

**Structural Factors Determining Short- and Long-Term Thermal Stability  
Limits of Bulk and Metal-Oxide Supported Ionic Liquids with  
1-*n*-Butyl-3-Methylimidazolium [BMIM]<sup>+</sup> Cation**

**by**

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## ABSTRACT

Ionic liquids (ILs) are the first choice in many applications such as synthesis, electrochemistry, and especially in catalysis because of their tunable physicochemical properties. In catalysis field, determination of thermal stability limits of metal-oxide supported ILs is crucial for proper choice of ILs at application conditions because determined stability limits of pure ILs are not applicable for these systems. Because, ILs directly interact with metal-oxides and these interactions influence thermal stability of ILs significantly.

In the first part of this study, structural factors determining thermal stability of ILs with 1-*n*-butyl-3-methylimidazolium, [BMIM]<sup>+</sup>, cation on SiO<sub>2</sub>, TiO<sub>2</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and MgO were determined. Results show that thermal stability limits of ILs increase with decreasing inter-ionic interaction strength. Stability limits of ILs linearly increase with increasing acidity of C2 proton on imidazolium ring, controlling inter-ionic interaction strength. Moreover, anion size significantly influences stability limits. Presence of metal-oxide lowers stability limits significantly as surface acidity decreases with increasing point of zero charge (PZC) of metal-oxide. Based on these findings a model was developed as a function of PZC and  $\nu(\text{C2H})$  to estimate stability limits of [BMIM]<sup>+</sup>-based metal-oxide-supported ILs. Finally,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported ILs' long-term thermal stabilities were determined by isothermal TGA measurements based on 1 % mass loss after 6 h treatments. Long-term stability limits were lower more than 60 °C from short-term stability limits. Furthermore, activation energy  $E_a$  required for decomposition were determined from the results of isothermal treatments.

This study was the first step of the studies on catalysts with the IL-coated supported metal complexes.

## ÖZET

İyonik sıvılar, 100 °C derecenin altında sıvı fazda, iyonlar halinde bulunan tuzlar olarak tanımlanır. İyonik sıvılar, yapılarındaki anyon/kasyon gruplarının değiştirilerek istenilen fiziksel-kimyasal özellikleri sağlayabildikleri için uygulama alanlarında çeşitli avantajlar sağlarlar. İyonik sıvıların farklı metal-oksit destekler üzerindeki ısıl bozunma sıcaklıklarının tespiti, bu sıvıların katalizör sistemlerinde kullanımı ve maksimum uygulanabilir sıcaklıklarının belirlenmesi için çok önemlidir.

Bu çalışmadaki amaç, sabit katyona sahip (1-bütıl-3-metılımdazolyum) çeşitli anyonlarla oluşturulmuş iyonik sıvıların belirlenen metal-oksit destekler üzerindeki kısa ve uzun dönemli ısıl kararlılıklarının belirlenmesidir. Farklı asitlik değeri taşıyan iyonik sıvıların farklı yüzey yüküne sahip desteklerle nasıl bir etkileşim içerisinde olduğunun bulunması hedeflenmiştir. İyonik sıvılarla kaplanmış metal-oksitlerin ısıl kararlılıkları, termogravimetrik analiz (TGA) yöntemiyle belirlenmiştir. Isıl kararlılığın, iyonik sıvının yapısına bağılı olduğu gözlemlenmiştir. Bu kapsamda, metal-oksit desteklerinin yüzey asitliği ve imidazolyum katyonu üzerindeki C2 protonunun ısıl kararlılığı kontrol eden iki önemli faktör olduğu belirlenmiştir. Aynı zamanda anyon boyutunun da ısıl kararlılık üzerinde rol oynadığı belirlenmiştir. Dokuz iyonik sıvının dört metal-oksit ( $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\gamma\text{-Al}_2\text{O}_3$ ,  $\text{MgO}$ ) üzerindeki ısıl dayanıklılıkları kullanılarak matematiksel bir model geliştirilmiştir. Bu modelle benzer yapıya sahip iyonik sıvıların farklı yüzey asitliğine sahip metal-oksit destekler üzerindeki ısıl dayanıklılığının tahmin edilebilmesi hedeflenmiştir.

Bir sonraki adım olarak ise, dokuz iyonik sıvının izotermal-TGA yöntemiyle  $\gamma\text{-Al}_2\text{O}_3$  üzerindeki uzun dönemli ısıl dayanıklılıklarının belirlenmesi ve bozunma için gerekli olan aktivasyon enerjisinin iyonik sıvının yapısına bağılı olarak nasıl bir değişiklik gösterdiğinin

belirlenmesi hedeflenmiştir. Çalışmalar sonucunda uzun dönemli ısıl dayanıklılıkların kısa dönemli ısıl dayanıklılıklarından en az 60 °C düşük olduğu tespit edilmiştir. Bu çalışmanın sonuçlarına dayanarak, uygulama alanlarında çalışma koşullarına bağlı olarak daha uygun iyonik sıvıların seçilebilmesi öngörülmüştür.

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## NOMENCLATURE

|                                  |                                                 |
|----------------------------------|-------------------------------------------------|
| IL                               | ionic liquid                                    |
| [BMIM] <sup>+</sup>              | 1-butyl-3-methylimidazolium                     |
| [OAc] <sup>-</sup>               | acetate                                         |
| [DBP] <sup>-</sup>               | dibutyl phosphate                               |
| [TOS] <sup>-</sup>               | tosylate                                        |
| [HSO <sub>4</sub> ] <sup>-</sup> | hydrogen sulfate                                |
| [OS] <sup>-</sup>                | octyl sulfate                                   |
| [TfO] <sup>-</sup>               | trifluoromethane sulfonate                      |
| [BF <sub>4</sub> ] <sup>-</sup>  | tetrafluoroborate                               |
| [SbF <sub>6</sub> ] <sup>-</sup> | hexafluoroantimonate                            |
| [NTf <sub>2</sub> ] <sup>-</sup> | bis(trifluoromethylsulfonyl)imide               |
| T <sub>onset</sub> '             | maximum tolerable temperatures of ionic liquids |
| E <sub>HB</sub>                  | hydrogen bond interaction energy                |
| E <sub>a</sub>                   | activation energy                               |

## Chapter 1

### INTRODUCTION

As the title of this thesis declares, two main topics investigated in this study are short- and long-term thermal stability limits of bulk and supported ionic liquids (ILs) with 1-*n*-butyl-3-methylimidazolium cation, [BMIM]<sup>+</sup>, and structural factors controlling these thermal stability limits. In this general introduction I aim to give the reader an insight into the history, properties and applications of ionic liquids and following by the discussion on the applications of ILs in catalytic systems to explain the importance of the determination of structural factors controlling the thermal stability limits of supported ILs.

#### 1.1. Ionic Liquids

Ionic liquids are generally defined as the salts which melt at or below 100 °C and are composed of solely cation and anion pairs <sup>1</sup>.

##### 1.1.1. History of Ionic Liquids

The history of ionic liquids (ILs) started with the description of melting point of ethylammonium nitrate, [EtNH<sub>3</sub>][NO<sub>3</sub>], as 12 °C by P. Walden in 1914 <sup>2</sup>. In 1948, Hurley et al. <sup>3</sup> have developed the first ILs with chloroaluminate anions while they are trying to find an easier and cheaper way to electroplate aluminum. In 1970s and 1980s, the groups of Osteryoung <sup>4</sup> and Hussey <sup>5</sup> studied on the room temperature chloroaluminates, respectively. These melts were assigned as the first generation of ILs. However, these ILs had limitations because of their hygroscopic nature and requirement for an inert atmosphere during preparation and storage. Furthermore, one of the product of reaction of these molten salts with

water is corrosive HCl <sup>6</sup>. In the early 1980s molten chloroaluminate salts were used as non-aqueous polar solvents for the investigations of transition metal complexes by Hitchcock et al. <sup>7</sup>. Then in the mid 1980s, Fry et al. <sup>8</sup> and Boon et al. <sup>9</sup>, offered low melting point ILs as solvents for organic synthesis. In 1990s, the first publications about ILs used in homogeneous catalysis have appeared in literature by Chauvin et al. <sup>10</sup> and Carlin et al. <sup>11</sup> Furthermore, in 1992 Wilkes et al. <sup>12</sup> showed that the ILs could not be restricted with the molten chloroaluminate salts by preparing the first water-stable sample with the IL, 1-ethyl-3-methylimidazolium tetrafluoroborate, [EMIM][BF<sub>4</sub>]. This type of ILs named as second generation ILs because they could be prepared and stored without an inert atmosphere unlike the chloroaluminate samples <sup>13</sup>. However, this type of ILs also has disadvantages such as high sensitivity towards hydrolysis. For instance, Endres et al. <sup>14</sup> found that the undried IL [BMIM][PF<sub>6</sub>] attacked the gold substrate when hydrolyzed because of the formation of HF, and showed that the increase in the water content increases the aggressiveness of the reaction<sup>13</sup>. In 1996, Bonhôte et al. <sup>15</sup> published the synthesis of ILs with the anions containing CF<sub>3</sub> and other fluorinated alkyl groups. Although in this case these ILs are water stable, the high price of the starting material Li[(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N] seems to be a significant problem for their application on larger scales.

Although ILs still have some disadvantages in the synthesis and applications, the number of synthesized ILs synthesized exceeds 500. Furthermore, Gutowski et al. <sup>16</sup> claimed that 10<sup>18</sup> IL combination may exist because of the tunable characteristics of ILs. Among them 1,3-dialkylimidazolium salts are the ones most commonly used and investigated because of the higher availability <sup>13</sup>. In Figure 1.1, the attention that ILs gained can be seen with the exponential increase in the number of publications about ILs/molten salts especially in the last decade.

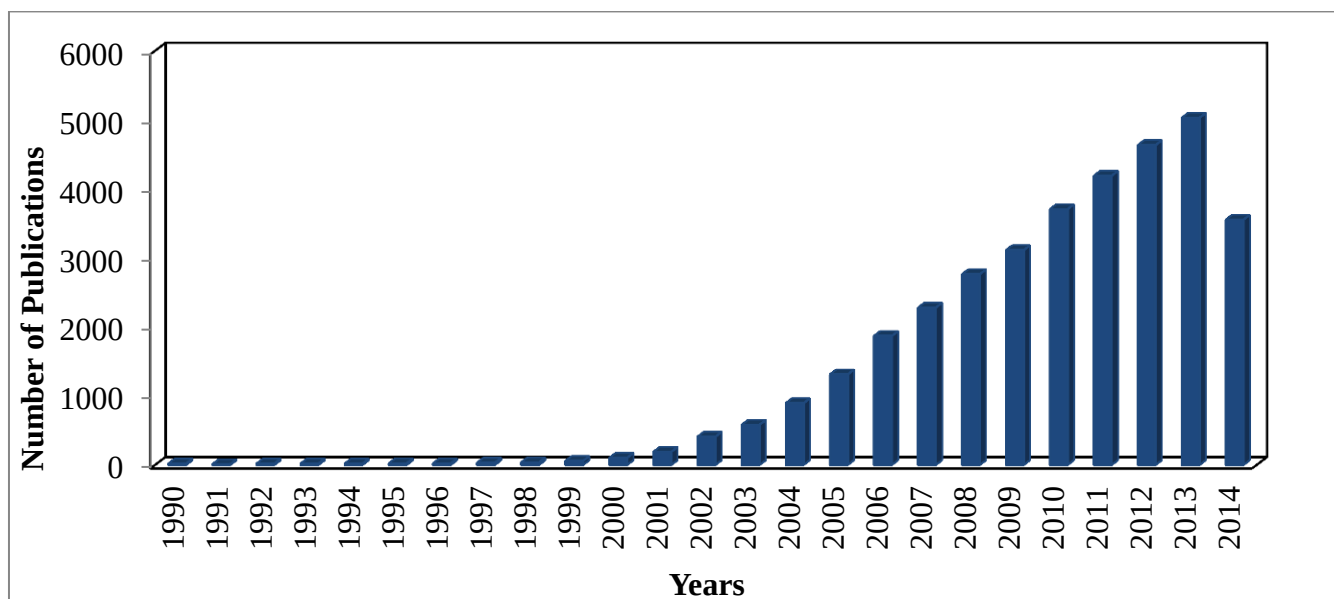


**Figure 1.1** Increase in the number of publications on ILs. Data for 2014 covers the publications till September.

### 1.1.2. Physical and Chemical Properties of Ionic Liquids

Because of the high number of available cations and anions,  $10^{18}$  different IL combinations are possible<sup>16</sup>. Changes in the selection of cation and anion pairs result in the variations in the physicochemical properties of ILs which led to the idea of ILs being “designer solvents”<sup>17</sup> and also increment in the application areas of ILs. Some of the physicochemical properties of ILs such as liquid range, heat capacities, hydrophilicities, densities and viscosities are controlled by the structural variations of the salts<sup>18</sup>. For instance, when the alkyl chain length of *n*-alkyl-methylimidazolium cations increases, viscosity<sup>15</sup> and hydrophobicity<sup>19</sup> of the ILs also increases; however a reverse effect is observed for the density of ILs as in the case of increasing anion size<sup>20</sup>. Beyond the tunable characteristic of physicochemical properties, all ILs provide extreme features such as very low vapor pressure (less than  $10^{-8}$  bar), dissolving ability for a wide range of compounds (including organic, inorganic, hydrophilic, hydrophobic, etc.)even the cellulose<sup>13</sup>. For instance, [BMIM][PF<sub>6</sub>] at

298.15 K has a vapor pressure of  $10^{-11}$  Pa <sup>21</sup>. Some of the ILs are composed of poorly coordinating ions so that they can be used as highly polar non-coordinating solvents and in some structural variations, ILs are immiscible with some of the organic solvents so that they can be used as non-aqueous polar alternatives for two phase systems <sup>18a</sup>. Some of these properties are as a result of ILs being liquids at very low temperatures unlike the ordinary ionic compounds for example, sodium fluoride has a m.p. of 993 °C <sup>13</sup>. These significant differences in the m.p. of ILs result from the structural combinations of ILs with exceptionally bulky, unsymmetrical organic cations and flexible inorganic charge delocalized anions as shown in Figure 1.2 and the most commonly used cations and anions are given in Figure 1.3. Unlike the other salts, ILs can not pack closely because of these properties of cation / anion pairs, resulting in the significant decrease in the m.p. of ILs.

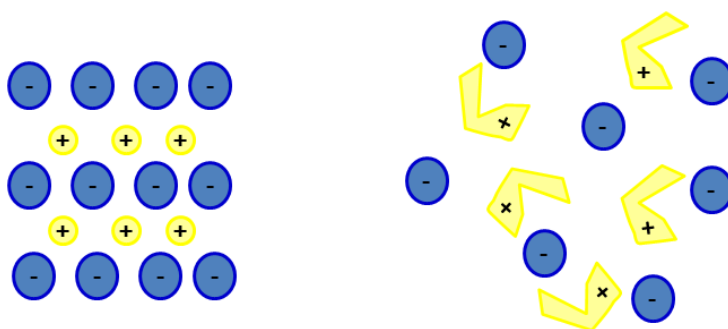
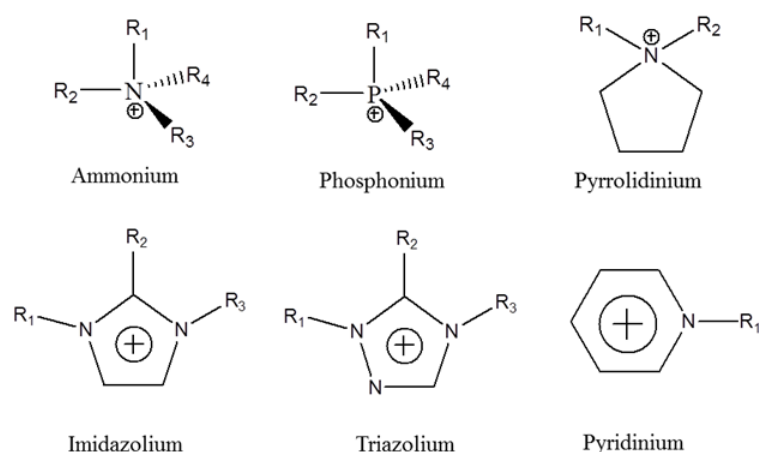


**Figure 1.2** Typical inorganic salt and ionic liquid structure



| Organic Anions                                                                                                                                                                                                                                                                                                                                                                                                                                            | Inorganic Anions                                                                                                                                                                                                                                                                                                                                                                                     |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup> , CH <sub>3</sub> OSO <sub>3</sub> <sup>-</sup> , C <sub>6</sub> H <sub>5</sub> OSO <sub>3</sub> <sup>-</sup> , CF <sub>3</sub> CO <sub>2</sub> <sup>-</sup> , C(CF <sub>3</sub> SO <sub>2</sub> ) <sub>3</sub> <sup>-</sup> , CF <sub>3</sub> SO <sub>3</sub> <sup>-</sup> , N(SO <sub>2</sub> CF <sub>3</sub> ) <sub>2</sub> <sup>-</sup> , BR <sub>4</sub> <sup>-</sup> , R <sub>3</sub> BOH <sup>-</sup> | F <sup>-</sup> , Cl <sup>-</sup> , Br <sup>-</sup> , I <sup>-</sup> , BF <sub>4</sub> <sup>-</sup> , PF <sub>6</sub> <sup>-</sup> , SbF <sub>6</sub> <sup>-</sup> , AsF <sub>6</sub> <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , ClO <sub>4</sub> <sup>-</sup> , CuCl <sub>2</sub> <sup>-</sup> , AuCl <sub>4</sub> <sup>-</sup> , ZnCl <sub>3</sub> <sup>-</sup> , SnCl <sub>3</sub> <sup>-</sup> |

**Figure 1.3** Most commonly used cations and anions.

ILs also have high conductivities ( $\sim 10 \text{ mS cm}^{-1}$ ) and a significantly large electrochemical window. While electrochemical potential of water has a value of about 1.2 V, some IL values are over 6 V at which the electrolyte is neither reduced nor oxidized at an electrode. Thus the electrodeposition of metals, semiconductors such as Al, Mg, Si, Ge, and rare earth elements at room temperature can be obtained from RTILs<sup>13</sup>. On the other hand, the most important disadvantage of ILs is their high viscosities at room temperature (ranging between about 10 cP to 500 cP) disabling to handle compared to organic solvents<sup>13</sup>.

The most important property of ILs investigated in this study is the high thermal stabilities of ILs. Although the thermal stability limits of ILs depend on the structural and peripheral factors, most of the ILs in bulk case are stable up to 400-450 °C<sup>22</sup>. However, Endres et al.<sup>14</sup> indicated that the thermal stability limits of ILs decrease in the case of long exposure to thermal treatment. Higher thermal stability of ILs coupled with extremely low vapor pressure enable to remove water content below 1 ppm in the IL by heating under

vacuum. The most commonly used cation and the interest of this study, ILs with imidazolium cation are generally hygroscopic which is an important factor controlling the thermal stability limits. When the water content in IL increases, thermal stability limit decreases. Maximum water contents of some imidazolium-based ILs are given in Table 1.1.

**Table 1.1** Maximum water contents of imidazolium based ILs with various anions.

| Abbreviations of ILs       | Maximum Water Content (ppm) |
|----------------------------|-----------------------------|
| [BMIM][PF <sub>6</sub> ]   | 2640                        |
| [BDMIM][PF <sub>6</sub> ]  | 2540                        |
| [PMIM][NTf <sub>2</sub> ]  | 3810                        |
| [BMIM][NTf <sub>2</sub> ]  | 3300                        |
| [DMIM][NTf <sub>2</sub> ]  | 1450                        |
| [BDMIM][NTf <sub>2</sub> ] | 6380                        |
| [BMIM][BF <sub>4</sub> ]   | 19500                       |
| [BMMIM][BF <sub>4</sub> ]  | 13720                       |

As seen in Table 1.1, the solubility of water in ILs with the same cation depends on the anion type, increasing in the order: PF<sub>6</sub> < NTf<sub>2</sub> < BF<sub>4</sub>. However, the solubility of organic solvents such as benzene, toluene and xylene in ILs increase with an increase in the alkyl chain length and size of the anions in reverse order: BF<sub>4</sub> < PF<sub>6</sub> < NTf<sub>2</sub><sup>23</sup>. As mentioned above, these tunable properties increase the application areas of ILs explained in details in the section 1.1.3.

### 1.1.3. Applications of Ionic Liquids

ILs being liquid at room temperature and nonvolatile and nonflammable has increased the interest on ILs as green solvents in the last two decades. With the increasing number of researches on the ILs, and thank to their tunable physicochemical properties, currently ILs are used also as catalyst or catalyst activators, electrolytes for batteries, heat transfer fluids and lubricants<sup>24</sup>. As mentioned in previous sections, ILs can dissolve cellulose, which previously was only known to be soluble in an explosive organic solvent. Cellulose is produced in nature in the amount of 1011 tons per year, making it the most abundant natural organic chemical and the most important source of bio-renewable chemicals<sup>25</sup>.

Another important application of the ILs is their use in batteries because of their high conductivity and wide electrochemical window. Traditional solvents used in electrolytes for Li batteries are aprotic because of the requirements of wide electrochemical windows for the cathode limit of the  $\text{Li/Li}^+$  potential. However, aprotic organic solvents are usually volatile and flammable compared to ILs which are neither volatile nor flammable with a wide electrochemical window<sup>14</sup>. Moreover, as a result of their electrochemical window and low vapor pressure ILs are very efficient for the electrodeposition of metals above 100 °C so that electrodeposition of water sensitive metals such as aluminum or titanium become possible.<sup>25</sup> ILs are also used in the nuclear industry<sup>13</sup> as separation media for nuclear fuel and as electrolytes for the recovery of uranium and lanthanides<sup>26</sup>. Furthermore, an application was developed by the company BASF named biphasic acid scavenging utilizing ionic liquids (BASIL<sup>TM</sup>). In this process 1-methylimidazole is used to scavenge the acid formed during the synthesis of alkoxyphenylphosphines from the chloride analogues and then recycled and introduced again into the system (common BASIL processes are given in Table 1.2).

**Table 1.2** The most common industrial modified reactions of BASIL process

| Reaction        | Scheme                                                                                                                                                                                                  |
|-----------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Acylation       | $\text{R}-\text{O}-\text{H} + \text{R}'-\overset{\text{O}}{\parallel}\text{C}-\text{Cl} \rightarrow \text{R}'-\overset{\text{O}}{\parallel}\text{C}-\text{O}-\text{R} + \text{HCl}$                     |
| Elimination     | $\text{R}-\text{CH}_2-\text{CH}_2-\text{Cl} \rightarrow \text{R}-\text{CH}=\text{CH}_2 + \text{HCl}$                                                                                                    |
| Phosphorylation | $\text{R}-\text{O}-\text{H} + \text{R}'-\overset{\text{O}}{\parallel}\text{P}(\text{R})-\text{Cl} \rightarrow \text{R}'-\overset{\text{O}}{\parallel}\text{P}(\text{R})-\text{O}-\text{R} + \text{HCl}$ |
| Sulfurylation   | $\text{R}-\text{O}-\text{H} + \text{R}'-\overset{\text{O}}{\parallel}\text{S}(\text{O})-\text{Cl} \rightarrow \text{R}'-\overset{\text{O}}{\parallel}\text{S}(\text{O})-\text{O}-\text{R} + \text{HCl}$ |
| Silylation      | $\text{R}-\text{O}-\text{H} + \text{---Si---Cl} \rightarrow \text{---Si---OR} + \text{HCl}$                                                                                                             |
| Deprotonation   | $\text{Ph}_3\text{P}^+\text{RCH}_2\text{H} \text{ Cl}^- \rightarrow \text{Ph}_3\text{P}^+=\text{RCH} + \text{HCl}$                                                                                      |

The interest of this study is the application of ILs in the catalytic systems which will be explained in the following sections in details.

## 1.2. Ionic Liquids in Catalytic Systems

For the use of ILs as catalysts or catalytic activators, they are thought to be the excellent media to dissolve and hold transition metal complexes since ILs are ionic, polar and

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weakly-coordinating compounds. In catalytic systems use of ILs are favored because of the some advantages provided:

- Increased selectivity
- Low vapor pressure
- Separation media (phase separation, extraction, distillation)
- High heat transfer
- High thermal stability
- Good electrochemical properties
- Possibility to immobilize catalyst
- Acceleration of reactions.

However, ILs also have some main problems to be used in catalytic systems:

- High costs of commercial ILs
- High viscosity
- Low solubility of gases in ILs
- Purification difficulties
- Limited knowledge about the ILs physicochemical properties.

The disadvantages and limitations of ILs in catalytic systems led to the born of new concepts one of which is the immobilization of ILs on supports to improve the applications of ILs in industry by eliminating the limitations. This concept is called as supported ionic liquids (SILs) which were used generally by coating of a thin layer of IL film on a solid support. In the following two sections, the most common methods of SILs, supported ionic liquid phase-SILP and solid catalysts with ionic liquid layer-SCILL, will be explained in details.

### 1.2.1. Supported Ionic Liquid Phase (SILP)

Supported ionic liquid phase (SILP) catalytic system composed of the immobilization of an IL on a high surface area porous solid and dissolution of a homogeneous catalyst in IL phase (in some cases ILs can be used as the catalysts also without dissolving an active species)<sup>27</sup>. In SILP, the resulting system is solid with the active species dissolved in and acts as a homogeneous system with the benefits of a heterogeneous system<sup>28</sup>. Because of the tunable physicochemical properties of ILs, SILP catalyst systems can be optimized according to the system conditions. Moreover, the amount of IL used in catalytic systems and cost of application are significantly decreased while the limitations such as selectivity, separation, reusability are handled. Therefore, SILP concept has replaced most of SIL concepts used before due to its improvements in the applications of catalytic systems. For a better understanding of SILP system, a simple representation is given in Figure 1.4.

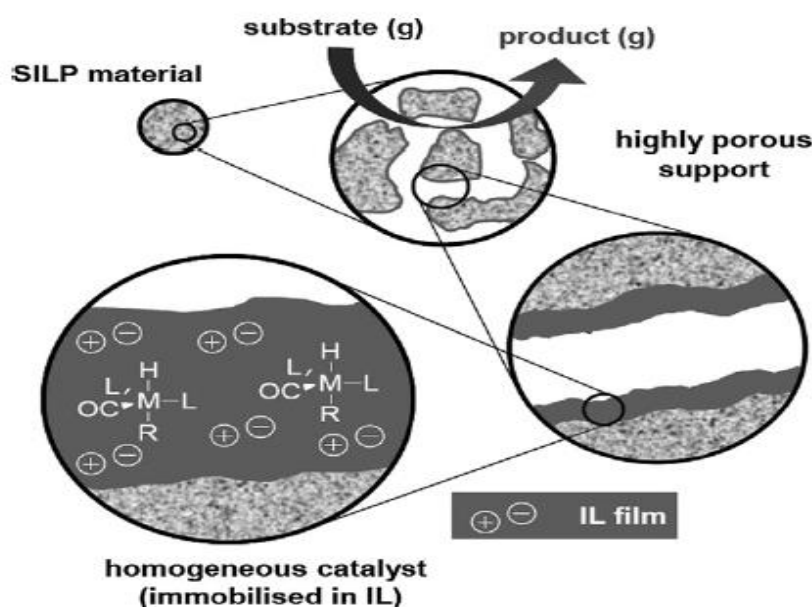


**Figure 1.4** Simplified representation of SILP system<sup>29</sup>.

In the applications of ILs in SILP systems, the choice of IL must depend on the reaction type and reaction conditions. Therefore, used ILs vary according to the reaction type,

reaction conditions such as reactor type, reaction temperature and pressure and etc. However, there are some cation and anion types that are much more favored in the applications of SILP due to their specific properties. The most commonly used cations are 1-ethyl-3-methyimidazolium ([EMIM]<sup>+</sup>), 1-butyl-3-methyimidazolium ([BMIM]<sup>+</sup>), and 1-hexyl-3-methyimidazolium ([HMIM]<sup>+</sup>). The most commonly used anions are [Cl]<sup>-</sup>, [Br]<sup>-</sup>, [BF<sub>4</sub>]<sup>-</sup>, [PF<sub>6</sub>]<sup>-</sup>, [NTf<sub>2</sub>]<sup>-</sup>. The most widely used ILs in SILP are [BMIM][BF<sub>4</sub>] and [BMIM][PF<sub>6</sub>] because of their high solvation power for polar catalysts complexes with a weak coordination strength<sup>28</sup>. Furthermore, the nature and the structure of supports used in SILP applications are also important factors to improve the activity and efficiency of the system. Therefore, the choice of the support also varies according to the reaction conditions, used ILs, used catalytically active particles and etc. The most commonly used supports are the ones that are almost both electronically and sterically inert towards the reactions such as porous silica gels with a surface area of 300-500 m<sup>2</sup>/g, crystalline silica-alumina materials (zeolites and clays), mesoporous silica materials and inorganic materials (Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>), polymer-based materials and a new concept with porous carbons and carbon nanotubes. However, inorganic materials are not preferred in most cases of SILP applications because of the low surface areas and pore volumes. Moreover, the chosen support may require further pre-treatments before the coating process of ILs on the surface to increase the selectivity and activity of the reaction. For instance, since the acidity of support is extremely important factor for the reaction, in some cases to adjust the acidity of silica support, some silanol groups are removed by thermal treatments. Acidity of support is very important to improve the selectivity and activity of the reaction. Therefore, pre-treatment of support gets a high importance. However, since most of these pre-treatments are done by thermal applications, according to the type of chosen support some precautions must be taken to protect the structure, pore size and active sites of the support. In the case of zeolites as support, temperature is very important factor to be careful

about because of the high dependency of the structure on the temperature. Since the choice of IL and support are reaction dependent, the interactions of support-IL-catalyst particles also change with the reaction conditions, the choice of IL and support and also the preparation of SILP catalysts. In Figure 1.5, the schematic representation of various support-IL-catalyst combinations are given.

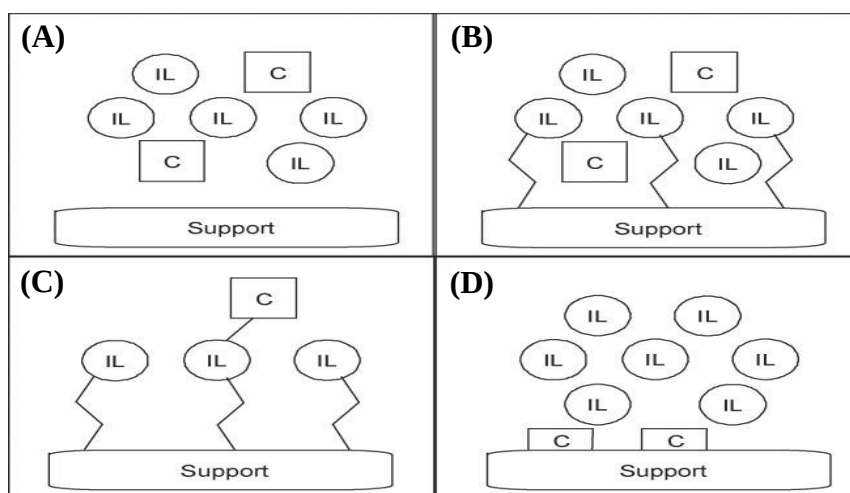


**Figure 1.5** Schematic representations of various support-IL-catalyst combinations.

The conformation in part (A) of Figure 1.5 occurs when the IL is deposited on the support as a multilayer and acts as an immobilizing medium for the catalyst like a homogeneous catalyst. This kind of conformation can be obtained simply by the impregnation method. If the support is first pre-treated with a monolayer of IL fragments and then catalysts are impregnated on the modified support, conformation in part (B) of Figure 1.5 is obtained. If IL is directly anchored on the support via covalent anchoring, the conformation in part (C) of Figure 1.5 is obtained and for conformation in part (D) of Figure 1.5, an IL is impregnated on the surface of classical heterogeneous catalysts such as covalently anchored catalysts or supported transition-metal nanoparticles (the last method is especially used in the preparation of different type of IL-assisted catalysts as discussed in the next section.)<sup>28</sup>.

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### 1.2.2. Solid Catalysts with Ionic Liquid Layer (SCILL)

Solid catalysts with ionic liquid layer (SCILL) concept is very similar to SILP, however; in SCILL porous solid itself is a heterogeneous catalyst and not an inert support used to immobilize the homogeneous catalyst by the IL. This method was developed to improve the selectivity of heterogeneous catalysts<sup>30</sup>. The activity and selectivity of solid catalyst may be changed with two methods depending on the coating of internal surface with IL. The first one is the co-catalytic effect where IL may have a positive influence on the chemical properties of catalyst. The second one is the physical solvent effect where IL may change the effective concentrations of reactant(s)/intermediate(s), compared to the uncoated catalyst. Since the solubility of liquid or gaseous reactants in IL can be altered by the choice of the cation and anion pairs the selectivity to the intermediate can be favored if the intermediate is less soluble in the IL than the reactant.<sup>30</sup> Some application areas under research were given in Table 1.3. Although both SILP and SCILL have several advantages in the catalytic applications, their main limitations arise from the stability of ILs on the support material during the application conditions. One limiting factor for these applications is that ILs tend to lose their structural integrity via thermal decomposition<sup>31</sup>, leaching out<sup>32</sup> or evaporation<sup>33</sup> during applications.

**Table 1.3** Some of the application areas of SILP and SCILL concepts

| Ionic Liquids                                                  | Abbreviation               | Catalyst                                                                                                | Support                                            | Application Areas                                                                                                                    |
|----------------------------------------------------------------|----------------------------|---------------------------------------------------------------------------------------------------------|----------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------|
| 1-N-(ferrocenylmethyl)imidazole hydrogen sulfate               | [FeMIM][HSO <sub>4</sub> ] | Ferrocenyl group                                                                                        | SiO <sub>2</sub>                                   | Synthesis of homo-allylic alcohols <sup>34</sup>                                                                                     |
| 1-butyl-3-methylimidazolium tetrafluoroborate                  | [BMIM][BF <sub>4</sub> ]   | Rh-tri(m-sulfonyl) triphenyl phosphine                                                                  | Al <sub>2</sub> O <sub>3</sub><br>Activated carbon | Biphasic hydroformylation catalysis <sup>35</sup>                                                                                    |
| 1-butyl-3-methylimidazolium hexafluorophosphate                | [BMIM][PF <sub>6</sub> ]   |                                                                                                         |                                                    |                                                                                                                                      |
| 1,2-dimethyl-3-butyl-imidazolium hexafluorophospate            | [BDMIM][PF <sub>6</sub> ]  |                                                                                                         |                                                    |                                                                                                                                      |
| 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide  | [EMIM][NTf <sub>2</sub> ]  | dibromo[3-(2,5-(2R,5R)-dimethylphospholanyl-1)-4-di-o-tolylphosphino-2,5-dimethylthio-phenyl] ruthenium | SiO <sub>2</sub>                                   | Asymmetric hydrogenation of methyl acetoacetate <sup>27a</sup>                                                                       |
| 1-butyl-3-methylimidazolium octylsulfate                       | [BMIM][OS]                 | Rh-complex/ triphenylphosphine trisulfonate cesium                                                      | SiO <sub>2</sub>                                   | Ethylene hydroformylation <sup>36</sup>                                                                                              |
|                                                                |                            | Rh-complex/ 3,3',3''-phosphinetriyltribenzenesul fonate                                                 |                                                    |                                                                                                                                      |
| 1-ethyl-3-methylimidazolium bis( trifluoromethylsulfonyl)imide | [EMIM][NTf <sub>2</sub> ]  | Ir, Ru and Rh complexes                                                                                 | porous carbons                                     | Asymmetric hydrogenation of double C =N and C= C bonds in trimethylindolenine, 2-methylquinoline and dimethylitaconate <sup>37</sup> |
| 1-butyl-3-methylimidazolium tetrafluoroborate                  | [BMIM][BF <sub>4</sub> ]   |                                                                                                         | mesoporous SiO <sub>2</sub>                        |                                                                                                                                      |
| 1-butyl-3-methylimidazolium hexafluorophosphate                | [BMIM][PF <sub>6</sub> ]   |                                                                                                         |                                                    |                                                                                                                                      |
| 1-butyl-3-methylimidazolium hexafluorophosphate                | [BMIM][PF <sub>6</sub> ]   | Rh complexes of the biphosphine ligand sulfoxantphos                                                    | SiO <sub>2</sub>                                   | Continuous flow gas-phase hydroformylation of propene <sup>27c</sup>                                                                 |
| 1-butyl-3-methylimidazolium                                    | [BMIM][OS]                 |                                                                                                         |                                                    |                                                                                                                                      |

|                                                                    |                  |                                                                  |                            |                                                                                          |
|--------------------------------------------------------------------|------------------|------------------------------------------------------------------|----------------------------|------------------------------------------------------------------------------------------|
| octylsulfate                                                       |                  |                                                                  |                            |                                                                                          |
| 1-Ethyl-3-methylimidazolium chloride                               | [EMIM][Cl]       | Highly acidic SILP catalysts                                     | SiO <sub>2</sub>           | Continuous gas-phase isopropylation of toluene and cumene <sup>38</sup>                  |
| 1-(3-trimethoxysilylpropyl)-3-methylimidazoliumchloride            |                  | V and Mo complexes                                               | SiO <sub>2</sub> (SBA-15)  | Selective oxidation of alcohols <sup>39</sup>                                            |
| 1-(3-trimethoxysilylpropyl)-3-methylimidazoliumhexafluorophosphate |                  |                                                                  |                            |                                                                                          |
| 1-N-ferrocenylmethyl benzimidazole chloride                        | [FemMerBenz][Cl] | Ferrocene tethered polymer supported ionic liquid phase catalyst | ferrocene tethered polymer | Intramolecular O-arylation of o-iodoanilides to corresponding benzoxazoles <sup>40</sup> |
| 1-N-methylimidazole chloride                                       | [MIM][Cl]        | Pd-porphyrin complex                                             | mesoporous SBA-15          | Solvent-free Heck reaction <sup>41</sup>                                                 |
| 1-butyl-3-methylimidazolium trifluoromethanesulfonate              | [BMIM][TfO]      | transition metal complexes (Ru, Ir, Os, Fe, Cu, Mo, Pd, Re, Rh)  | Silica 100                 | Very low temperature water–gas-shift reaction <sup>42</sup>                              |

### 1.3. Objective of Thesis

As mentioned above, ILs might lose their stabilities when they are coated on the support materials during the application conditions. The most common reason for the disintegration is the thermal decomposition of ILs during the applications at high temperatures. Although ILs are popular with their high thermal stability limits, used support materials usually catalyze their decomposition reaction by lowering the stability limits. Furthermore, thermal stability limits of ILs are also controlled by the structural factors. Therefore, the aim of the thesis was chosen as the determination of the short- and long-term thermal stability limits of metal-oxide supported ILs with 1-butyl-3-methylimidazolium, [BMIM]<sup>+</sup> cation and then the determination of the structural factors controlling these stability limits.

In this thesis, the experimental methods including the preparation of samples were given in Chapter 2. Then, the structural factors controlling the thermal stability limits of bulk and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported ILs with [BMIM]<sup>+</sup> cation was investigated in Chapter 3. As a next step of the investigation, support effect on the thermal stability limits of ILs with [BMIM]<sup>+</sup> cation was studied with the metal-oxides SiO<sub>2</sub>, TiO<sub>2</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, MgO, CeO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> and a simple mathematical model to estimate the thermal stability limits of supported ILs were given in Chapter 4. These two chapters have been published in *Thermochemica Acta* and *Chemical Engineering Science*, respectively and they have been reformatted to meet the requirements of this thesis. In Chapter 5, isothermal long-term thermal stability limits of ILs supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and activation energies ( $E_a$ ) required for decomposition were investigated. In order to determine the activation energy of the decomposition of supported ILs,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was chosen as the representative metal-oxide and isothermal treatments were performed on the [BMIM]<sup>+</sup>-based ILs coated on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

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## Chapter 2

### EXPERIMENTAL METHODS

#### 2.1. Sample Preparation

Metal-oxides, ILs and solvent (acetone) used in this study were purchased from Sigma Aldrich with the highest available purity. The used metal-oxides, SiO<sub>2</sub> (CAS Number 112945-52-5), TiO<sub>2</sub> (anatase-CAS Number 1317-70-0),  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (CAS Number 1344-28-1), MgO (CAS Number 1309-48-4), Fe<sub>2</sub>O<sub>3</sub> (CAS Number 1309-37-1), and CeO<sub>2</sub> (CAS Number 1306-38-3) have the purity levels of 99.9 %, 99 %, 98 %, 99 %, 99 %, and 99.9 % respectively. [BMIM][HSO<sub>4</sub>] 94.5%, [BMIM][OAc] 95 %, [BMIM][OS] 95 %, [BMIM][DBP] 96%, [BMIM][SbF<sub>6</sub>] 97 %, [BMIM][TOS] 97 %, [BMIM][BF<sub>4</sub>] 98 %, [BMIM][NTf<sub>2</sub>] 98 %, [BMIM][TfO] 98 %, were the nine ILs used in this study.

##### 2.1.1. Calcination of Metal-oxides

Although all metal-oxides were bought with the highest available purity, calcination process was performed for each metal-oxide in order to remove the presence of possible organic impurities. SiO<sub>2</sub>, TiO<sub>2</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and MgO were calcined under oxygen atmosphere for 5h at 520, 500, 500 and 700 °C, respectively while CeO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> were calcined at 400 and 450 °C, respectively, for 2 h. After the calcination process each metal-oxide was sealed and stored for further use.

### 2.1.2. IL-Loading on Metal-oxides

ILs were coated on the calcined metal-oxide supports via incipient wetness impregnation method which is a commonly used technique for the synthesis of heterogeneous catalysts. 200 mg of each IL was dissolved in 5 mL acetone. IL-solvent mixtures were added dropwise on top 1 g of freshly calcined support materials and shook slightly to prevent the bubble formation. The prepared mixtures were set aside for 2 h to settle down. Then the remaining solvent in the prepared samples was evaporated in vacuum oven at 70 °C for 24 h to obtain powder samples. Thermal stability limits of ILs were taken into consideration for the determination of drying procedure as indicated Clough *et al.*<sup>1</sup> so that the all supported ILs were dried at 70 °C to prevent the possible decomposition. IL-loading of the prepared powder samples were determined as approximately 16.7 wt. % according to the analyses of scanning electron microscopy coupled with energy dispersive X-ray spectroscopy mapping results.

## 2.2. Characterization Methods

Point of zero charge determination was performed on the freshly calcined metal-oxides and they were characterized by Brunauer–Emmett–Teller surface area analyses (BET) to determine the pore volume and surface area. Prepared supported-IL samples were characterized by thermogravimetric analyses (TGA), fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy coupled with energy-dispersive X-Ray spectroscopy (SEM/EDX), and Bruner-Emmett-Teller (BET) methods. The details of each technique were given in the corresponding sections.

### 2.2.1. Point of Zero Charge (PZC) Determination–Dynamic Light Scattering (DLS)

Point of zero charge (PZC) is the pH value at which point the surface has a zero net total particle charge <sup>2</sup>. PZC is a good measure of surface acidity, which could be determined with simple acid base titration <sup>3</sup> via a dynamic light scattering (DLS) instrument.

Light scattering results from the interaction of light and electrical field of a small particle dispersed in a solution. An incident photon induces an oscillating dipole in the electron cloud and with the changes in the dipole energy is radiated in all directions producing the scattered light. During the measurements of PZC values on DLS instrument, particle electrophoresis which is the movement of charged particles relative to dispersant under applied electrical field took as the basis <sup>4</sup>. Furthermore, in order to perform measurements on DLS instrument, the sample has to meet some requirements such as different refractive index than used dispersant, transparent dispersion and etc. The image of the dynamic light scattering instrument with the titrator was given in Figure 2.1.



**Figure 2.1** The image of Zetasizer Nanoseries-DLS instrument coupled with Malvern Multipurpose titrator <sup>5</sup>.

In this study, PZC measurements were performed on a Zetasizer Nanoseries-DLS instrument coupled with Malvern Multipurpose titrator. For the PZC measurements, 4 mg of each calcined metal-oxide was dispersed in 20 g of 0.1 M KNO<sub>3</sub> solution, sonicated for 5 min and then titrated with 0.25 M NaOH and HNO<sub>3</sub> as described Gulicovski et.al.<sup>3</sup>. Software set up was as follows:

- Measurement type was chosen as pH/titration/Zeta potential
- Refractive indexes of SiO<sub>2</sub>, TiO<sub>2</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, MgO, CeO<sub>2</sub>, and Fe<sub>2</sub>O<sub>3</sub> were set as 1.46, 2.90, 1.76, 1.74, 2.20, and 2.94, respectively.
- Absorbance values of SiO<sub>2</sub>, TiO<sub>2</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, MgO, CeO<sub>2</sub>, and Fe<sub>2</sub>O<sub>3</sub> were set as 0.01, 1.0, 0.01, 0.1, 0.01, and 0.1, respectively.
- General options were fixed to Smoluchowski.
- Temperature was set to 25°C and equilibrium time was set to 120 s.
- Cell type was chosen as clear disposable Zeta cell.
- Measurements were performed in automatic base in between minimum value of 10 and maximum value of 100 scans.
- Titrations were performed with 0.5 M NaOH and HNO<sub>3</sub> solutions.
- Initial sample volume was set as 20 mL.
- Measurements were performed from pH 11 to 2 for each metal-oxide.
- Instrument pH tolerance was set as 0.2 for SiO<sub>2</sub> and TiO<sub>2</sub>, as 0.05 for Al<sub>2</sub>O<sub>3</sub>, MgO, CeO<sub>2</sub>, and Fe<sub>2</sub>O<sub>3</sub>.
- Increase range of pH was set as 0.2 for SiO<sub>2</sub>, TiO<sub>2</sub>, and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and while it is decreased to 0.1 for MgO, CeO<sub>2</sub>, and Fe<sub>2</sub>O<sub>3</sub>.

### 2.2.2. Thermogravimetric Analyses (TGA)

Thermogravimetry (TG) is the branch of thermal analysis methods which examines the mass change of a sample as a function of temperature in the scanning mode or as a function of time in the isothermal mode. Although some of the thermal phenomenon do not results in the change in mass of the sample such as melting or crystallization, there are some very important exceptions such as absorption-desorption, oxidation-reduction and decomposition. TG is used to characterize thermal stability of materials by using the difference before and after treatment under various conditions <sup>6</sup>. Thermal stability might be lost because of the decomposition <sup>7</sup>, evaporation <sup>8</sup> or leach out <sup>9</sup> of some samples during the thermal treatment. TGA makes a continuous weighing of the small sample in an inert atmosphere such as nitrogen or argon as the temperature is increased in the furnace at a programmed linear rate. TG curves are normally plotted with % mass change on the vertical axis and temperature (T) or time (t) on the horizontal axis. The mass change of a material are strongly dependent on the operating conditions such as heating rate, sample amount, sample pan type, flowing inert gas type, volume of sample and the scanning rate have significant influences on the characteristics of the recorded TG curve <sup>8, 10</sup>.

In this study, TGA measurements were performed on a TA Instruments TGA Q500 and Seiko Instruments Inc. (SII) EXSTAR TG/DTA 6300 model instruments. The measurements were started by opening the nitrogen gas valve and set up the flow of the nitrogen as 300 mL/min. Then, the reference pan and a clean, empty platinum pan were placed on the reference and sample platforms. The zero button located on the software was used to tare the weight of the empty pans. The measurement parameters were set as follows: a heating rate of 10 °C/min within a temperature range of 25 to 800 °C with the ramp mode. Then, approximately 15 mg of sample were placed in platinum pan on sample compartment

and purged with nitrogen for 1 h at 25 °C and then the ramp was started from 25 to 800 °C. In order to visualize the TGA measurements and its working principle, the schematic of the instrument was given in Figure 2.2.

Temperature limits obtained from the interception of two linear functions one originating from the zero weight loss level and the other one tangential to the declining portion of the weight change line (mentioned above as the common plot type), were named as  $T_{\text{onset}}$ . However, these  $T_{\text{onset}}$  limits generally overestimate the real thermal decomposition temperature depending on the experimental conditions such as high heating rate<sup>8</sup>. Because of this overestimation, thermal stability limits of ILs were determined from the onsets of derivative weight % change lines. The determined stability limits were named  $T'_{\text{onset}}$  and to be more conservative about the short-term thermal stability limits,  $T'_{\text{onset}}$  values were used in this study. All measurements were repeated three times under identical conditions to determine the reproducibility. The measurements indicate that all results were reproducible within an error range of  $\pm 3$  °C. A representative image of  $T_{\text{onset}}$  and  $T'_{\text{onset}}$  values determination of a representative IL was given on Figure 2.3.

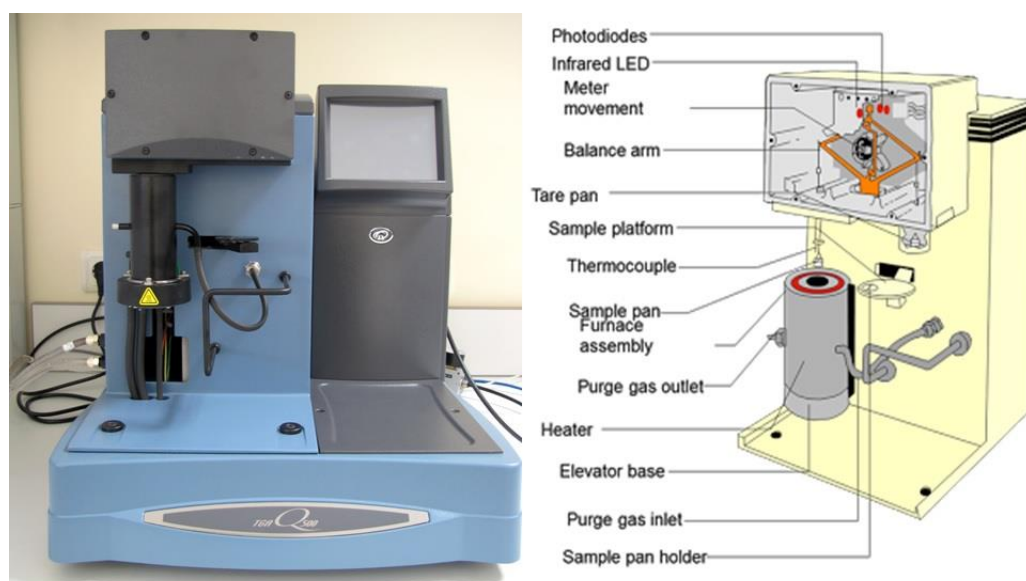


**Figure 2.2** Image of TGA instrument TG Q 500 (left)<sup>11</sup> and the schematic of the instrument (right)<sup>12</sup>.

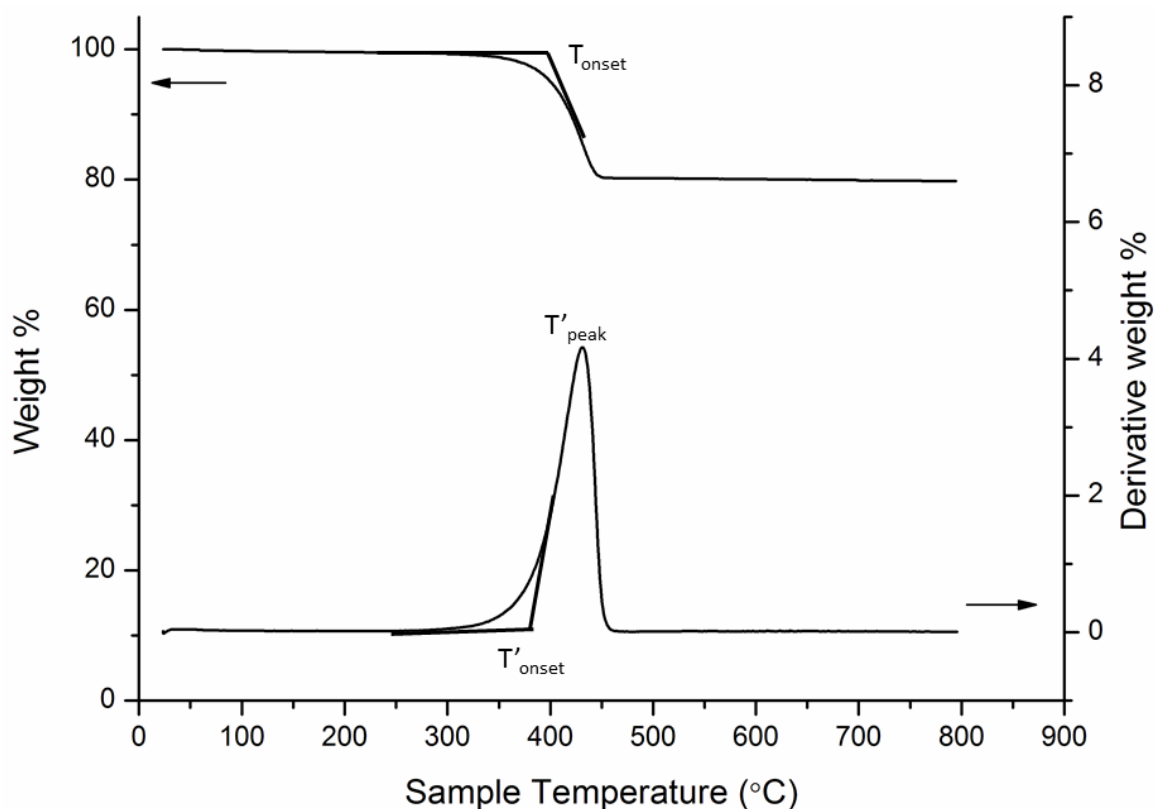


**Figure 2.3** A representative image of  $T_{\text{onset}}$  and  $T'_{\text{onset}}$  values determination of ILs

### 2.2.3. Fourier Transform Infrared Spectroscopy (FT-IR)

Infrared spectroscopy (IR spectroscopy) is the technique which uses the infrared region of the electromagnetic spectrum for characterization. Infrared region of the spectrum consists of the light with a longer wavelength and lower frequency than visible light. It covers a range of techniques, mostly based on absorption spectroscopy. The infrared portion of the electromagnetic spectrum is usually divided into three parts as near infrared, mid infrared and far infrared according to their relation to the visible spectrum. Near infrared has the highest energy and can excite vibrations in between wavenumbers  $4000\text{--}14000\text{ cm}^{-1}$ . The mid infrared, can be used to find out the fundamental vibrations of a sample in between wavenumbers  $400\text{--}4000\text{ cm}^{-1}$ . The far infrared has the lowest energy and usually used for the

rotational spectroscopy in between the wavenumbers 10–400  $\text{cm}^{-1}$ . Wavenumber defines the number of waves per unit length. Thus, wavenumbers are directly proportional to frequency and also the energy of the IR absorption. IR absorption data is generally plotted with wavenumber on x axis and absorption/transmission intensity on y axis <sup>13</sup>.

Although IR spectroscopy has been used for more than 70 years, Fourier transform spectrometers (FT-IR) have recently replaced these dispersive instruments for most applications due to their superior speed and sensitivity so that it enables to analyze the most difficult samples. Unlike dispersive IR spectrometers, FT-IR examines all frequencies simultaneously.

FT-IR mainly composed of three compartments which are radiation source, interferometer and detector. The same types of radiation sources are used for both dispersive and Fourier transform spectrometers. However, the source is more often water-cooled in FTIR instruments to provide better power and stability. The main difference in FT-IR is the replacement of monochromator with an interferometer, which divides radiant beams, generates an optical path difference between the beams and then recombines them in order to produce repetitive interference signals measured as a function of optical path difference by a detector <sup>14</sup>. The most commonly used interferometer is a Michelson interferometer. It consists of three active components which are a moving mirror, a fixed mirror, and a beamsplitter. The two mirrors are perpendicular to each other <sup>14</sup>. The beamsplitter which is a semi-reflecting device generally produced by depositing a thin film of germanium onto a flat KBr substrate. Radiation of IR source is collimated and directed to the interferometer, and impinges on the beamsplitter. At the beamsplitter, half of the beam is transmitted to the fixed mirror and the other half of the beam is reflected towards the moving mirror. After these divided beams are reflected from each mirror, they are recombined at the beamsplitter <sup>14</sup>.

Attenuated Total Reflection (ATR) technique enables to examine the surface of the samples and it is mounted to a FTIR spectrometer. The principle of ATR is based total internal reflection. The most important part of the ATR is the prism where the sample is directly placed. The angle of incidence of the light beam is arranged according to reflect the total beam at the prism-sample interface. Then, the beam leaving the prism is attenuated by the sample as a result of selective absorption at certain wavelengths <sup>15</sup>. A simplified optical layout of a typical FTIR spectrometer is illustrated in Figure 2.4.

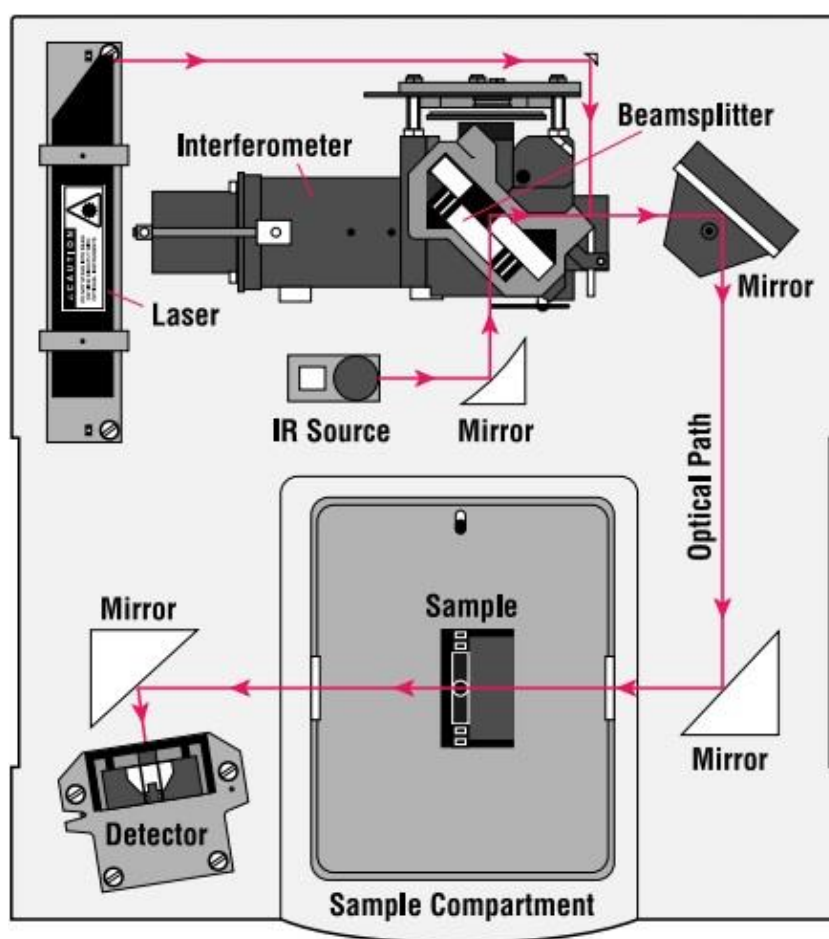


**Figure 2.4** The simplified optical layout of the typical FT-IR spectrometer <sup>14</sup>.

In this study, Thermo Scientific Nicolet iS10 model and Bruker Vertex v80 model FT-IR spectrometers with an attenuated total reflection (ATR) cell were used to collect IR

spectra. Approximately, 1 mg of each supported IL sample was placed on the ATR prism and each IR spectrum was collected in air at room temperature with a resolution of  $4\text{ cm}^{-1}$  and an average of 512 scans. Relative ATR shifts were corrected according to the wavelength dependent factor- penetration depth of the IR beam of the spectrometer- to adjust the relative peak intensities. Penetration depth of the spectrometer is given in the equation below where  $d_p$ ,  $\lambda$ ,  $\theta$ ,  $n_1$ , and  $n_2$  are the penetration depth, wavelength, incident angle, respectively.

$$d_p = \frac{\lambda}{2\pi n_1 \sqrt{\sin^2 \theta - \left(\frac{n_2}{n_1}\right)^2}}$$

In order to assign the peaks, the study of Noack *et al.*<sup>16</sup> on the peak assignments of bulk imidazolium ILs was used. A representative image of the determination of the main peaks on the absorbance spectrum of IL was given in Figure 2.5.

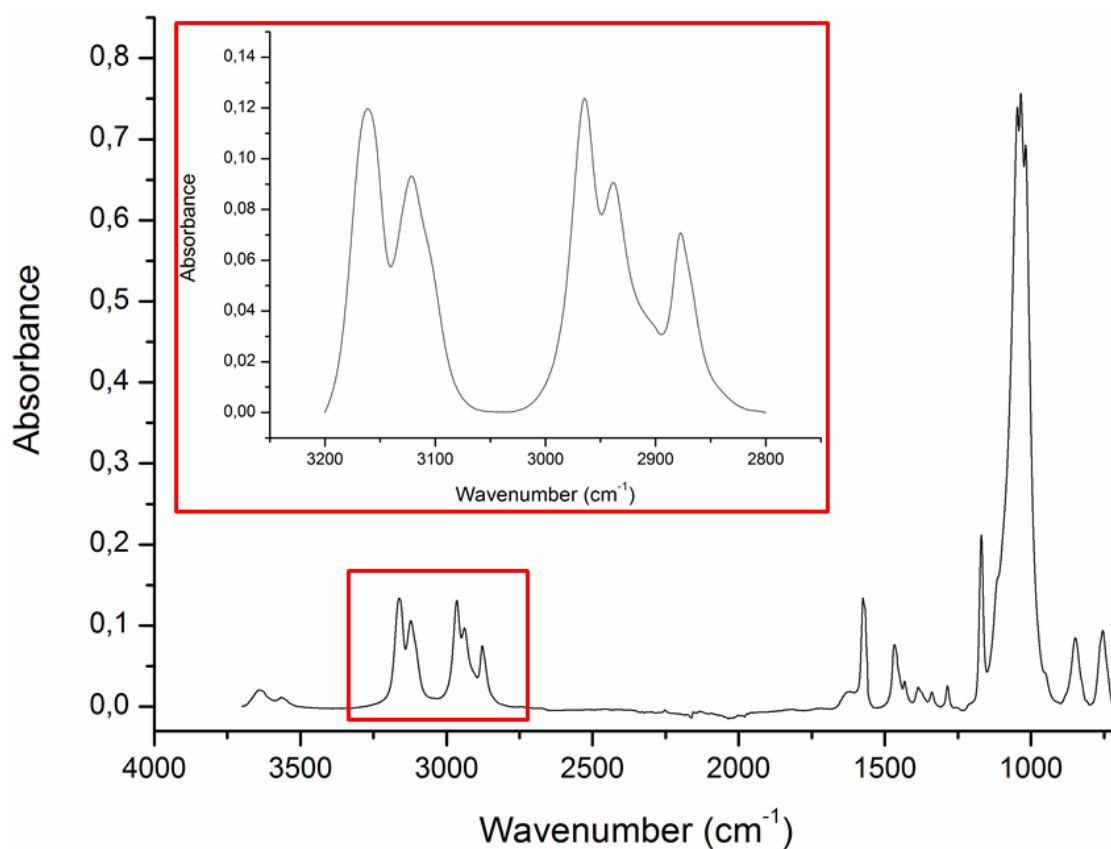


**Figure 2.5** A representative image of main peak assignments on the absorbance spectra of ILs.

#### **2.2.4. Scanning Electron Microscopy Coupled with Energy-Dispersive X-Ray Spectroscopy (SEM/EDX)**

Scanning electron microscopy (SEM) was first developed by Max Knoll in 1935<sup>17</sup>. SEM enables to collect the topography and composition images of the sample surface by using a high-energy beam of electrons. The difference of SEM from the other microscope is the electrons used to form images instead of light. This difference gives some advantages to SEM over traditional microscopes such as large field of depth which provides to focus on various specimens at the same time, higher resolution to magnify the samples to higher levels<sup>18</sup>.

The electron beam is produced at the top of the microscope by an electron gun and the beam goes through a vertical path to the microscope which is evacuated. By traveling through electromagnetic fields and lenses, beam reaches to the sample in a sequence of horizontal strips. When the electrons interact with the atoms on the sample surface, the signals of these interactions can be interpreted by the computer which directly gives information about the surface topography. SEM images can be produced by four different types of signals which belong to backscattered electrons, secondary electrons, x-rays and visible light (cathodoluminescence)<sup>18-19</sup>. During the electron beam scans on the sample surface, some of the high energy electrons produce inelastic interactions with the sample atoms which results in the scatter of electrons from the surface. When these scattered electrons lose very low energy during this process, they are called back-scattered electrons and they limit the focus of the microscope on the sample<sup>20</sup>. The resolution of the images depends on the radius where the backscattered electrons are produced. Furthermore, the intensity of the backscattered electron signal is affected by the composition of the sample<sup>21</sup>. During the electron beam scans, as a result of the interaction of high energy electrons with the valence electrons of the sample atoms, these valence electrons are released from the atoms. If the

electrons have energies less than 50 eV, they are named as secondary electrons which forms the most commonly used images in SEM technique.<sup>22</sup> The image of SEM and the layout of the microscope were given in Figure 2.6.

The X-ray images are collected by interactions of the electrons and sample surface by converting the X-rays into voltage signals. The signals further amplified and shaped by a linear amplifier and then passed to a computer x-ray analyzer where the data is displayed as a histogram of intensity by voltage.<sup>23</sup> Energy dispersive X-ray spectroscopy (EDX) enables to find out the particular elements on the sample surface and also their relative proportions such as atomic %.

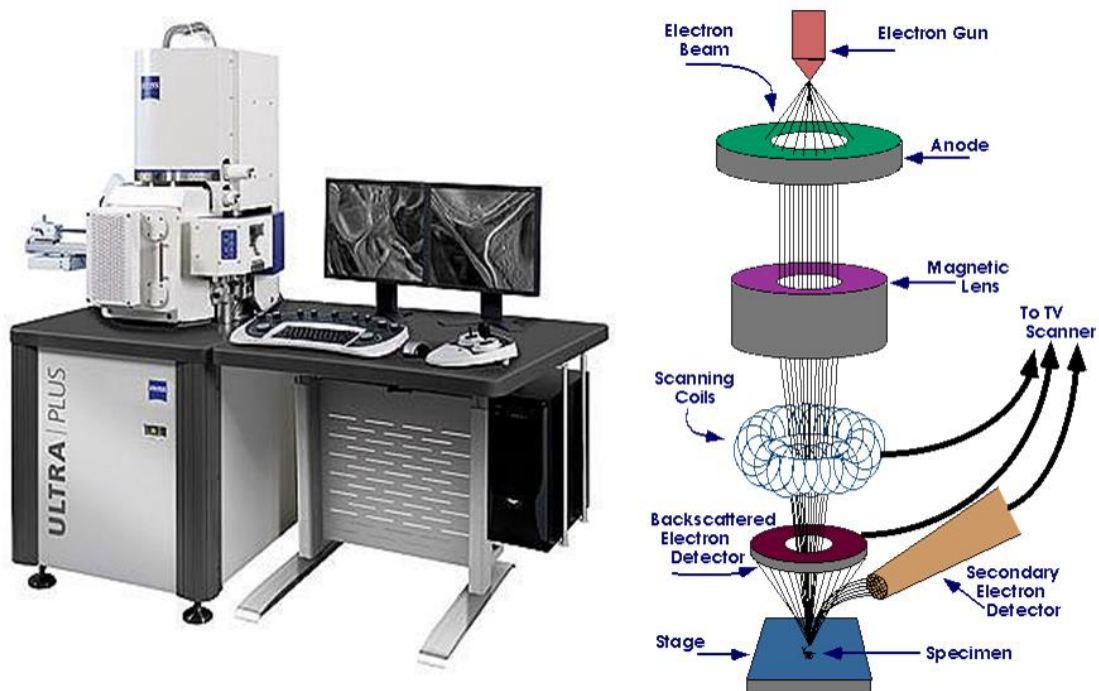


**Figure 2.6** The image of scanning electron microscopy (left)<sup>23</sup> and the layout of the microscope (right)<sup>18</sup>.

In this study, SEM images were collected with a Zeiss Ultra Plus (FESEM) Model Scanning electron microscope with a SE detector by following the procedure given below.

- Samples were applied on a carbon tape to prevent the charging effect of supports
- The chamber where the samples were loaded was evacuated till it reaches to  $10^{-6}$  mbar.
- Accelerating voltage (EHT) was set as 5 kV for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 1 kV for SiO<sub>2</sub>, TiO<sub>2</sub> and MgO.
- SEM images were collected with SE detector at the magnifications of 30K $\times$  and 100K $\times$ .
- Working distance for the samples coated on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was 5.3 mm while for the samples on SiO<sub>2</sub>, TiO<sub>2</sub> and MgO, working distance was within the range of 3.1-3.4 mm.
- All EDX images were collected at a magnification of 100K $\times$  with an EHT of 5 kV and working distance of 6.7 mm for ILs on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, EHT of 10 kV and working distance in the range of 5.0-5.7 mm for ILs on SiO<sub>2</sub>, TiO<sub>2</sub> and on MgO.

#### **2.2.5. Brunauer–Emmett–Teller Surface Area Analyses (BET)**

The specific surface area, pore volume of a porous powder material is determined by Brunauer–Emmett–Teller (BET) method which depends on the physical adsorption of a gas on the surface of the sample. Physical adsorption results from Van der Waals forces between the gas molecules and the surface of the sample. Measurements are usually performed at the temperature of liquid nitrogen and the amount of gas adsorbed on the surface monolayer can be measured by the volumetric or continuous flow procedure. BET measurements can be performed as multipoint or single point.

In multipoint measurements, the data are interpreted at least three different  $P/P_0$  values according to the BET adsorption isotherm given in equation 1 where  $P_0$ ,  $P$ ,  $V_a$ ,  $V_m$ ,  $C$  are the saturated pressure of adsorbate gas, partial pressure of adsorbate gas, volume of gas adsorbed at standard temperature and pressure, volume of gas to produce a monolayer on the surface, respectively. For single point measurements,  $V_a$  value obtained from the single measurement of  $P/P_0$  value and then surface area is calculated from the equation 2. Before each measurement the surface of the sample has to be outgassed to remove the gases or vapors physically adsorbed on the surface. Outgassing conditions such as temperature and time have to be chosen according to the sensitivity of the sample for an accurate measurement of sample properties.<sup>24</sup>

$$\frac{1}{[V_a(\frac{P_0}{P}-1)]} = \frac{C-1}{V_m C} \frac{P}{P_0} + \frac{1}{V_m C} \quad (\text{Equation 1})$$

$$S = \frac{V_m N_a}{m \cdot 22400} \quad (\text{Equation 2})$$

In this study, BET analyses were performed on Quantachrome Instrument Quadrasorb SI model instrument. Sample amounts loaded into the instrument differ from 0.17 to 0.28 g. Samples were degassed for 4 h at 60 °C which is far below the determined stability limit of the least stable IL on each support. Analyses were performed in 9 mm-small bulbs. Measurements were repeated at 60 different points for each sample in between  $10^{-5}$  – 0.3  $P/P_0$ . Micropore analyses were performed at 40 different points for each sample in between  $10^{-5}$  – 0.01  $P/P_0$ . 10 different points were measured in between the 0.01 – 0.05  $P/P_0$  and also 0.05 – 0.3  $P/P_0$ .

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## Chapter 3

### STRUCTURAL FACTORS CONTROLLING THERMAL STABILITY OF IMIDAZOLIUM IONIC LIQUIDS WITH 1-N-BUTYL-3-METHYLMIDAZOLIUM CATION ON $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

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#### Abstract

Structural factors determining thermal stability limits of imidazolium ionic liquids (ILs) with 1-*n*-butyl-3-methylimidazolium, [BMIM]<sup>+</sup>, cation on one of the most commonly used metal-oxide support,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, were determined by thermogravimetric analysis complemented by infrared (IR) spectroscopy. IR results show that inter-ionic interaction strength in ILs increases as their anion structure varies in the following order: [NTf<sub>2</sub>]<sup>−</sup> < [SbF<sub>6</sub>]<sup>−</sup> < [BF<sub>4</sub>]<sup>−</sup> < [TfO]<sup>−</sup> < [OS]<sup>−</sup> < [HSO<sub>4</sub>]<sup>−</sup> < [TOS]<sup>−</sup> < [DBP]<sup>−</sup> < [OAc]<sup>−</sup>. TGA data illustrate a strong dependence of thermal stability limits on inter-ionic interactions. Thermal stability limits of both bulk and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported [BMIM]<sup>+</sup>-based ILs increase with decreasing inter-ionic interaction strength. Thermal stability limit of IL with octyl sulfate anion was lower than that of analogous IL with hydrogen sulfate anion, because of its exceptionally large anion size. Moreover, the effect of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> on IL thermal stability conditions becomes dominant with decreasing inter-ionic interactions in ILs.

**Keywords:** SCILL; SILP; imidazolium ionic liquid; thermal stability limit

### 3.1. Introduction

Ionic liquids (ILs) are considered as new generation green solvents with extremely low volatility consisting of organic/inorganic cation/anion pairs with almost endless structure combinations. Such high degree of structural flexibility offers tunable chemical and physical properties<sup>1-4</sup>. With these tunable properties, they are excellent choice for a wide range of applications, such as synthesis<sup>5</sup>, catalysis<sup>6</sup>, electrochemistry<sup>7</sup> and separation<sup>8</sup>. ILs are immobilized on a support material in some of these emerging application areas<sup>9,10</sup>. In catalytic applications, for example, ILs are utilized in either supported ionic liquid phase (SILP) catalysts<sup>11-13</sup> or solid catalysts with ionic liquid layer (SCILL)<sup>14-16</sup>. They are coated on support materials, which are usually cheap high-surface area metal-oxides, in both of these applications.

Practically, ILs are required to protect their structural integrity at any application conditions. The structural integrity is lost either when ILs thermally decompose<sup>17</sup> or when they partially evaporate (in general, accompanied by partial decomposition<sup>10</sup>) or leach out from the system<sup>18</sup>. Thermal stability limits of bulk ILs have been studied extensively. Results of these studies generally illustrate that both cation and anion influence the thermal stability limits of ILs significantly. A recent review article by Maton et al. presents a thorough analysis of the literature on thermal stability of bulk ILs<sup>18</sup>. Among the number of studies, data presented by Ngo et al. illustrate an interesting point<sup>19</sup>. Their thermogravimetric analysis (TGA) indicate that thermal decomposition temperatures of imidazolium-based ILs change by more than 100 °C when the pan material used for TGA measurements was changed from alumina to aluminum. Following this report, Kosmulski et al. investigated such phenomenon in more detail and illustrated that thermal decomposition temperature of imidazolium ILs decrease in the presence of acidic silica<sup>20</sup>.

According to their results bulk 1-*n*-butyl-3-methylimidazolium triflate was thermally stable at 200 °C. However, addition of acidic silica resulted in thermal decomposition at the same temperature<sup>20</sup>. These results indicate that structural factors determining thermal stability of ILs are not only limited with the structure of cation/anion pair but also include interactions of ILs with their environment. These interactions become more prominent when the IL-assisted materials are considered. In catalytic applications of ILs, for example in SILP or SCILL type catalysts, ILs interact with active metal sites and metal-oxide supports. Thus, stability limits determined for bulk ILs are not directly applicable to these systems. For such systems, structural factors determining thermal stability limits of ILs on metal-oxide supports are required to be elucidated. Here, we report our TGA results on nine different imidazolium-based ILs supported on one of the most commonly used catalytic metal-oxide supports,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. ILs were chosen from a family of those with the same cation, 1-*n*-butyl-3-methylimidazolium, [BMIM]<sup>+</sup>, and with varying anions. Each IL structure was characterized by Fourier Transform Infrared (FT-IR) spectroscopy to elucidate structural factors determining the differences in thermal stability limits of both bulk and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported [BMIM]<sup>+</sup>-based ILs.

## 3.2. Materials and Methods

### 3.2.1. Materials and Sample Preparation

ILs,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, acetone and methanol were purchased from Sigma-Aldrich with the highest available purity.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was calcined at 500 °C for 5 h in flowing O<sub>2</sub>. Temperature ramp rate was 3 °C/min for the calcination process. 200 mg of corresponding IL was dissolved in 5 ml of either acetone or methanol. 1 g freshly calcined  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was immersed into prepared IL-solvent mixture. Resulting mixture was dried in a vacuum oven for a day at 70 °C and powder IL coated

metal-oxide samples were obtained. Such drying procedure was confirmed by checking the derivative onset temperature of each compound which was significantly higher than 70 °C as suggested by Clough et al.<sup>26</sup>. The corresponding IL loading was approximately 16.7 wt. %.

### 3.2.2. FT-IR Spectroscopy

Thermo Scientific Nicolet iS10 model FT-IR spectrometer with an attenuated total reflection (ATR) cell was used to collect IR spectra. Each IR spectrum, average of 512 scans, was collected in air at room temperature with a resolution of 4 cm<sup>-1</sup>. Peak assignments were done according to literature<sup>21</sup>.

### 3.2.3. Scanning Electron Microscopy Coupled with Energy-Dispersive X-Ray Spectroscopy (SEM/EDX)

Zeiss Ultra Plus (FEG-SEM) Model Scanning electron microscope with a SE detector was used for SEM imaging. Samples were applied on a carbon tape and the images were obtained at magnifications of 30K $\times$  and 100K $\times$  with an accelerating voltage (EHT) of 5 kV and a working distance of 6.7 mm. All EDX images were collected at a magnification of 100K $\times$  with an EHT of 5 kV and working distance of 6.7 mm.

### 3.2.4 Thermogravimetric Analysis

TGA measurements were performed on a TA Instruments TGA Q500 model instrument at a heating rate of 10 °C/min in flowing nitrogen within a temperature range of 24 to 800 °C. Approximately 15 mg of samples were placed in platinum pans and purged with nitrogen for 1 h. Onset temperature values ( $T_{\text{onset}}$ ) reported here were obtained from the interception of two linear functions, one originating from the zero weight loss level and the other one tangential to the

declining portion of the weight change line. Because  $T_{\text{onset}}$  typically overestimates the thermal decomposition temperature, especially at this relative high heating rate, all of our analyses were based on the  $T'_{\text{onset}}$  values obtained from the onsets of derivative weight % change lines. Reproducibility measurements performed under identical conditions indicate that results are reproducible within an error range of  $\pm 3$  °C.

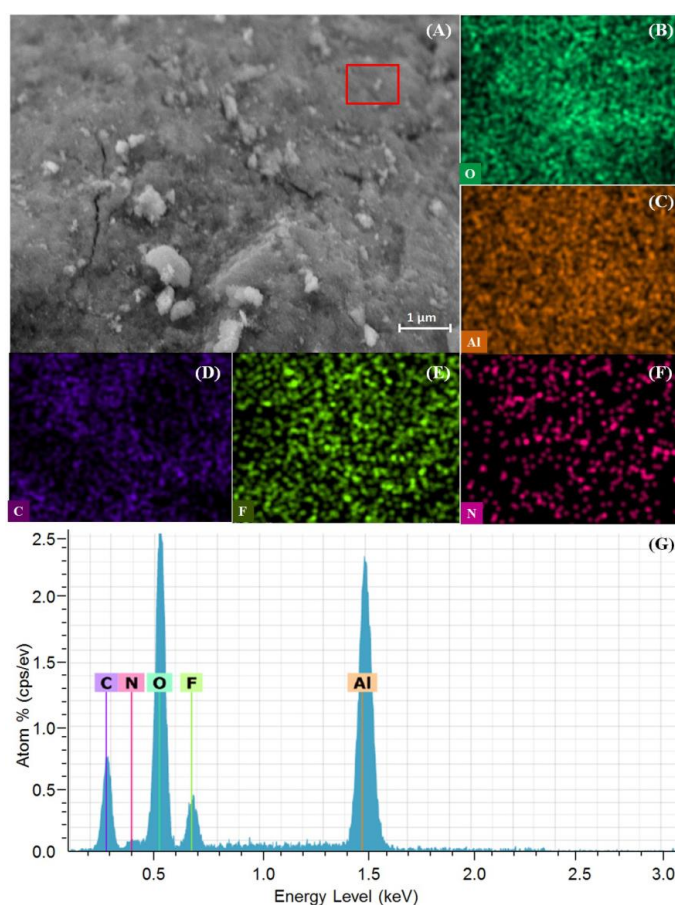


**Figure 3.1** (A) A representative SEM image of [BMIM][BF<sub>4</sub>] on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. EDX map showing the distribution of individual atoms: (B) Oxygen; (C) Aluminum; (D) Carbon; (E) Fluorine; and (F) Nitrogen. (G) Atomic distribution diagram by EDX.

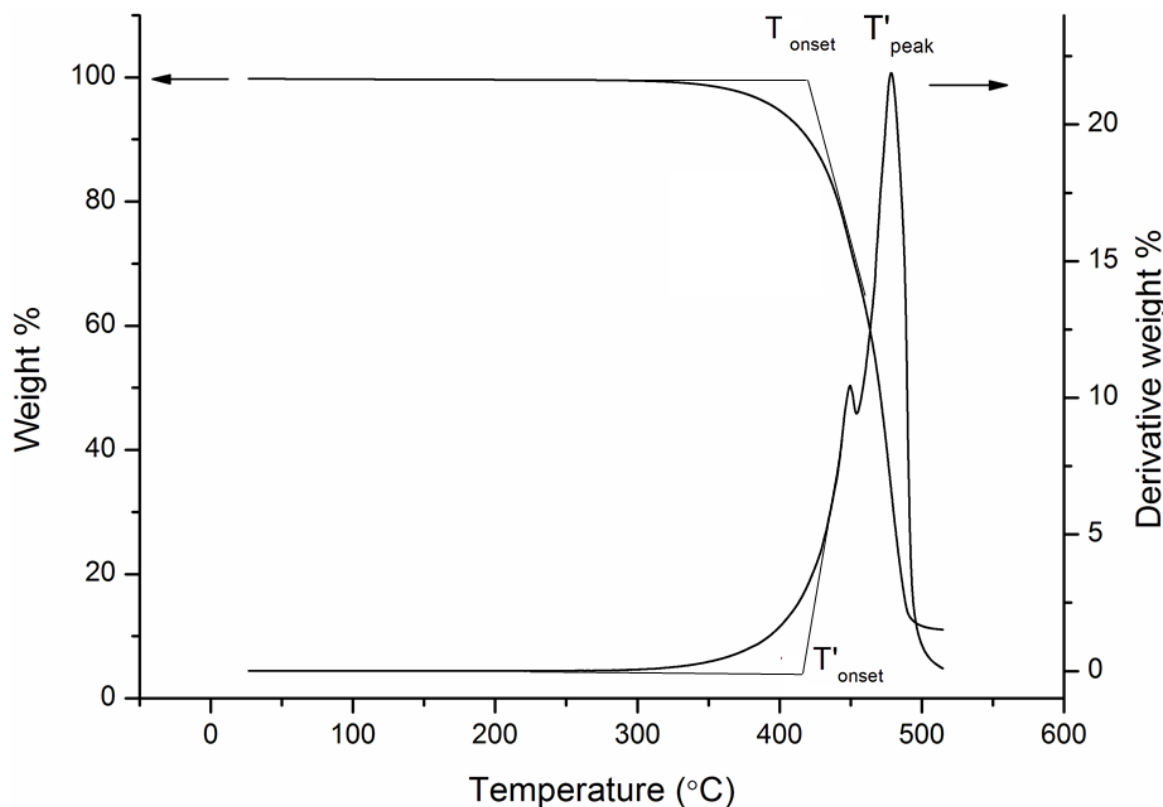


**Figure 3.2** Determination of  $T_{\text{onset}}$ ,  $T'_{\text{onset}}$ , and  $T'_{\text{peak}}$  values on a representative TGA data obtained for [BMIM][NTf<sub>2</sub>].

### 3.3. Results and Discussion

When comparing the thermal stability limits of different ILs on metal-oxides, having a uniform distribution of ILs on surfaces is crucial. Any inconsistency in the distribution of these layers might alter IL-metal-oxide interactions significantly resulting in incomparable results. The uniformity of IL distribution was confirmed by SEM imaging complemented by EDX mapping performed on several random locations on each sample. Figure 3.1 shows a representative SEM/EDX image set that was obtained for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported [BMIM][BF<sub>4</sub>]. The EDX mapping (shown in Figure 3.1-B to F) confirms the uniform distribution of O and Al atoms of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and C, F, and N atoms of [BMIM][BF<sub>4</sub>] over the surface. Moreover, analyzing the relative areas

under individual peaks in EDX atomic density distribution plots confirms the stoichiometric IL loading within 5 % error at every random location of samples investigated. Furthermore, thickness values of IL layers for each sample estimated by the BET-determined surface area and pore volume values are consistent with the expected values calculated from the IL amount per unit surface area of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for each samples. Details on the BET measurements are provided in the Appendix A1. Thus, we infer that  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported ILs investigated here have comparable uniformity in terms of IL layer distribution.

Any mass loss measured during TGA is linked to either thermal decomposition or evaporation of ILs during temperature ramp in continuous flow of nitrogen gas <sup>22,23</sup>. In either case, structural integrity is lost <sup>18</sup>. Here we refer the temperature at which such changes start to occur to the thermal stability limit, which can be typically indexed by  $T_{\text{onset}}$ ,  $T'_{\text{onset}}$ , and  $T'_{\text{peak}}$  values as given on a representative TGA profile obtained for [BMIM][NTf<sub>2</sub>] in Figure 3.2. These values for both bulk and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported ILs are given in Table 3.1. Among these,  $T'_{\text{onset}}$  provide more conservative limits than the other two, thus we prefer them over the others.

It is known that onset values depend strongly on the operating factors of TGA, such as heating rate, type of gas flowed, sample amount and sample pan type as discussed in recent literature <sup>24,25</sup>. Presence of such factors directly limits the comparison of data from different sources with different experimental parameters. Thus, we performed our measurements under identical conditions to obtain self-consistent and comparable results. Moreover, we focus directly on evaluating the effects of structural factors on short-term thermal stability limits in rather relative manner. As an on-going study, we are also investigating long-term stability limits of metal-oxide-supported ILs by isothermal gravimetric measurements. However, such isothermal measurements are not suitable for the purpose of this present study. Because, here our aim is to

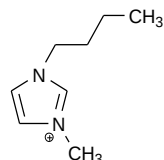
obtain comparable quantitative values for the stability limits with high temperature resolution.

Only such high resolution values obtained by dynamic measurements can help to elucidate any

**Table 3.1.** Structural details\*, TGA results and FT-IR fingerprints of [BMIM]<sup>+</sup>-based ILs investigated.

| Anion Structure | Ionic Liquid Name                                                        | Abbreviation              | Bulk ILs (°C)      |                     |                    | $\gamma$ -Al <sub>2</sub> O <sub>3</sub> -supported ILs (°C) |                     |                    | $\nu(\text{C2H})$ (cm <sup>-1</sup> ) | $\nu(\text{C4,5H})$ (cm <sup>-1</sup> ) |
|-----------------|--------------------------------------------------------------------------|---------------------------|--------------------|---------------------|--------------------|--------------------------------------------------------------|---------------------|--------------------|---------------------------------------|-----------------------------------------|
|                 |                                                                          |                           | T <sub>onset</sub> | T' <sub>onset</sub> | T' <sub>peak</sub> | T <sub>onset</sub>                                           | T' <sub>onset</sub> | T' <sub>peak</sub> |                                       |                                         |
|                 | 1- <i>n</i> -Butyl-3-methylimidazolium acetate                           | [BMIM][OAc]               | 222                | 210                 | 246                | 173                                                          | 135                 | 221                | 3056                                  | 3140                                    |
|                 | 1- <i>n</i> -Butyl-3-methylimidazolium dibutyl phosphate                 | [BMIM][DBP]               | 274                | 258                 | 293                | 173                                                          | 162                 | 206                | 3077                                  | 3145                                    |
|                 | 1- <i>n</i> -Butyl-3-methylimidazolium tosylate                          | [BMIM][TOS]               | 346                | 334                 | 379                | 244                                                          | 218                 | 288                | 3102                                  | 3148                                    |
|                 | 1- <i>n</i> -Butyl-3-methylimidazolium hydrogen sulfate                  | [BMIM][HSO <sub>4</sub> ] | 348                | 335                 | 389                | 240                                                          | 220                 | 277                | 3103                                  | 3148                                    |
|                 | 1- <i>n</i> -Butyl-3-methylimidazolium octyl sulfate                     | [BMIM][OS]                | 314                | 286                 | 353                | 189                                                          | 170                 | 237                | 3105                                  | 3149                                    |
|                 | 1- <i>n</i> -Butyl-3-methylimidazolium trifluoromethanesulfonate         | [BMIM][TfO]               | 382                | 382                 | 420                | 303                                                          | 273                 | 337                | 3115                                  | 3153                                    |
|                 | 1- <i>n</i> -Butyl-3-methylimidazolium tetrafluoroborate                 | [BMIM][BF <sub>4</sub> ]  | 381                | 376                 | 396                | 317                                                          | 263                 | 389                | 3122                                  | 3161                                    |
|                 | 1- <i>n</i> -Butyl-3-methylimidazolium hexafluoroantimonate              | [BMIM][SbF <sub>6</sub> ] | 387                | 385                 | 413                | 317                                                          | 269                 | 363                | 3123                                  | 3166                                    |
|                 | 1- <i>n</i> -Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide | [BMIM][NTf <sub>2</sub> ] | 421                | 412                 | 478                | 303                                                          | 296                 | 340                | 3124                                  | 3159                                    |

\*Cation structure, [BMIM]<sup>+</sup>:



direct dependency of thermal stability limits on quantified structural parameters of ILs. A heating rate of 10 °C/min clearly differentiates results of present study from any long-term stability limits measured by isothermal or slow heating gravimetric measurements and moves our focus to rather short-term limits. These short-term limits can be considered as the upper temperature limits at which bulk and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported ILs can be exposed under preparation and working conditions. In any case structural factors determining such limits are needed to be elucidated to be able to set the operating conditions.

Although the ILs considered here have the same cation, their structures differ in terms of anion structures.  $T'_{\text{onset}}$  values for the bulk ILs range from 210 to 412 °C as given in Table 3.1. Thus, we infer that anion structure has a significant effect on thermal stability limits as discussed by Clough et al.<sup>26</sup>. According to these results [BMIM][NTf<sub>2</sub>] and [BMIM][OAc] has the highest and lowest short-term thermal stability limits, respectively. Moreover, results summarized in Table 3.1 further indicate that ILs considered here are thermally stable on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> up to a temperature range of 135 to 296 °C. These values are significantly lower than those of bulk ILs. For example, bulk [BMIM][NTf<sub>2</sub>] has a  $T'_{\text{onset}}$  value of 412 °C, however, it decreases to 296 °C when the same IL is supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. These results indicate that not only the anion structure but also the interactions of ILs with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> control their thermal stability limits when they are coated on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, consistent with the results of Ngo et al.<sup>19</sup> and Kosmulski et al.<sup>20</sup>.

For both bulk and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported [BMIM]-based ILs, the short-term thermal stability limits decrease as the anion structure changes in the following order: [NTf<sub>2</sub>]<sup>-</sup> > [TfO]<sup>-</sup> ~ [SbF<sub>6</sub>]<sup>-</sup> ~ [BF<sub>4</sub>]<sup>-</sup> > [HSO<sub>4</sub>]<sup>-</sup> > [TOS]<sup>-</sup> > [OS]<sup>-</sup> > [DBP]<sup>-</sup> > [OAc]<sup>-</sup>. Here we note that the TGA results of [TfO]<sup>-</sup>, [SbF<sub>6</sub>]<sup>-</sup>, and [BF<sub>4</sub>]<sup>-</sup> are not distinguishable within the error range of our measurements. Among these, fluorinated anions such as [NTf<sub>2</sub>]<sup>-</sup>, [SbF<sub>6</sub>]<sup>-</sup>, [BF<sub>4</sub>]<sup>-</sup>, and [TfO]<sup>-</sup>

are known as weak hydrogen-bond acceptors, which result in non-coordinating ILs when combined with imidazolium ring. Thus, we infer that changes in anion structure affect the interactions between cation/anion pairs as well as those between ILs and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. To probe and quantify these effects, the acidity levels of individual ILs were considered. The most acidic proton on imidazolium cation is the proton located at C2 position, which is the carbon atom between two N atoms of imidazolium ring<sup>21,27</sup>. This proton is responsible for strongly localized and directional hydrogen bond between cation and anion. Thus, it contributes to the inter-ionic cohesive energy, which decreases with increasing acidity of this proton, *i.e.* with increasing C2–H bond strength<sup>21,27</sup>. Acidity of this proton was quantified by the stretching vibration frequency of C2–H bond,  $\nu(\text{C2H})$ . Because all of the ILs considered here have the same cation, any change in the anion structure results in change in the inter-ionic interaction strength and acidity of C2H. In general, a higher  $\nu(\text{C2H})$  value represents a higher energy of the C2–H bond, thus a higher C2H acidity<sup>28,29</sup>.  $\nu(\text{C2H})$  values of bulk ILs, given in Table 3.1, varies from 3056 cm<sup>-1</sup> for IL with [OAc]<sup>-</sup> anion to 3124 cm<sup>-1</sup> for IL with [NTf<sub>2</sub>]<sup>-</sup> anion. These IR results of bulk ILs confirm that acidity of C2H decreases in the order [NTf<sub>2</sub>]<sup>-</sup> > [SbF<sub>6</sub>]<sup>-</sup> > [BF<sub>4</sub>]<sup>-</sup> > [TfO]<sup>-</sup> > [OS]<sup>-</sup> > [HSO<sub>4</sub>]<sup>-</sup> > [TOS]<sup>-</sup> > [DBP]<sup>-</sup> > [OAc]<sup>-</sup> consistent with data presented by Lungwitz et al.<sup>30</sup>. Because  $\nu(\text{C2H})$  stretching frequency is inversely correlated with the cohesive energy between anion and cation, we predict the inter-ionic interaction strength changes in the reverse order: [NTf<sub>2</sub>]<sup>-</sup> < [SbF<sub>6</sub>]<sup>-</sup> < [BF<sub>4</sub>]<sup>-</sup> < [TfO]<sup>-</sup> < [OS]<sup>-</sup> < [HSO<sub>4</sub>]<sup>-</sup> < [TOS]<sup>-</sup> < [DBP]<sup>-</sup> < [OAc]<sup>-</sup>. This conclusion is consistent with the recent report by Cláudio et al.<sup>31</sup> tabulating the hydrogen-bond basicity of [BMIM]<sup>+</sup>-based ILs estimated by COSMO-RS simulations. As an extension to our analysis focusing on C2H acidity, we also plotted hydrogen-bond interaction energy values ( $-E_{\text{HB}}$ ) against our  $\nu(\text{C2H})$  values both in Figure 3.3 and 3.4. These plots confirm a strong inverse correlation between  $-E_{\text{HB}}$  and C2H acidity. Thus,

we confirm that hydrogen bond basicity of the anion is directly controlled by C2H acidity of the imidazolium ring as expected. As  $\nu(\text{C2H})$  values increase, inter-ionic interaction energies of the IL decrease significantly accompanied by a strong decrease in  $-E_{\text{HB}}$  values.

Figure 3.3 further presents the variation of  $T'_{\text{onset}}$  values of both bulk and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported ILs with increasing  $\nu(\text{C2H})$  frequency. Again the data present a strong correlation between  $T'_{\text{onset}}$  and C2–H bonding strength. Thermal stability limits of bulk ILs increase linearly with increasing C2–H bonding strength. Thus, we infer that C2H acidity of imidazolium ring is one of the structural factors determining short-term thermal stability limits.

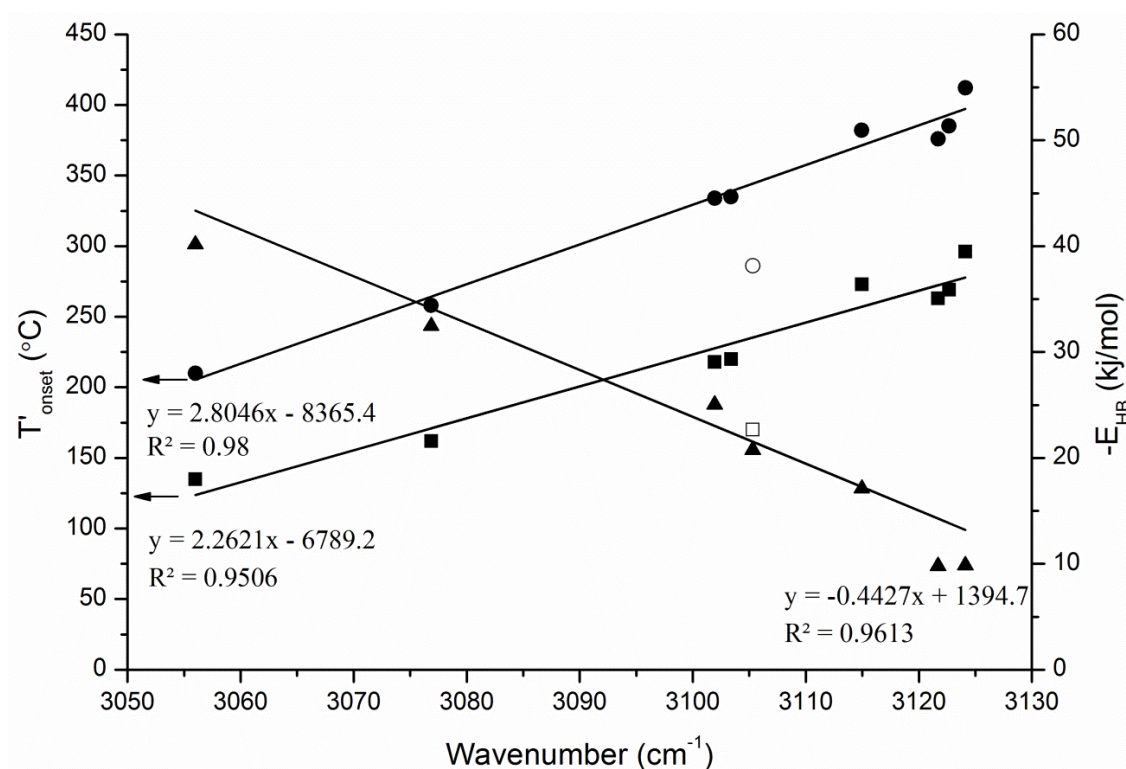


**Figure 3.3.** Variation of thermal stability limits ( $T'_{\text{onset}}$ ) of bulk and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported ILs with increasing  $\nu(\text{C2H})$ ; bulk ILs (●) and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported ILs (■); open symbols indicate the values of [BMIM][OS]. Secondary y-axis shows the variation of hydrogen-bond interaction energy ( $-E_{\text{HB}}$ ) (▲) with increasing C2–H stretching vibration.  $-E_{\text{HB}}$  data are taken from <sup>31</sup>.

This structural parameter controls the inter-ionic interactions, thus as the inter-ionic interactions become stronger, initiation of decomposition reaction becomes easier, resulting in significant reductions in thermal stability limits. It is known that thermal decomposition of bulk ILs occur either by a nucleophilic or basic attack of the anion on the cation (as such in E2 Hofmann elimination or in S<sub>N</sub>2 nucleophilic substitution mechanisms) or by the reaction of anion fragments with the cation<sup>26,32–34</sup>. In either case, the decomposition reaction becomes easier with increasing anion-cation interactions as our data confirm. It can be concluded by analyzing the shapes of TGA profiles that thermal decomposition mechanisms observed in bulk and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported ILs involve at least a two-step process as seen in Figure 3.2 and in Appendix A1. I. Ivan et al. reported that the hemolytic bond scission between nitrogen and the alkyl group is critical in the thermal stability of poly(N-vinylimidazole) polymers by combining differential scanning calorimetry, TGA coupled with mass spectrometry, and pyrolysis-gas chromatography/mass spectrometry<sup>35</sup>. Such decomposition mechanisms could also play role in the ILs considered here. We suggest that a detailed follow-up investigation combining different techniques, as reported by Ivan et al.<sup>35</sup>, complemented by quantum chemical calculations could reveal the elementary steps of the decomposition mechanisms of individual ILs.

Similar to the bulk ILs,  $T'_{\text{onset}}$  values of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported ILs presented in Figure 3.3 also show a linear alignment with C2H frequency. Here we note that IL with octyl sulfate anion, [OS]<sup>-</sup>, is an exception both in the case of bulk and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported ILs.  $T'_{\text{onset}}$  for this IL is approximately 50 °C lower than that of the IL with hydrogen sulfate, [HSO<sub>4</sub>]<sup>-</sup>, although  $\nu(\text{C2H})$  values of these two analogous ILs are close to each other (3105 and 3103 cm<sup>-1</sup>, respectively). Because, both of these ILs have the same cation, such difference in their  $T'_{\text{onset}}$  values is directly attributed to the size difference between their anions. As the size of anion becomes larger, there is an increased chance of anion to interact either with cation or  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>,

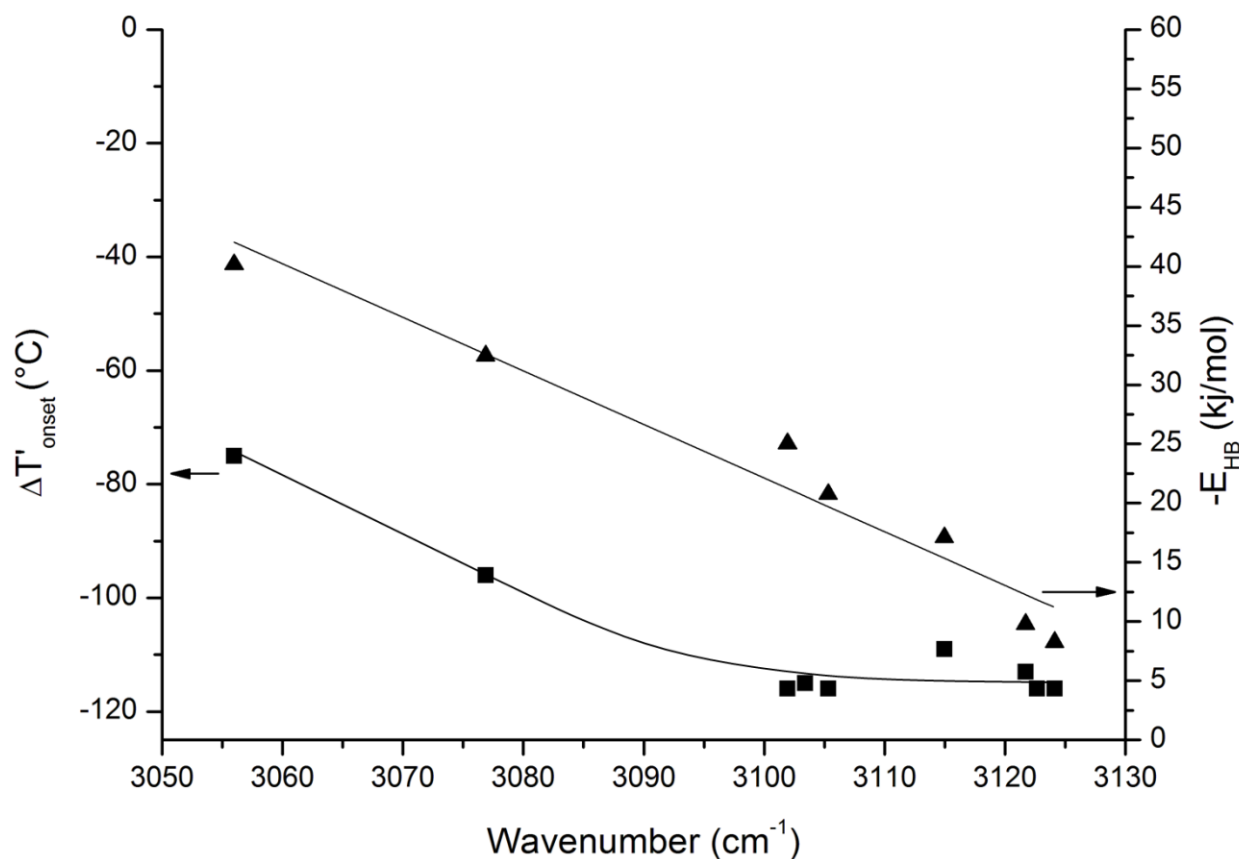


**Figure 3.4** Difference of  $T'_{\text{onset}}$  values between bulk and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported ILs ( $\Delta T'_{\text{onset}}$ ) as a function of increasing  $\nu(\text{C2H})$ . Secondary y-axis illustrates the variation of hydrogen-bond interaction energy ( $-E_{\text{HB}}$ ) with increasing  $\nu(\text{C2H})$ .  $-E_{\text{HB}}$  data are taken from <sup>31</sup>.

causing the IL to start decomposing at a lower temperature than analogous ILs with smaller anions. Thus, we infer that anion size is another factor that influences the thermal stability limits of both bulk and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported ILs, although it does not necessarily affect the C2H acidity significantly.

One interesting behavior that is apparent in Figure 3.3 is that variation of  $T'_{\text{onset}}$  values with increasing  $\nu(\text{C2H})$  for bulk ILs has a higher slope than that of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported ILs. Aiming at exploring why these slopes are different, difference of  $T'_{\text{onset}}$  values between bulk and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported ILs ( $\Delta T'_{\text{onset}}$ ) were investigated as a function of  $\nu(\text{C2H})$  of bulk ILs

(Figure 3.4). Data show that as  $\nu(\text{C2H})$  increases from 3056 to 3102  $\text{cm}^{-1}$ ,  $\Delta T'_{\text{onset}}$  value decreases from -75 to -116 °C and then remains almost constant within a frequency range of 3102 to 3124  $\text{cm}^{-1}$ . This decrease in  $\Delta T'_{\text{onset}}$  confirms that  $T'_{\text{onset}}$  of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported ILs deviate more from their bulk values with increasing C2H acidity, corresponding to a decrease in inter-ionic interaction energy. Thus, we infer that as cation-anion interaction weakens, interaction between  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and IL becomes dominant affecting their thermal stability limits more significantly.

### 3.4. Conclusions

Structural factors determining short-term thermal stability limits of a wide range of bulk and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported [BMIM]-based ILs were determined by TGA measurements complemented by FT-IR spectroscopy. Results presented here illustrate a strong influence of anion structure on thermal stability limits. As the acidic strength of the C2 proton on the imidazolium ring increases, the inter-ionic interaction strength decreases. Such decrease in inter-ionic interaction strength results in an increase in thermal stability limits of both bulk and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported ILs. In addition, when ILs are coated on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, the influence of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> on thermal stability limits becomes dominant as the inter-ionic interactions weaken, accompanied by an increase in C2H acidity. Besides these electronic structural factors, physical factors, such as the anion size, also play an important role in determining thermal stability limits. We suggest that determination of these structural factors and their effects on thermal stability limits are crucial in choosing proper ILs stable on metal-oxide supports at the application conditions.

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## Chapter 4

### A MODEL TO PREDICT MAXIMUM TOLERABLE TEMPERATURES OF METAL- OXIDE-SUPPORTED [BMIM]<sup>+</sup>-BASED IONIC LIQUIDS

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#### Abstract

The thermal stability limits of metal-oxide-supported ionic liquids (ILs) with 1-*n*-butyl-3-methylimidazolium cation, [BMIM]<sup>+</sup>, on most commonly used metal-oxides, SiO<sub>2</sub>, TiO<sub>2</sub>, γ-Al<sub>2</sub>O<sub>3</sub> and MgO are determined. Data show that stability limits of bulk and metal-oxide-supported ILs linearly increase with increasing acidity of C2 proton on imidazolium ring, controlling the inter-ionic interaction strength. Moreover, data also show that the presence of metal-oxide lowers the stability limits considerably. This effect becomes more significant as the surface acidity of the metal-oxide decreases from SiO<sub>2</sub> to MgO. This decrease in stability limits with increasing point of zero charge (PZC) of metal-oxide indicates that the interaction between IL and metal-oxide becomes the dominant factor rather than the inter-ionic interactions. Based on these findings a simple mathematical expression was developed as a function of PZC and inter-ionic interaction strength probed by  $\nu(\text{C2H})$  to predict the stability limits of [BMIM]<sup>+</sup>-based ILs immobilized on metal-oxides. Performance of the model was tested on several different ILs supported on different metal-oxides, including Fe<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub>. Results show that the model successfully predicts the maximum operating or tolerable temperatures of supported-[BMIM]<sup>+</sup>-based ILs with an average relative error less than 4.3 %. We suggest that the model developed here can help to choose proper ILs that are stable at the operating conditions of systems including ILs immobilized on metal-

oxides, such as in solid catalysts with ionic liquid layer (SCILL) or in supported ionic liquid phase (SILP) catalysts.

**Keywords:** SCILL; SILP; imidazolium ionic liquid; thermal stability limit, metal-oxide.

#### 4.1. Introduction

Ionic liquids (ILs) have gained tremendous attention in the last two decades thank to their tunable physicochemical properties suitable for numerous application areas, such as electrochemistry <sup>1</sup>, synthesis <sup>2</sup>, and catalysis <sup>3</sup>. Among these application areas, in catalysis, they offer new opportunities for immobilization of homogenous type catalysts on metal-oxides <sup>4</sup> as in supported ionic liquid phase (SILP) catalyst <sup>5</sup> or they can be utilized as a selective layer over the supported metal catalysts to offer enhanced selectivity as in solid catalysts with ionic liquid layer (SCILL) <sup>6</sup>. One limiting factor for these applications is that ILs tend to lose their structural integrity through thermal decomposition <sup>7</sup>, leaching out <sup>8</sup> or evaporation <sup>9</sup> under application conditions. Thermal stability of ILs has been investigated extensively <sup>8,10</sup>. There are several thorough review articles summarizing thermal stability data of ILs available in the literature <sup>8,11</sup>. In addition to these, very recently a detailed analysis on the stability limits of 66 different ILs was presented <sup>10</sup>. Furthermore, by using QSPR method on the literature values of 586 different ILs, quantitative structure-property relationship for the thermal decomposition temperatures of ILs was developed <sup>12</sup>. Thus, for bulk ILs, especially for most commonly studied imidazolium ILs, thermal stability limits are mostly identified. However, one of the main drawbacks of these studies is the fact that they only report the results of stability measurements, and do not focus on elucidating general criteria regarding structural factors controlling the stability limits. Although it was reported that the designation of such general criteria for assessing the thermal stability limits of ILs is not possible <sup>13</sup>,

understanding of such factors is crucial for their selection or rational design for specific applications requiring harsh operating conditions.

One other crucial aspect is that the thermal stability limits measured for bulk ILs do not necessarily represent their stability limits when they are coated on metal-oxides, such as in the case of SILP or SCILL systems. When they are coated on metal-oxides, there might be strong interactions between ILs and metal-oxides resulting in significant changes in their stability limits. In other words, metal-oxides might catalyze the thermal decomposition reaction lowering the stability limits significantly. The influence of alumina on thermal stability was proved by replacing pan-material used for the thermogravimetric analyses (TGA) measurements<sup>14</sup>. Upon replacement of aluminum pans with alumina, thermal stability of imidazolium-based ILs decreased approximately 100 °C. Following this study, thermal stability limits of ILs in the presence of acidic silica was investigated<sup>15</sup>. According to their results bulk 1-*n*-butyl-3-methylimidazolium triflate was thermally stable at 200 °C. Addition of acidic silica triggered the decomposition mechanism at a lower temperature than the case in bulk IL. Similarly, it was illustrated that the maximum tolerable temperature of bulk 1-butyl-3-methylimidazolium hexafluorophosphate, [BMIM][PF<sub>6</sub>], changes significantly when immobilized on SiO<sub>2</sub> (although it was reported to be even more stable than its bulk state when immobilized on Al<sub>2</sub>O<sub>3</sub>)<sup>16</sup>. These studies illustrate that thermal stability of ILs depend not only on the structural factors of ILs but also on other interactions with the environment, such as interactions between ILs and metal-oxides. Determination of such structural factors controlling thermal stability limits of ILs on metal-oxides is crucial for the proper choice of ILs for applications involving immobilization of ILs on metal-oxides.

Here, we report such structural factors based on nine different ILs supported on commonly used metal-oxide materials, SiO<sub>2</sub>, TiO<sub>2</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and MgO. ILs were chosen with

the same cation, 1-*n*-butyl-3-methylimidazolium, [BMIM]<sup>+</sup>, with various anions. By systematically changing the anion type and metal-oxide material, structural parameters controlling the stability limits were elucidated. Based on these findings a simple mathematical expression has been developed to predict the thermal stability limits of [BMIM]<sup>+</sup>-based ILs on metal-oxides, as a function of inter-ionic interactions in ILs (quantified by stretching infrared (IR) fingerprint of the acidic proton on imidazolium ring) and the surface acidity of metal-oxides (quantified by the point of zero charge (PZC)). The information provided here can be helpful in picking a proper IL which is stable at operating conditions for SCILL and SILP type catalysts.

## 4.2. Materials and Methods

### 4.2.1. Materials

All ILs, metal-oxides (SiO<sub>2</sub>, TiO<sub>2</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, MgO, Fe<sub>2</sub>O<sub>3</sub>, and CeO<sub>2</sub>), acetone and methanol were purchased from Sigma-Aldrich with the highest available purity. SiO<sub>2</sub>, TiO<sub>2</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and MgO were calcined for 5 h in flowing O<sub>2</sub> at 520, 500, 500, and 700 °C, respectively. CeO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> were calcined at 400 and 450 °C, respectively, for 2 h under O<sub>2</sub> flow. 200 mg of IL was dissolved in 5 mL of either methanol or acetone. IL-solvent mixtures were immersed in 1 g of freshly calcined metal-oxides. Remaining solvent in the prepared samples was evaporated in vacuum oven at 70 °C for 24 h to obtain powder samples. Thermal stability limits of ILs were taken into consideration for the determination of drying procedure as indicated in the literature<sup>17</sup>. IR spectra of the dried samples show none to almost negligible solvent/water peaks confirming the performance of the drying process. IL-loading of powder samples was approximately 16.7 wt. %.

### 4.2.2. Methods

#### 4.2.2.1. PZC Determination of Metal-oxides

PZC measurements were performed on a Zetasizer Nanoseries-Dynamic Light Scattering (DLS) instrument coupled with Malvern Multipurpose titrator. 4 mg of each metal-oxide was dispersed in 20 g of 0.1 M KNO<sub>3</sub> solution and ultrasonicated for approximately 5 min to improve dispersions. Dispersed samples were titrated with 0.25 M NaOH and HNO<sub>3</sub> as described in the literature<sup>18</sup>. Instrument pH increment was set to 0.2 for the measurements of SiO<sub>2</sub>, TiO<sub>2</sub>, and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and that for backwards measurements was 0.1 for MgO, CeO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>. Tolerance was set to 0.2 for SiO<sub>2</sub> and TiO<sub>2</sub>; to 0.05 for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, MgO, CeO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>. Refractive indexes used during measurements are 1.46, 2.90, 1.76, 1.74, 2.20, and 2.94 for metal-oxides SiO<sub>2</sub>, TiO<sub>2</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, MgO, CeO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>, respectively. Absorbance values used during measurements are 0.01, 1.0, 0.01, 0.1, 0.01, and 0.01 for metal-oxides SiO<sub>2</sub>, TiO<sub>2</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, MgO, CeO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>, respectively.

#### 4.2.2.2. FT-IR Spectroscopy

Thermo Scientific Nicolet iS10 model FT-IR spectrometer with an attenuated total reflection (ATR) cell was used to collect IR spectra. Each IR spectrum was collected in air at room temperature with a resolution of 4 cm<sup>-1</sup> and an average of 512 scans. 32 scans were collected as background before each measurement. Peak assignments were done according to literature<sup>19</sup>. Relative ATR shifts were corrected according to the wavelength dependent factor- penetration depth of the IR beam of the spectrometer to adjust the relative peak intensities.

#### 4.2.2.3. Scanning Electron Microscopy Coupled with Energy-Dispersive X-Ray Spectroscopy (SEM/EDX)

SEM images were collected by a Zeiss Ultra Plus (FEG-SEM) scanning electron microscope with a SE detector. Samples were applied on carbon tape to prevent the charging

effect of supports. Images were collected at the magnifications of 30K' and 100K' with an accelerating voltage (EHT) of 5 kV for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, of 1 kV for SiO<sub>2</sub>, TiO<sub>2</sub>, and MgO. Working distance for the samples coated on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was 5.3 mm while for the samples on SiO<sub>2</sub>, TiO<sub>2</sub>, and MgO, it was within the range of 3.1-3.4 mm. All EDX images were collected at a magnification of 100K' with an EHT of 5 kV and working distance of 6.7 mm for ILs on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, EHT of 10 kV and a working distance in the range of 5.0-5.7 mm for ILs on SiO<sub>2</sub>, TiO<sub>2</sub>, and on MgO.

#### 4.2.2.4. TGA Measurements

TGA measurements were performed on a TA Instruments Q500 model TGA instrument with a heating rate of 2 and 10 °C/min in flowing nitrogen within a temperature range of 24 to 600 °C for supported-ILs. Approximately 15 mg of sample was placed in a platinum pan and purged with nitrogen for 1 h. Temperature limits obtained from the interception of two linear functions, one originating from the zero weight loss level and the other one tangential to the declining portion of the weight change line, were named as  $T_{\text{onset}}$ . However, these  $T_{\text{onset}}$  limits generally overestimate the thermal decomposition temperature depending on the experimental conditions, such as high heating rates<sup>9a</sup>, (see a comparison in Appendix A2). Because of this overestimation, thermal stability limits of ILs were determined from the onsets of derivative weight % change lines. The determined stability limits were named  $T'_{\text{onset}}$ , which are usually slightly lower than  $T_{\text{onset}}$  values and are not affected by the differences in heating rates within the reported measurement error below (Appendix A2). Thus,  $T'_{\text{onset}}$  values were conservatively considered as the maximum operating or tolerable temperatures of the samples. Reproducibility measurements indicate that all results were reproducible within an error range of  $\pm 3$  °C.

### 4.3. Results and Discussion

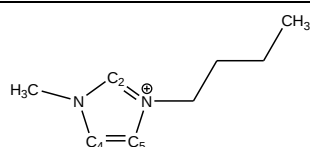
Typically, stability limits determined by fast-scan TGA measurements depend mainly on the sample amount, pan material, heating rate, and type of carrier gas<sup>8-9,13</sup>. As these parameters directly govern the outcomes of dynamic measurements, comparison of the data collected under different experimental conditions is quite difficult. Thus, we performed TGA measurements under identical conditions to achieve reproducible and consistent results for assessing qualitatively the relationship between structural parameters and thermal stability limits. Because we utilized fast-scan TGA measurements, the stability limits determined are rather short-term limits, setting the maximum temperatures that such metal-oxide-supported ILs can tolerate for a short period of time. For long-term stability limits, such as temperature at which 1% mass loss per year or month occurs, a more detailed kinetics study as performed by Heym et al.<sup>20</sup> and Seeberger et al.<sup>9a</sup> is required. The maximum tolerable temperatures are in general 20 to 50 °C higher than the results of isothermal TGA measurements of the bulk ILs<sup>21</sup>. It was illustrated that thermal stability limit measured for bulk 1-butyl-3-methylimidazolium methyl sulfate varies within approximately 50 °C when the heating rate was increased from 2 to 16 °C/min<sup>22</sup>. However, measurements that we performed at a heating rate of 2 °C/min on metal-oxide-supported ILs reproduced the same  $T'_{\text{onset}}$  results as the ones with a heating rate of 10 °C/min within  $\pm 3$  °C measurement error (comparison is given in Appendix A2). Thus, we infer that the artifacts of TGA are less pronounced on these metal-oxide supported samples. Since slow heating rates promote evaporation over thermal decomposition<sup>20</sup>, we preferred the heating rate of 10 °C/min to characterize the dynamic structural dependency, which otherwise would not be possible to distinguish by isothermal TGA or slow heating measurements<sup>23</sup>. Moreover, we also note that any detected mass losses result either from thermal decomposition of ILs or their evaporation from the metal-oxide in flowing gas<sup>20, 24</sup>. In either case, structural integrity

of the IL/metal-oxide system is lost. Previously, we reported the dependency of thermal stability limits of [BMIM]<sup>+</sup>-based bulk ILs on their corresponding anion structures (given in Table 4.1).

**Table 4.1.** [BMIM]<sup>+</sup>-based ILs with the structural details and FT-IR fingerprints.

| IL                                                                       | abbreviation | anion structure | $\nu(\text{C2H})$<br>(cm <sup>-1</sup> ) | $\nu(\text{C4,5H})$<br>(cm <sup>-1</sup> ) |
|--------------------------------------------------------------------------|--------------|-----------------|------------------------------------------|--------------------------------------------|
| 1- <i>n</i> -Butyl-3-methylimidazolium acetate                           | [BMIM][OAc]  |                 | 3056                                     | 3140                                       |
| 1- <i>n</i> -Butyl-3-methylimidazolium dibutyl phosphate                 | [BMIM][DBP]  |                 | 3077                                     | 3145                                       |
| 1- <i>n</i> -Butyl-3-methylimidazolium tosylate                          | [BMIM][TOS]  |                 | 3102                                     | 3148                                       |
| 1- <i>n</i> -Butyl-3-methylimidazolium hydrogen sulfate                  | [BMIM][HSO4] |                 | 3103                                     | 3148                                       |
| 1- <i>n</i> -Butyl-3-methylimidazolium octyl sulfate                     | [BMIM][OS]   |                 | 3105                                     | 3149                                       |
| 1- <i>n</i> -Butyl-3-methylimidazolium trifluoromethanesulfonate         | [BMIM][TfO]  |                 | 3115                                     | 3153                                       |
| 1- <i>n</i> -Butyl-3-methylimidazolium tetrafluoroborate                 | [BMIM][BF4]  |                 | 3122                                     | 3161                                       |
| 1- <i>n</i> -Butyl-3-methylimidazolium hexafluoroantimonate              | [BMIM][SbF6] |                 | 3123                                     | 3166                                       |
| 1- <i>n</i> -Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide | [BMIM][NTf2] |                 | 3124                                     | 3159                                       |

Cation structure;



Accordingly, maximum tolerable temperatures of [BMIM]<sup>+</sup>-based bulk ILs decrease in the following order of anions: [NTf<sub>2</sub>]<sup>-</sup> > [TfO]<sup>-</sup> ~ [SbF<sub>6</sub>]<sup>-</sup> ~ [BF<sub>4</sub>]<sup>-</sup> > [HSO<sub>4</sub>]<sup>-</sup> > [TOS]<sup>-</sup> > [OS]<sup>-</sup> > [DBP]<sup>-</sup> > [OAc]<sup>-</sup> <sup>23</sup>. Furthermore, FT-IR characterization of bulk ILs (individual spectra are given in Appendix A2) showed that frequencies of C2, C4 and C5 protons on the imidazolium ring shift upon varying the anion structure. These protons on imidazolium ring specify the hydrogen bond donating ability of ILs <sup>25</sup> and involve in H-bonding between cation and anion <sup>26</sup>. It was illustrated that all interactions in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide are in between CH of the imidazolium ring and SO<sub>2</sub> group on the [NTf<sub>2</sub>]<sup>-</sup> anion <sup>27</sup>. Consistent with the explanations found in the literature, higher shift, either blue- or red-shift, was observed on the stretching vibrational frequency of C2 protons rather than those of C4,5 protons by changing the anion structure because of stronger interactions with anions through C2 protons <sup>28</sup>. Thus, we focus on C2 proton to probe the inter-ionic interactions <sup>29</sup>.

As illustrated in our previous study <sup>23</sup>, given in Figure 4.1, there is a strong correlation between C2H stretching frequency ( $\nu(\text{C2H})$ ) and the thermal stability limits of bulk ILs, which are inversely related to the hydrogen-bond interaction energies (EHB) <sup>30</sup>. In the aspects of  $\nu(\text{C2H})$  in bulk ILs, the acidity of C2H of ILs decreases in the order [NTf<sub>2</sub>]<sup>-</sup> > [SbF<sub>6</sub>]<sup>-</sup> > [BF<sub>4</sub>]<sup>-</sup> > [TfO]<sup>-</sup> > [OS]<sup>-</sup> > [HSO<sub>4</sub>]<sup>-</sup> > [TOS]<sup>-</sup> > [DBP]<sup>-</sup> > [OAc]<sup>-</sup> and thermal stability limits of ILs follow the same trend with the only exception of [OS]<sup>-</sup> anion, because of its extremely large size. Because  $\nu(\text{C2H})$  stretching frequency is inversely correlated with the cohesive energy between anion and cation <sup>26</sup>, the inter-ionic interaction strength changes in the reverse order: [NTf<sub>2</sub>]<sup>-</sup> < [SbF<sub>6</sub>]<sup>-</sup> < [BF<sub>4</sub>]<sup>-</sup> < [TfO]<sup>-</sup> < [HSO<sub>4</sub>]<sup>-</sup> < [TOS]<sup>-</sup> < [DBP]<sup>-</sup> < [OAc]<sup>-</sup> <sup>23</sup>. Thus, our data suggested that the bulk ILs become thermally more stable as inter-ionic interaction strength decreases as shown in Figure 4.1.

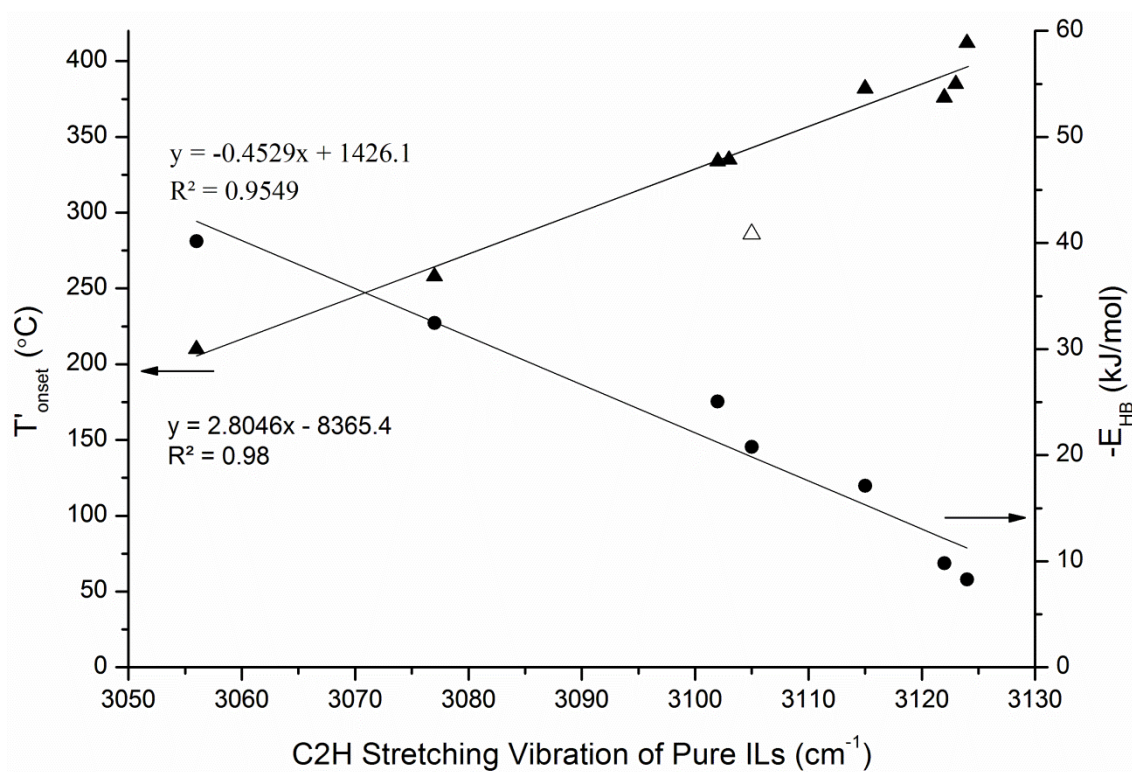


**Figure 4.1.** Our previously reported data <sup>23</sup> showing the correlation between thermal stability limits ( $T'_{\text{onset}}$ ) of bulk ILs and the vibrational frequencies of C2 protons of bulk ILs (hydrogen-bond interaction energies ( $E_{\text{HB}}$ ) <sup>30</sup>).

Here, we extend this approach to metal-oxide-supported ILs to reveal the effects of surface interactions on the thermal stability limits of supported ILs.

#### 4.3.1. Thermal Stability Limits of [BMIM]<sup>+</sup>-based ILs on Metal-oxide Supports

The uniformity of IL distribution in metal-oxide-supported samples was confirmed by SEM imaging complemented by EDX mapping performed on several random locations on each sample. Figure 4.2 shows a representative SEM/EDX image set that was obtained for [BMIM][BF<sub>4</sub>] on SiO<sub>2</sub>, TiO<sub>2</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and MgO. All EDX maps (representative ones are given in Figure 4.2) confirm the uniform distribution of C and F atoms of [BMIM][BF<sub>4</sub>] over the corresponding metal-oxide surface. Consistently, analyses of the relative peak areas in EDX atomic density distribution plots confirm the stoichiometric IL loading within 5 % error

at every random location of each sample. The IL-loading in metal-oxide-supported samples corresponds to an IL-layer thickness of less than 0.8 nm on SiO<sub>2</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (with a surface area of 212 and 209 m<sup>2</sup>/g, respectively), less than 1.5 nm on MgO (with a surface area of 99 m<sup>2</sup>/g), and less than 2.8 nm on TiO<sub>2</sub> (with a surface area of 55 m<sup>2</sup>/g). These thickness values, calculated according to surface area of metal-oxides and density of ILs, indicate single to a few molecular layers of IL confirming the presence of interactions between metal-oxides and ILs<sup>31</sup>. If the thickness exceeds tens of nanometers, with increasing IL loading or decreasing metal-oxide surface area, it is expected to have very little influence of metal-oxide on the thermal stability limits of ILs, as some IL will exist without interfacial interactions with the surface.

Table 4.2 summarizes the thermal stability limits of metal-oxide-supported ILs on SiO<sub>2</sub>, TiO<sub>2</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and MgO in comparison with those of corresponding bulk ILs<sup>23</sup>. As in the case of bulk ILs, IL with [NTf<sub>2</sub>]<sup>-</sup> anion is one of the most stable and those with [OAc]<sup>-</sup> and [DBP]<sup>-</sup> anions are the two least stable ones when supported on metal-oxides. Moreover, data also illustrate that the thermal stability of corresponding ILs change significantly depending on the type of metal-oxide. For instance, T'<sub>onset</sub> value of bulk [BMIM][NTf<sub>2</sub>] is 412 °C, it decreases to 360, to 352, to 296, and to 206 °C when the same IL is supported on SiO<sub>2</sub>, on TiO<sub>2</sub>, on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and on MgO, respectively. This trend is valid for all ILs in such a way that the largest amount of deviation from the bulk T'<sub>onset</sub> value occurs when the ILs are supported on MgO, suggesting a stronger effect of MgO on the thermal stability behavior of ILs.

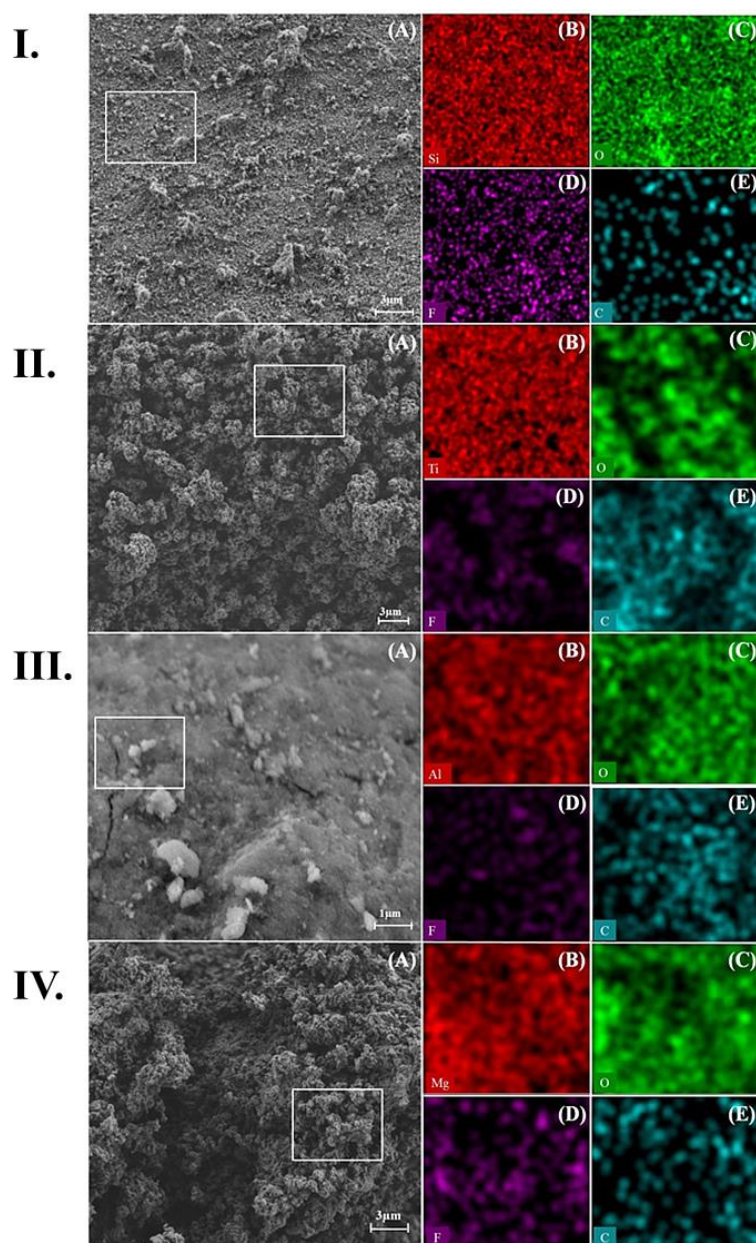


**Figure 4.2.** A representative SEM image of IL [BMIM][BF<sub>4</sub>] on SiO<sub>2</sub> (IA), TiO<sub>2</sub> (IIA), γ-Al<sub>2</sub>O<sub>3</sub> (IIIA) and MgO (IVA). EDX mapping shows the distribution of each element on the surface: (IB) silicon; (IIB) titanium; (IIIB) aluminum; (IVB) magnesium; (IC, IIC, IIIC, IVC) oxygen; (ID, IID, IIID, IVD) fluorine; (IE, IIE, IIIE, IVE) carbon.

**Table 4.2.** Thermal stability limits,  $T'_{\text{onset}}$ , of bulk ILs and of ILs supported on SiO<sub>2</sub>, TiO<sub>2</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and MgO

| ILs                       | $T'_{\text{onset}}$ (°C) |                     |                     |                                               |             |
|---------------------------|--------------------------|---------------------|---------------------|-----------------------------------------------|-------------|
|                           | Bulk*                    | on SiO <sub>2</sub> | on TiO <sub>2</sub> | on $\gamma$ -Al <sub>2</sub> O <sub>3</sub> * | on MgO      |
|                           |                          | (PZC = 1.7)         | (PZC = 4.5)         | (PZC = 7.6)                                   | (PZC = 9.8) |
| [BMIM][OAc]               | 210                      | 191                 | 187                 | 135                                           | 127         |
| [BMIM][DBP]               | 258                      | 222                 | 246                 | 162                                           | 143         |
| [BMIM][TOS]               | 334                      | 303                 | 322                 | 218                                           | 176         |
| [BMIM][HSO <sub>4</sub> ] | 335                      | 318                 | 312                 | 220                                           | 164         |
| [BMIM][OS]                | 286                      | 271                 | 268                 | 170                                           | 165         |
| [BMIM][TfO]               | 382                      | 352                 | 350                 | 273                                           | 204         |
| [BMIM][BF <sub>4</sub> ]  | 376                      | 331                 | 341                 | 263                                           | 209         |
| [BMIM][SbF <sub>6</sub> ] | 385                      | 337                 | 363                 | 269                                           | 209         |
| [BMIM][NTf <sub>2</sub> ] | 412                      | 360                 | 352                 | 296                                           | 206         |

\* Our previously reported data <sup>23</sup>

Figure 4.3 illustrates strong correlations between thermal stability of supported ILs on each metal-oxide and the corresponding  $\nu(\text{C2H})$  of individual ILs, as in the case of bulk ILs <sup>23</sup>. In general, an increase in  $\nu(\text{C2H})$  results in an increase in the  $T'_{\text{onset}}$  values of both bulk and supported-ILs. This behavior proves that as the inter-ionic interaction gets weaker with increasing  $\nu(\text{C2H})$ , IL becomes thermally more stable on metal-oxides. Only exception here is [BMIM][OS], which has an exceptionally large anion, and thus behaves differently than the other ILs. Thus, we exclude it from our analyses. The slope of this correlation shows how strongly the thermal stability limits of ILs are correlated with the inter-ionic interaction energies (probed by  $\nu(\text{C2H})$ ). A steeper slope indicates a higher dependency of stability limits on interaction energies between the ions of IL. Figure 4.3(A to D) shows that the steepness of this correlation gets lower from bulk ILs to metal-oxide-supported ILs as the metal-oxide changes in the following order: SiO<sub>2</sub> ~ TiO<sub>2</sub> >  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> > MgO. This trend is, inversely related with the amount of deviation from the stability limits of bulk. Thus, we infer that as the slope

of this correlation decreases the effect of IL/metal-oxide interaction becomes dominant in controlling the ILs' thermal stability rather than the inter-ionic interactions.

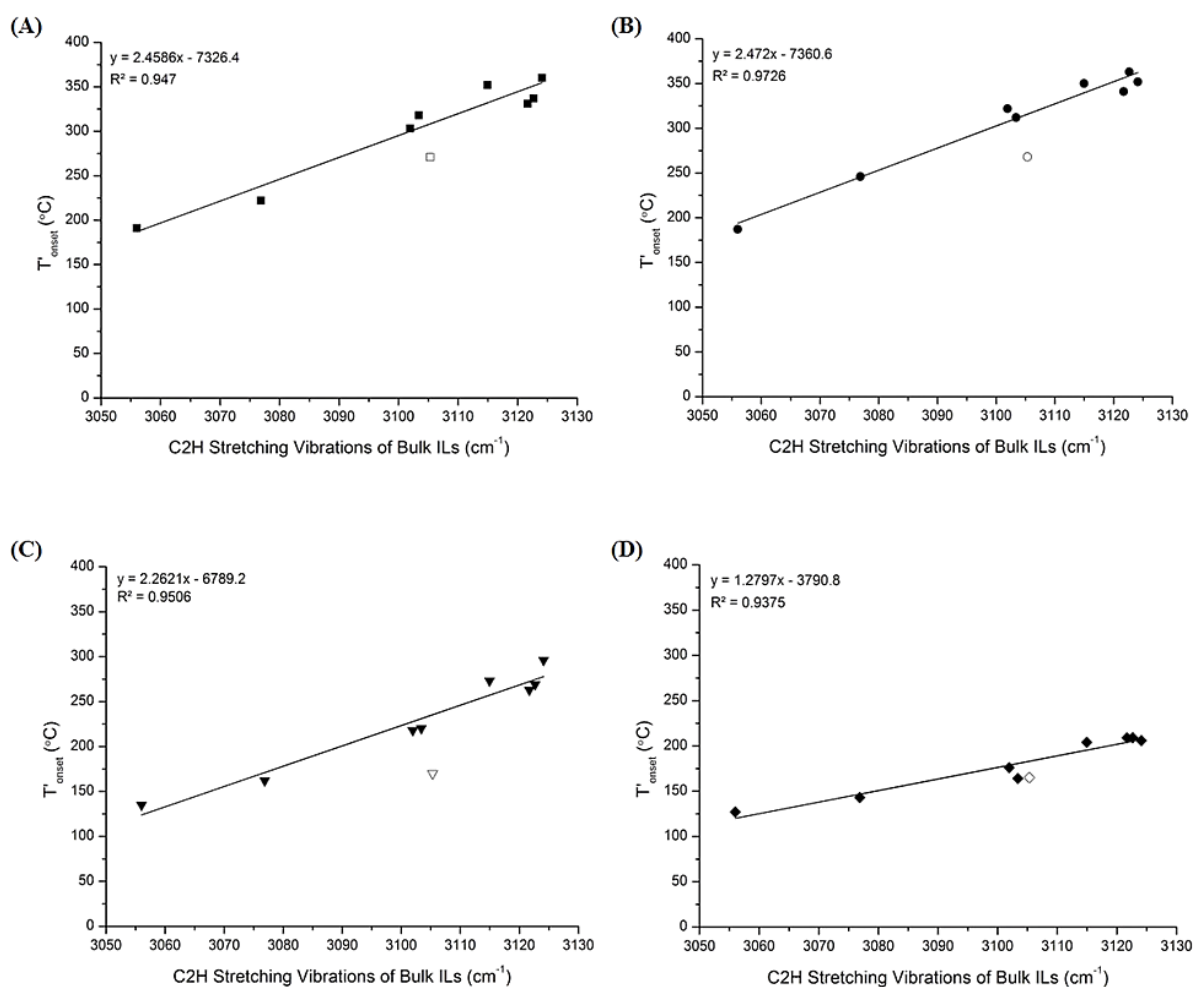


**Figure 4.3.** Variation of  $T'_{\text{onset}}$  values of metal-oxide-supported ILs with increasing acidity of C2 proton; SiO<sub>2</sub>-supported ILs (■); TiO<sub>2</sub>-supported ILs (●);  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported ILs (▼); MgO-supported ILs (◆); open symbols indicate  $T'_{\text{onset}}$  values of [BMIM][OS], which are excluded in the analyses.

#### 4.3.2. Derivation of a Model to Predict the Maximum Tolerable Temperatures of [BMIM]<sup>+</sup>-based ILs on Metal-oxide Supports

One of the main factors controlling the IL/metal-oxide interaction is the surface acidity of metal-oxides. PZC is a good measure of surface acidity, thus, we performed simple

acid-base titration <sup>18</sup> to quantify the surface acidity of individual metal-oxides. According to these measurements and consistent with literature data <sup>32</sup>, the PZC values of metal-oxides increase from a pH of 1.7 for SiO<sub>2</sub> to 4.5 for TiO<sub>2</sub>, to 7.6 for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and to 9.8 for MgO.

Aiming to investigate the effect of surface acidity on thermal stability limits of metal-oxide-supported ILs we plotted the slopes of individual lines of correlations between stability limits and inter-ionic interactions for each metal-oxide versus the corresponding PZC value of metal-oxides (Figure 4.4). Data show that slopes on SiO<sub>2</sub> and on TiO<sub>2</sub> are almost constant and slightly lower than that of the bulk ILs. However, as the metal-oxide becomes more basic starting from  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to MgO the slope decreases significantly. This decrease in slope is associated with a larger amount of deviation in  $T'_{\text{onset}}$  values of the supported-ILs from their corresponding bulk values. Thus, we infer that when the metal-oxide surface gets more basic with increasing PZC value, interactions between ILs and metal-oxides become more dominant in controlling the thermal stability of supported-ILs. Consequently the dependence of stability limits on inter-ionic interactions (probed by C2 proton acidity) becomes less important than the case in bulk ILs. This shift in dominant structural factors suggests a change in the mechanism of thermal decomposition reaction of ILs on metal-oxides. Apparently the proton abstraction ability of basic MgO plays a role in initiating the decomposition of ILs on this support. This behavior is evident from a large deviation from the decomposition temperatures of bulk ILs.

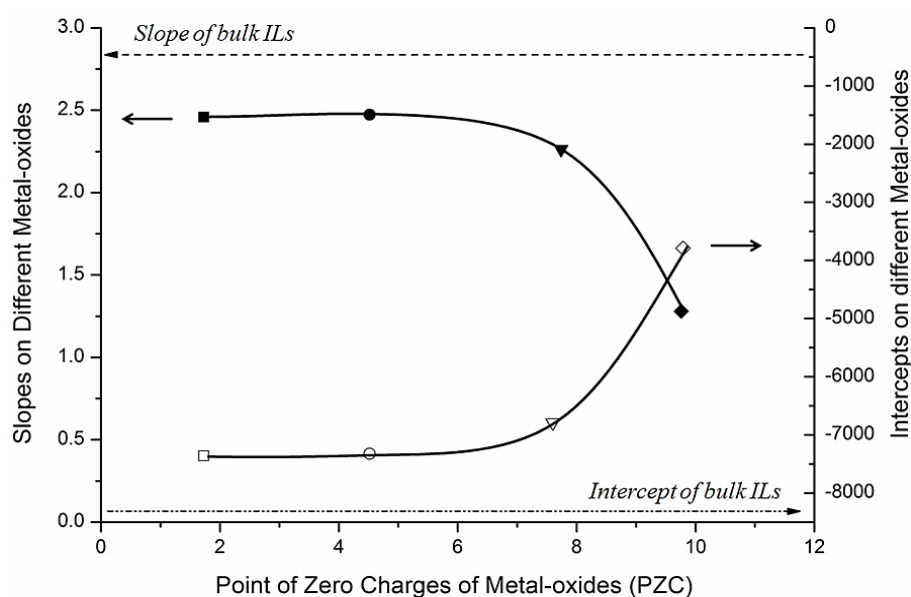


**Figure 4.4.** Variation of slopes and intercept values of thermal stability lines of supported ILs, given in Figure 4.3, as a function of PZC of metal-oxides. Closed symbols indicate slope values as follows: SiO<sub>2</sub>-supported ILs (■); TiO<sub>2</sub>-supported ILs (●); γ-Al<sub>2</sub>O<sub>3</sub>-supported ILs (▼); MgO-supported ILs (◆) and (----) dashed line on top shows the slope of bulk ILs. Open symbols indicate the intercept values of supported ILs and (-----) dashed-dotted line at the bottom indicates the intercept of bulk ILs.

One other aspect of Figure 4.4 is the variation of intercept values of the individual lines in Figure 4.3 for each metal-oxide versus the corresponding PZC value of metal-oxides. This variation illustrates an increase in intercept values with increasing PZC of the metal-oxide. Aiming to develop a simple mathematical expression for the estimation of  $T'_{\text{onset}}$  of metal-oxide-supported ILs as a function of inter-ionic interaction energy and PZC of the metal-oxides, we fitted each of these variations in Figure 4.4 into third order polynomials (with  $R^2 = 1$ ) and derived the model given below for  $T'_{\text{onset}}$  in the form of  $y = mx + n$ , where  $m$  and  $n$  are represented in terms of these third order polynomials as a function of PZC for slope and intercept, respectively, and  $x$  is the stretching frequency of C2 proton of bulk ILs,  $\nu(\text{C2H})$ .

$$\begin{aligned} \text{Model } T'_{\text{onset}}(\nu(\text{C2H}), \text{PZC}) = & [(-0.007699 \times (\text{PZC})^3 + 0.096313 \times (\text{PZC})^2 - 0.3649 \times (\text{PZC}) \\ & + 2.8518) * \nu(\text{C2H})] + [24.3402 \times (\text{PZC})^3 - 308.5932 \times (\text{PZC})^2 + 1176.0588 \times (\text{PZC}) - \\ & 8587.6487] \end{aligned}$$

The performance of this model in predicting the  $T'_{\text{onset}}$  values of supported-ILs is illustrated in Figure 4.5. Data show that the model accurately estimates the thermal stability limits presented in Table 2 with less than 4 % average relative error (individual relative errors for each supported-IL sample is provided in Appendix A2) and with a maximum relative error of 10.7 % for [BMIM][DBP] on SiO<sub>2</sub>, possibly because of its relatively large anion just like [BMIM][OS]. These relative error values are comfortably comparable with those of group contribution methods derived for bulk ILs<sup>12,33</sup>. We further investigated the performance of this model by analyzing identical samples prepared using different metal-oxides, Fe<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub>. We picked ILs with [DBP]<sup>-</sup>, [BF<sub>4</sub>]<sup>-</sup>, and [NTf<sub>2</sub>]<sup>-</sup> anions and prepared their corresponding supported samples on these metal-oxides. Here, we consider [BMIM][DBP] as the worst case scenario, because it gives the highest error in our analyses, as discussed above. The TGA measurements under identical conditions show that  $T'_{\text{onset}}$  values of these ILs on Fe<sub>2</sub>O<sub>3</sub> are 171, 308, and 313 °C for [BMIM][DBP], [BMIM][BF<sub>4</sub>], and [BMIM][NTf<sub>2</sub>], respectively. Using  $\nu(\text{C2H})$  values of 3077, 3122, and 3124 cm<sup>-1</sup> for [BMIM][DBP], [BMIM][BF<sub>4</sub>] and [BMIM][NTf<sub>2</sub>], respectively, and 6.8 for PZC, our model estimates the  $T'_{\text{onset}}$  values as 188, 296, and 301 °C, for these Fe<sub>2</sub>O<sub>3</sub>-supported ILs, respectively. Furthermore, on CeO<sub>2</sub>,  $T'_{\text{onset}}$  values were 158, 252, and 266 °C and our model estimates these values as 153, 238, and 242 °C for [BMIM][DBP], [BMIM][BF<sub>4</sub>], and [BMIM][NTf<sub>2</sub>], respectively, for a measured PZC value of 8.7 for CeO<sub>2</sub>. When the data obtained for ILs-supported on Fe<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub> are included, the average relative error and the maximum

relative error are 4.3 % and 10.7 %, respectively. Here, we note that the model is not valid for IL with [OS]<sup>-</sup>, as its  $T'_{\text{onset}}$  values on different metal-oxides do not follow the same trend with the other ILs as shown with open symbols in Figure 4.3. As discussed in our previous study this behavior is because of its extraordinarily large anion<sup>23</sup>. Thus, we exclude its values in our error calculations.

As an extension, we further investigated the performance of our model on ILs with different cations than [BMIM]<sup>+</sup>. For instance, 1-ethyl-3-methylimidazolium tetrafluoroborate, [EMIM][BF<sub>4</sub>], was selected as it is one of the commonly used ILs<sup>34</sup>. Experimental  $T'_{\text{onset}}$  values of [EMIM][BF<sub>4</sub>] on SiO<sub>2</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and MgO are determined as 345, 272, and 182 °C, respectively and our model estimates the corresponding  $T'_{\text{onset}}$  values as 359, 275, and 205 °C, respectively. Moreover, the model estimated  $T'_{\text{onset}}$  values of 1,3-dimethylimidazolium methyl sulfate, [DMIM][MS], supported on SiO<sub>2</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and MgO as 330, 248, and 190 °C, respectively, and the corresponding measured values are 342, 228, and 171 °C, respectively. These values indicate that the model can predict not only the  $T'_{\text{onset}}$  of metal-oxide-supported ILs with [BMIM]<sup>+</sup> cation, but also those of supported ILs with not so different cation structures within acceptable error range, provided that the anion is not oversized and the cation has not so large alkyl groups attached. We believe that the model can be utilized to pick proper [BMIM]<sup>+</sup>-based ILs suitable for specific operating conditions of corresponding systems, such as those of SCILL and SILP type catalysts.

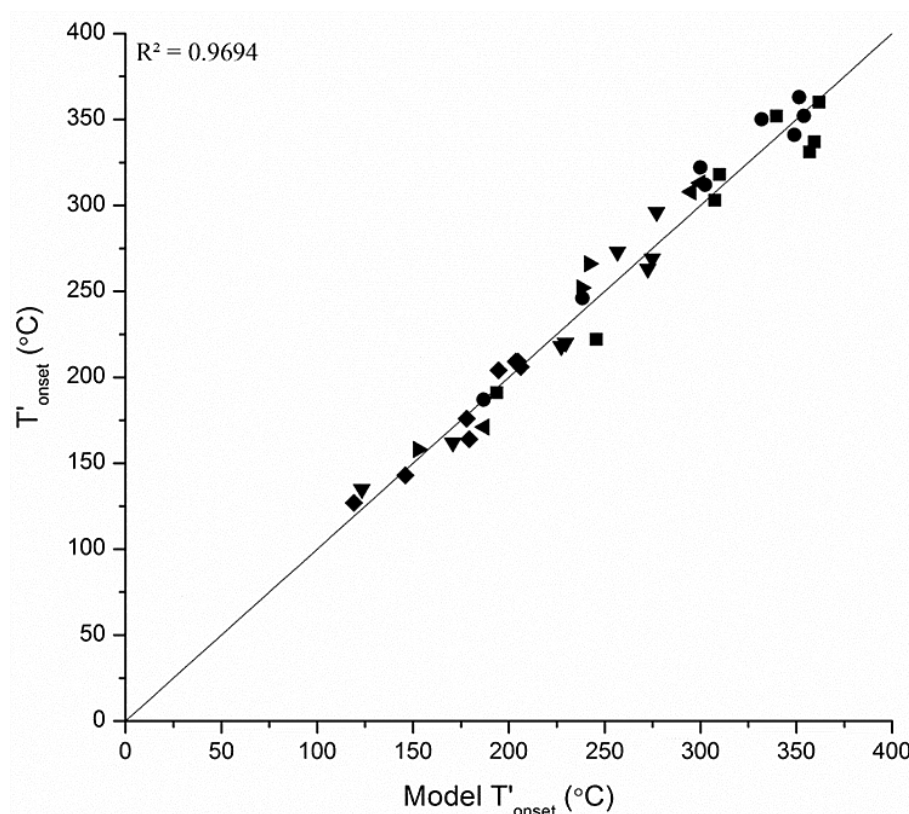


**Figure 4.5.** Comparison of model  $T'_{\text{onset}}$  values with experimental results: SiO<sub>2</sub>-supported ILs (■); TiO<sub>2</sub>-supported ILs (●);  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported ILs (▼); MgO-supported ILs (◆); Fe<sub>2</sub>O<sub>3</sub>-supported ILs (◄); CeO<sub>2</sub>-supported ILs (►). Solid line indicates the 45° line.  $R^2$  was calculated excluding the  $T'_{\text{onset}}$  values of [BMIM][OS].

#### 4.4. Conclusion

Structural factors controlling thermal stability limits of [BMIM]<sup>+</sup>-based ILs supported on the most commonly used metal-oxide, SiO<sub>2</sub>, TiO<sub>2</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and MgO were determined. Data show that stability limits are strongly controlled by the interaction between anion and cation of the IL and by that between IL and metal-oxide. Control of the latter factor becomes dominant with decreasing surface acidity of the metal-oxide. Based on these findings a simple mathematical expression was developed to predict the maximum temperatures that [BMIM]<sup>+</sup>-based ILs on metal-oxides can tolerate for short-terms, as a function of inter-ionic interactions in ILs quantified by stretching IR fingerprints of the C2H acidic proton of the imidazolium

ring and the surface acidity of metal-oxides quantified by the PZC value. The model provided here can be utilized for picking a proper IL which can tolerate the operating conditions of systems involving direct interactions of ILs with metal-oxides, such as in the case of SCILL and SILP type catalysts.

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## Chapter 5

### LONG-TERM THERMAL STABILITIES OF [BMIM]<sup>+</sup>-BASED ILS ON $\gamma$ -Al<sub>2</sub>O<sub>3</sub>\*

#### Abstract

ILs with the same cation 1-butyl-3-methylimidazolium and varying anions supported on one of the most commonly used metal-oxide  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Since short-term limits are not sufficient enough for the applications of ILs in catalytic systems such as SILP and SCILL, long-term thermal stabilities of nine [BMIM]<sup>+</sup>-based ILs supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was determined from the isothermal TGA measurements based on the 1 % mass loss after 6 h treatments. Long-term stability limits were found to be lower more than 60 °C from the short-term stability limits determined by fast-scan TGA measurements. This difference strongly depends on the anion type as seen in the case of IL with [HSO<sub>4</sub>]<sup>-</sup> anion. Furthermore, from the results of these isothermal treatments, rate of decomposition of these ILs at any temperature and activation energy  $E_a$  required for the decomposition were determined. These calculated  $E_a$  values were found to be exponentially related to the  $\nu(\text{C2H})$  vibration of bulk ILs which controls the short-term thermal stability limits of these ILs with a linear relationship. Both short and long-term analyses results showed that decomposition of ILs strongly depend on the inter-ionic interactions. Decrease in inter-ionic interaction (probed by C2H vibration) with the varying anion type results in the increased thermal stability.

**Keywords:** SCILL; SILP; imidazolium ionic liquid; long-term thermal stability limit; isothermal TGA; activation energy of decomposition

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\* This chapter is written in the format of a manuscript to be submitted for publication

### 5.1. Introduction

Ionic liquids (ILs) have gained tremendous attention with their unique properties which can be tuned by the different combinations of anions and cations in the structure. Remarkable numbers of investigations have been performed on the determination of these tunable properties of ILs such as thermal stability limits, solubility, density, viscosity and etc.<sup>1</sup>.

With the increasing number of research, application areas of ILs have expanded in a wide range such as electrochemistry<sup>2</sup>, synthesis<sup>3</sup> and catalysis<sup>4</sup>. In some fields of catalysis, ILs are immobilized on the support materials with high surface area such as metal-oxides<sup>5</sup>. Supported ionic liquid phase (SILP)<sup>6,7</sup> and solid catalysts with ionic liquid layer (SCILL)<sup>8,9</sup> are the two of the most common fields of immobilized ILs on support materials. However, ILs tend to lose their structural integrity via decomposition<sup>10</sup>, leaching out<sup>11</sup> or evaporation<sup>12,13</sup> from the system during application conditions. Heym et al.<sup>14</sup> suggest to control evaporation of ILs by replacing the inert gas flowing during TGA analyses.

Thermal stability limits and experiment conditions are two of the main factors which determine the application conditions of supported ILs. Although thermal stability limits of bulk ILs are investigated comprehensively<sup>11,15</sup>, stability limits of ILs immobilized on support materials still require more studies. Ngo et. al<sup>16</sup> proved the influence of alumina on the thermal stability by just replacing the aluminum pan-material used for TGA. Upon the replacement of aluminum pans with alumina, imidazolium based ILs thermal stability decreased around 100 °C. Following this study, Kosmulski et al.<sup>17</sup> investigated the decrease in the thermal stability of ILs in the presence of acidic silica. According to their results bulk 1-*n*-butyl-3-methylimidazolium triflate was thermally stable at 200 °C. Addition of acidic silica

triggered the decomposition mechanism at the same temperature and decomposition was observed at lower temperature. Laura Rodriguez-Perez et al.<sup>18</sup> have illustrated the short-term thermal stability (thermogravimetric analysis results-TGA) of bulk IL, 1-butyl-3-methylimidazolium hexafluorophosphate, [BMIM][PF<sub>6</sub>] changes significantly when immobilized on metal-oxide SiO<sub>2</sub> but stays almost the same on metal-oxide Al<sub>2</sub>O<sub>3</sub>. Moreover, Lemus et al.<sup>19</sup> have investigated the effect of support material on the thermal stability of IL 1-octyl-3-methylimidazolium hexafluorophosphate, [OMIM][PF<sub>6</sub>] with the metal-oxides SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>. Thermal stability of bulk IL [OMIM][PF<sub>6</sub>] decreased from 350 °C to 310, 215, 195 °C when they are supported on TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, respectively. However, all of these studies indicate only the short-term results. Recent studies on long-term stabilities of ILs showed that thermal stability limits of ILs significantly decreases when treated in longer time periods. For instance short-term thermal stability limits of bulk 1-butyl-3-methylimidazolium tetrafluoroborate, [BMIM][BF<sub>4</sub>], ranges from 360 to 435 °C<sup>20-23</sup> while its long-term limits (1 % mass loss in 10 h) are reported much lower around 216 °C<sup>15</sup>. Furthermore, kinetics studies were performed on this IL to confirm the stability limits also calculating the activation energy (E<sub>a</sub>) of decomposition which ranges in between 108.4-195 kJ/mol<sup>15,24</sup>.

Studies indicate that environmental interactions play a key role in both short- and long-term stability limits of ILs together with the structural factors so that the determination of these interactions and factors are very crucial for the application areas of ILs immobilized on support materials such as SILP and SCILL systems. In this study, we aimed to determine the long-term thermal stability limits of nine different [BMIM]<sup>+</sup>-based ILs supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and also E<sub>a</sub> required for the decomposition reactions. Therefore, ILs used in this study were chosen with the same cation, 1-*n*-

butyl-3-methylimidazolium, [BMIM]<sup>+</sup>, with various anions in order to compare with the short-term results of our previous study<sup>21</sup>. We suggest that the investigated results can be used in catalytic application areas since they are all analyzed in consistency with each other and also give the long-term results rather than the short-term.

## 5.2. Materials and Methods

### 5.2.1. Materials and Sample Preparation

ILs,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, acetone and methanol were purchased from Sigma-Aldrich with the highest available purity.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was calcined at 500 °C for 5 h in flowing O<sub>2</sub>. Temperature ramp rate was 3 °C/min for the calcination process. 200 mg of corresponding IL was dissolved in 5 mL of either acetone or methanol. 1 g freshly calcined  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was immersed into prepared IL-solvent mixture. Resulting mixture was dried in a vacuum oven for a day at 70 °C and powder IL coated metal-oxide samples were obtained. Such drying procedure was confirmed by checking the derivative onset temperature of each compound which was significantly higher than 70 °C as suggested by Clough et al.<sup>25</sup>. The corresponding IL loading was approximately 16.7 wt. %.

### 5.2.2. Scanning Electron Microscopy Coupled with Energy-Dispersive X-Ray Spectroscopy (SEM/EDX)

Zeiss Ultra Plus (FEG-SEM) Model Scanning electron microscope with a SE detector was used for SEM imaging. Samples were applied on a carbon tape and the images were obtained at magnifications of 30K $\times$  and 100K $\times$  with an accelerating voltage (EHT) of 5 kV and a working distance of 6.7 mm. All EDX images were collected at a magnification of 100K $\times$  with an EHT of 5 kV and working distance of 6.7 mm.

### 5.2.3. Thermogravimetric Analysis

TGA measurements were performed on a Seiko Instruments Inc. (SII) EXSTAR TG/DTA 6300 instrument at a heating rate of 5 °C/min in flowing nitrogen. Approximately 15 mg of samples were placed in platinum pans and purged with nitrogen for 1 h. In order to get rid of the absorbed/adsorbed water in the system, the samples were dried at 70 °C for 1 h. Then, the samples were heated up to the determined temperatures and waited at these temperatures for 6 h. These temperatures were determined according to the  $T'_{\text{onset}}$  values obtained in previous study<sup>21</sup>. Each supported IL, treated at three different temperatures which were generally 20, 40, 60 °C lower than the  $T'_{\text{onset}}$  value. By using these TGA results, temperature required for 1 % decomposition of IL after 6 h was determined and also the activation energy ( $E_a$ ) required for the decomposition reaction was determined as explained by Clough et al<sup>25</sup>.

### 5.2.4. FT-IR Spectroscopy

Thermo Scientific Nicolet iS10 model FT-IR spectrometer with an attenuated total reflection (ATR) cell was used to collect IR spectra. Each IR spectrum, average of 512 scans, was collected in air at room temperature with a resolution of 4 cm<sup>-1</sup>. Peak assignments were done according to literature<sup>26</sup>.

## 5.3. Results and Discussion

In literature, thermal stability limits of bulk ILs are generally determined by fast-scan TGA measurements so that these limits indicate the short-term stabilities rather than the long-term stability limits. For long-term stability limits, such as temperature at which 1% mass loss per year/month/day occurs, a more detailed kinetics study is required<sup>12,27</sup>. Thermal stability limits obtained by fast-scan TGA measurements are in general 20 to 50 °C higher than the results of isothermal TGA measurements of the bulk ILs<sup>28</sup>. In our previous study we determined the short-term thermal stability limits of nine [BMIM]<sup>+</sup>-based ILs on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and

also the structural factors controlling the thermal stability limits<sup>21</sup>. However, determination of the long-term thermal stability limits of ILs is very crucial for the applications of ILs to choose the proper IL at specific operating conditions. Here, we extend this study to reveal the long-term thermal stability limits of these nine ILs on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> from 1% mass loss during 6h-isothermal TGA treatments and also the required activation energy ( $E_a$ ) for the decomposition reactions.

Long-term stabilities of ILs ( $T_{0.01/6h}$ ) were determined from the isothermal TGA experiments using the method of Baranyai et al.<sup>29</sup>. Time required for 1 % mass loss of samples ( $t_{0.99}$ ) were determined from the isothermal TGA results. These  $t_{0.99}$  values were plotted against the temperature values of isothermal treatments. From these plots  $T_{0.01/6h}$  were determined as explained by Baranyai et al.<sup>29</sup>. When  $T_{0.01/6h}$  of ILs were compared with the short-term results ( $T'_{onset}$ ), it was found that the stability limits decreased more than 60 °C varying according to the anion type as indicated by Cieniecka-Roslonkiewicz et al.<sup>28</sup>. However, for the IL with [HSO<sub>4</sub>]<sup>-</sup> anion, there was a significant difference in the stability limits which might result from the hygroscopic structure of anion. Fumino et al proved that the [EMIM][EtSO<sub>4</sub>] had more inter-ionic interactions compared to [EMIM][NTf<sub>2</sub>] because of the hydrogen bonds at different strength in between cation and anion<sup>30</sup>. Thus, with the increasing treatment time inter-ionic interactions of IL with [HSO<sub>4</sub>]<sup>-</sup> anion might get more dominant and result in a much lower  $T_{0.01/6h}$  value.

Furthermore, from Arrhenius equation by using the isothermal TGA data, the rate of the decomposition at any rate evaluated<sup>31</sup>. This method allows rapid and accurate prediction of the decomposition rate at any temperature. Where ILs thermally decompose via the reaction of one cation with one anion, generating volatile degradants, it is assumed that the concentration of cations and anions IL does not change. Therefore, decomposition is accepted

as pseudo zeroth order. Plotting  $\ln(d\alpha/dt)$  against  $1/T$  gives a linear fit with a gradient equal to  $-E_a/R$  and a y-axis intercept equal to  $\ln(A)$  ( $E_a$  stands for the activation energy). The plot of  $\ln(d\alpha/dt)$  against  $1000/T$  for representative IL [BMIM][BF<sub>4</sub>] on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was given in Figure 5.1.

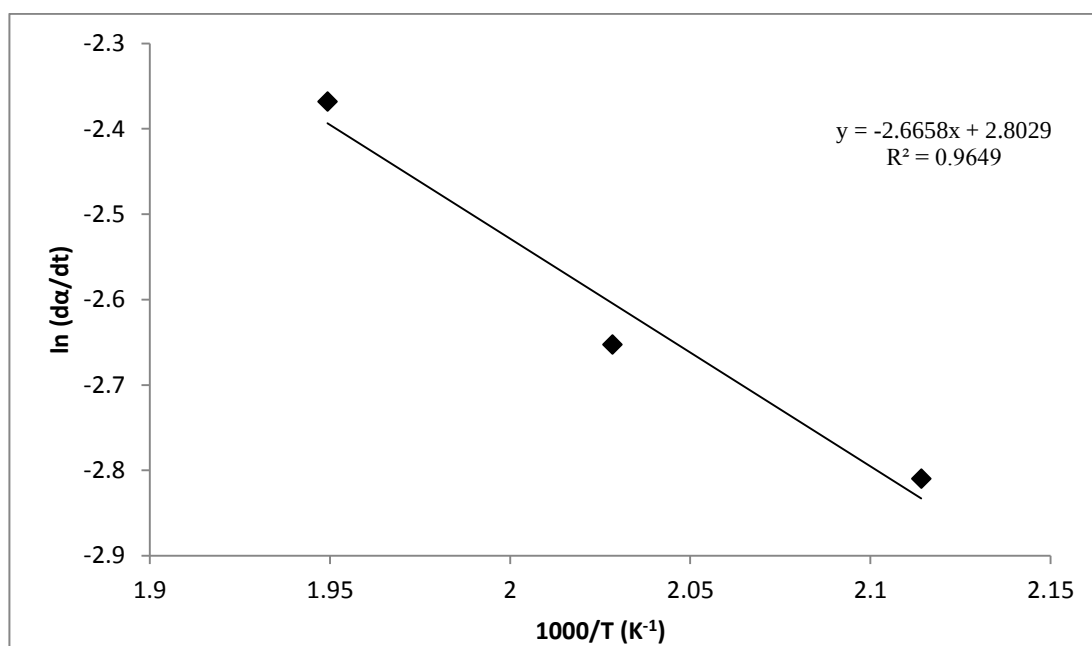


**Figure 5.1.** Thermal decomposition kinetics of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported [BMIM][BF<sub>4</sub>] determined from isothermal TGA experiments.  $E_a = 22.2$  kJ/mol

From this graph  $E_a$  of [BMIM][BF<sub>4</sub>] supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was determined as 22.2 kJ/mol. Kinetic studies on the bulk IL [BMIM][BF<sub>4</sub>] showed that  $E_a$  of decomposition ranges in between 108.4-195 kJ/mol.<sup>15,24</sup> Thus the difference in between the  $E_a$  values of bulk IL and that of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported IL indicates the interaction in between IL and metal-oxide controlling the thermal stability limits of IL as indicated in our previous studies<sup>21,32</sup>. ILs used in this study, short-term ( $T'_{\text{onset}}$ ) and long-term ( $T_{0.01/6h}$ ) thermal stability limits and calculated activation energies of these ILs were given in Table 5.1. For the ILs with [OS]<sup>-</sup> and [SbF<sub>6</sub>]<sup>-</sup> anions, calculation of  $E_a$  could not be possible. Furthermore, influence of inter-ionic

interactions on both  $T'_{\text{onset}}$  and  $T_{0.01/6h}$  were compared in the Figure 5.2. As can be seen from the Figure 5.2., inter-ionic interactions probed by C2H vibration is inversely related with the short- and long-term thermal stabilities confirming the results of our previous studies <sup>21</sup>. Increasing C2H vibration, decreasing inter-ionic interactions result in the increased thermal stability of ILs in each case.

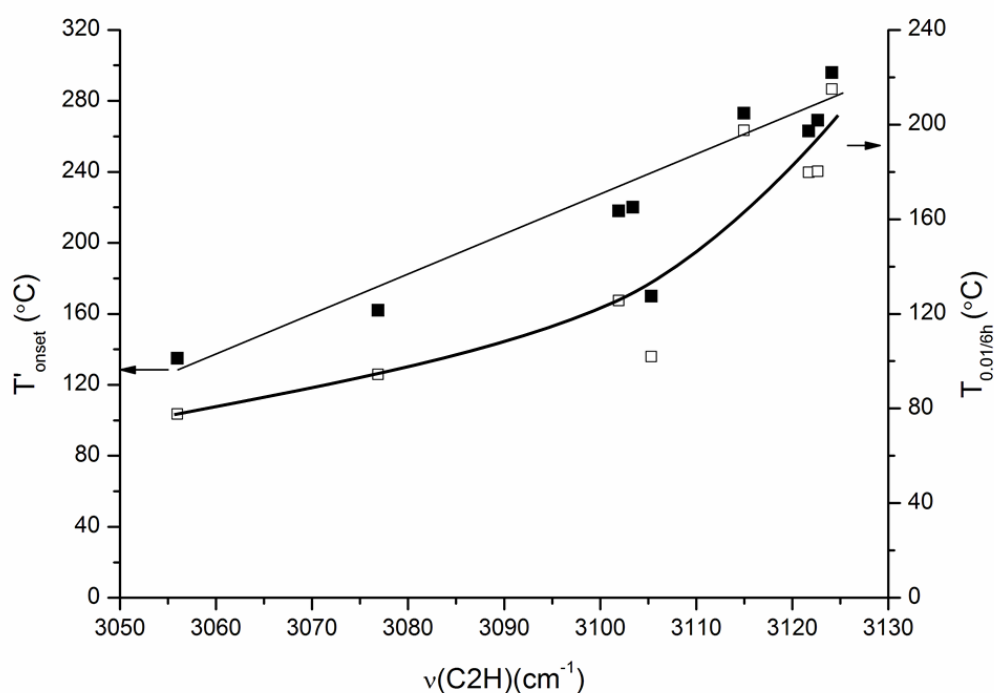


**Figure 5.2.** Influence of inter-ionic interactions probed by C2H vibration on the short-term ( $T'_{\text{onset}}$ ) and long-term ( $T_{0.01/6h}$ ) thermal stabilities. Data of IL with [OS]<sup>-</sup> anion was excluded from the trendlines.

**Table 5.1.** Short- and long-term stabilities of ILs supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and activation energies required for decomposition.

| ILs                       | T' <sub>onset</sub> (°C) | T <sub>0.01/6h</sub> (°C) | E <sub>a</sub> (kJ/mol) |
|---------------------------|--------------------------|---------------------------|-------------------------|
| [BMIM][OAc]               | 135                      | 127                       | 15.9                    |
| [BMIM][DBP]               | 162                      | 143                       | 13.1                    |
| [BMIM][TOS]               | 218                      | 176                       | 14.9                    |
| [BMIM][HSO <sub>4</sub> ] | 220                      | 164                       | 9.2                     |
| [BMIM][OS]                | 170                      | 165                       | -                       |
| [BMIM][TfO]               | 273                      | 204                       | 18.3                    |
| [BMIM][BF <sub>4</sub> ]  | 263                      | 209                       | 22.2                    |
| [BMIM][SbF <sub>6</sub> ] | 269                      | 209                       | -                       |
| [BMIM][NTf <sub>2</sub> ] | 296                      | 206                       | 29.2                    |

In the highlights of our previous study <sup>21</sup> (in Chapter 3), these calculated E<sub>a</sub> were compared with the C2H vibration of bulk ILs ( $\nu$ (C2H)) since this proton is responsible for strongly localized and directional hydrogen bond between cation and anion. Thus, it contributes to the inter-ionic cohesive energy, which decreases with increasing acidity of this proton, *i.e.* with increasing C2–H bond strength <sup>26,30</sup>. Although T'<sub>onset</sub> values were found to be linearly related to the C2H vibration of bulk ILs <sup>21</sup>, E<sub>a</sub> values displayed an exponential increase with increasing  $\nu$ (C2H) (in Figure 5.3.). This may result from the changes in the interactions because of the longer treatment periods. Thus longer treatment period may induce the other factors controlling thermal stability limits so that an exponential relation is obtained rather than the linear one as in the case of the relation between T'<sub>onset</sub> and  $\nu$ (C2H).

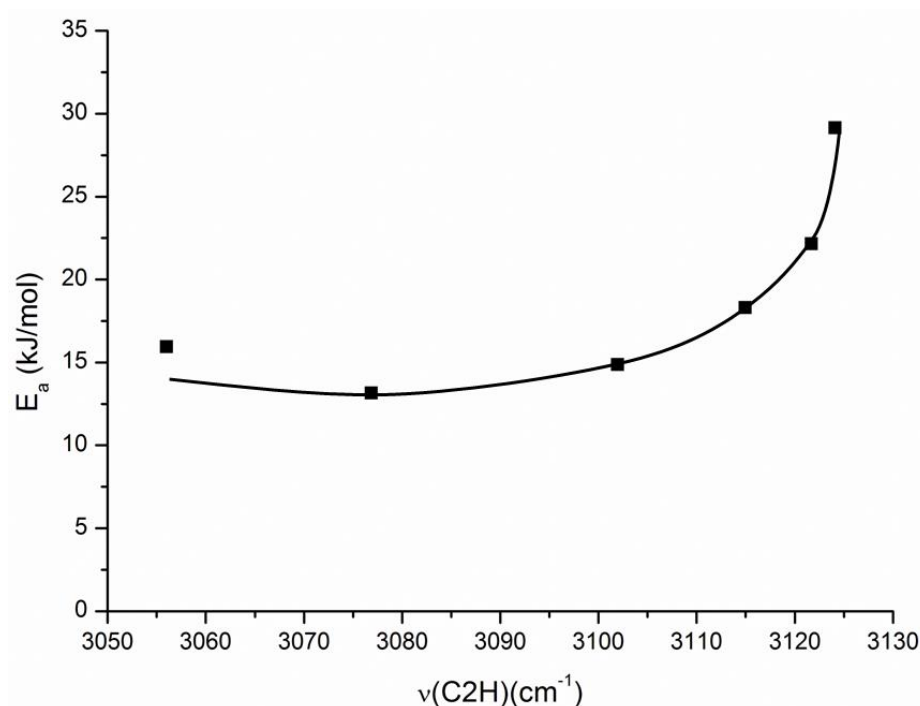


**Figure 5.3.** Relation between  $E_a$  and C2H vibrations of ILs supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> which control the thermal stability limits

#### 5.4. Conclusions

ILs with the same cation 1-butyl-3-methylimidazolium and varying anions supported on one of the most commonly used metal-oxide  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was used for the investigations of long-term thermal stabilities. Since short-term thermal stability limits are not sufficient enough for the applications of ILs in catalytic systems such as SILP and SCILL, long-term thermal stabilities of nine [BMIM]<sup>+</sup>-based ILs supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was determined from the isothermal TGA measurements. Long-term stability limits were found to be lower more than 60 °C from the short-term stability limits determined by fast-scan TGA measurements. Furthermore, from the results of these isothermal treatments, rate of decomposition of these ILs at any temperature and activation energy  $E_a$  required for the decomposition were determined. These calculated  $E_a$  values were found to be exponentially related to the  $\nu(\text{C2H})$

vibration of bulk ILs which controls the short-term thermal stability limits of these ILs with a linear relationship. Both short- and long-term analyses results showed that decomposition of ILs strongly depend on the inter-ionic interactions. In either case, decrease in inter-ionic interaction (probed by C2H vibration) with the varying anion type results in increased thermal stability.

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## Chapter 6

### CONCLUSION and FUTURE DIRECTIONS

Over the last decade, considerable efforts have been devoted to studies of ionic liquids (ILs) for a variety of applications due to their versatile and tunable physicochemical properties. Among their applications in catalysis, IL-coated porous metal-oxide supported metal catalysts demonstrate greater catalyst activity and higher selectivity for desired products as compared to their conventional counterparts. However, their incorporation predominantly depends upon electronic structure on both IL and support. Furthermore, their catalytic applications are limited by their thermal stability that becomes lower as compared to their pure-state thermal stability because of the interactions between ILs and supports and designates the upper operating temperature.

In the first part of the study, maximum tolerable thermal stability limits of nine ILs supported on  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\gamma\text{-Al}_2\text{O}_3$ , and  $\text{MgO}$  were determined via fast-scan TGA measurements and some structural factors and peripheral interactions controlling the stability limits were elucidated. (These results were accepted as the short-term thermal stability limits because they were performed via fast-scan TGA method.) The acidic strength of the C2 proton on the imidazolium ring increases, the inter-ionic interaction strength decreases. Such decrease in inter-ionic interaction strength results in an increase in thermal stability limits of both bulk and metal-oxide supported ILs. Results show that stability limits are strongly controlled by the interaction between anion and cation of the IL and by that between IL and metal-oxide. Control of the latter factor becomes dominant with decreasing surface acidity of the metal-oxide. Besides these electronic structural factors, physical factors, such as the anion

size, also play an important role in determining thermal stability limits. Based on these findings a simple mathematical expression was developed to predict the maximum temperatures that [BMIM]<sup>+</sup>-based ILs on metal-oxides can tolerate for short-terms, as a function of inter-ionic interactions in ILs quantified by stretching IR fingerprints of the C2H acidic proton of the imidazolium ring and the surface acidity of metal-oxides quantified by the PZC value. Furthermore, from the results of these isothermal treatments, rate of decomposition of these ILs at any temperature and activation energy  $E_a$  required for the decomposition were determined. These calculated  $E_a$  values were found to be exponentially related to the  $\nu(\text{C2H})$  vibration of bulk ILs which controls the short-term thermal stability limits of these ILs with a linear relationship. Both short- and long-term analyses showed that decomposition of ILs strongly depend on the inter-ionic interactions. In either case, decrease in inter-ionic interaction (probed by C2H vibration) with the varying anion type results in increased thermal stability. The factors elucidated in the thesis and also the model provided here can be utilized for picking a proper IL which can tolerate the operating conditions of systems involving direct interactions of ILs with metal-oxides, such as in the case of SCILL and SILP type catalysts. However, in order to improve the selection criteria of proper ILs at different operating conditions, more investigations are required. Some of ideas for the investigations were listed below as the next steps of this study.

- For the applications of ILs in catalytic fields, maximum tolerable temperatures of a wide range of IL must be determined and viability of these structural factors and peripheral interactions must be controlled. For instance, control of C2H vibration and influence of metal-oxide on thermal stability limits must be tried for a wider range of ILs so that a generalization can be obtained for the applications at specific conditions.

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- The model developed to predict the thermal stability limits of supported ILs can be improved by coating the same ILs on different types of metal-oxides with different surface acidities because PZC of the metal-oxide was determined as one of the main factors controlling these limits. Thus, the error in the prediction of thermal stability limits might be decreased.
  - In the last part of the study, long-term thermal stabilities of nine ILs supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was determined through isothermal TGA measurements by calculating the 1% mass loss after 6 h treatments. This study showed that there is a significant difference in between thermal stability limits obtained from fast-scan TGA and isothermal TGA measurements. Therefore, long-term thermal stability limits of ILs supported on the other metal-oxides must be performed via isothermal measurements. Furthermore, 6 h treatment may not be sufficient for the applications of ILs in catalytic systems. After determination of the stability limits for 6 h, the treatment period must be extended systematically to observe the time effect on the stability limits.
  - Determination of the decomposition pathways of supported ILs is also very crucial for the choice of proper ILs for the application areas. So that decomposition pathways of ILs supported on different type of metal-oxides can be determined by systematically changing the anion type, anion size, and nucleophilicity.
  - This study is based on the influence of the anion since the cation was kept constant. For the comparison of the cation influence, a simple change on cation can be performed such as alkyl chain length and the steps of this study can be repeated. So that the influences of cation and anion on the thermal stability limits of IL-assisted systems can be elucidated and the choice of proper IL at application conditions can be more guaranteed.

- 
- These studies were performed as the first step of the studies on catalysts with the IL-coated supported metal complexes. These catalysts will be used to tune the selectivity and activity of several reactions. Therefore, thermal stability of these catalysts and also the factors controlling these limits must be determined as a next step. Since inter-ionic interactions and surface acidity are the two main factors controlling the thermal stability limits of supported ILs, in the presence of metal complex, a significant difference in the short- and long-term stabilities of these catalysts is expected. Because the dominant factors on the stability is expected to significantly change in the presence of various metal complexes.

**Chapter 3****APPENDIX 3A****STRUCTURAL FACTORS CONTROLLING THERMAL STABILITY OF  
IMIDAZOLIUM IONIC LIQUIDS WITH 1-N-BUTYL-3-METHYLIMIDAZOLIUM  
CATION ON  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>****Brunauer–Emmett–Teller (BET) Pore Volume and Surface Area Analysis**

BET analyses were performed on a Quantachrome Instrument Quadrasorb SI model instrument by Yıldız Technical University Analyses Laboratory. Sample amounts loaded into the instrument differ from 0.17 to 0.28 g. Samples were degassed at 60 °C for 4 h. Analyses were performed in 9 mm-small bulbs, measurements were repeated at 60 different points for each sample in between  $10^{-5}$  – 0.3 P/Po. Micropore analyses were performed at 40 different points for each sample in between  $10^{-5}$ –0.01 P/Po. 10 different points were measured in between the 0.01 – 0.05 P/Po and also 0.05–0.3 P/Po. Detailed results for each sample are provided at the end of the document. Approximate thicknesses for IL layers for each of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>–supported samples were estimated by dividing the difference between pore volumes of supported samples and unloaded  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> into the surface area of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Table SD-1 summarizes these values as well as the expected values obtained by dividing the volume of ILs used for sample preparation into surface area of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (expected IL thickness) assuming a uniform IL dispersion over  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for each sample. The comparison confirms that the BET-determined thickness values are approximately the same as the expected values within error, with an exception of

[BMIM][SbF<sub>6</sub>], for which we could not find a density value. Individual measurement results were given below with the IL names indicated as sample ID.

**Table SD-1.** BET determined and expected values of IL coating layer thickness on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

| IL                         | Sample # | Thickness of IL Coating Layer Å |                                                                                                 |                |
|----------------------------|----------|---------------------------------|-------------------------------------------------------------------------------------------------|----------------|
|                            |          | Calculated by BET results       | Expected values by IL loading per unit surface area of $\gamma$ -Al <sub>2</sub> O <sub>3</sub> | Relative error |
| [BMIM][SbF <sub>6</sub> ]* | 1        | -                               | -                                                                                               | -              |
| [BMIM][DBP]                | 2        | 5.94                            | 7.22                                                                                            | 17.69          |
| [BMIM][HSO <sub>4</sub> ]  | 3        | 5.61                            | 6.03                                                                                            | 6.88           |
| [BMIM][BF <sub>4</sub> ]   | 4        | 5.78                            | 6.33                                                                                            | 8.66           |
| [BMIM][OS]                 | 5        | 5.81                            | 7.09                                                                                            | 18.05          |
| [BMIM][TOS]                | 6        | 6.30                            | 6.66                                                                                            | 5.43           |
| [BMIM][NTf <sub>2</sub> ]  | 7        | 5.60                            | 5.35                                                                                            | 4.66           |
| [BMIM][TfO]                | 8        | 5.88                            | 5.93                                                                                            | 0.98           |
| [BMIM][Ac]                 | 9        | 7.18                            | 7.51                                                                                            | 4.31           |

\*Density value could not be found.

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Optimizing particle performance

### Analysis

Operator: operator Date: 5/8/2014

Sample ID: [BMIM][SbF<sub>6</sub>]

Sample Desc: 32-01-C-N-Sb-F-Al<sub>2</sub>O<sub>3</sub>

Sample weight: 0.2385 g

Analysis Time: 860.3min

Void Vol.: He Mode. Cell: 9mm small bulb

Outgas Time: 4.0hrs

Analysis gas: Nitrogen

Press. Tolerance: 0.050/0.000 (ads/des)

Filename:

Comment:

End of run:

OutgasTemp:

Bath Temp:

Equil time:

### Report

Operator: operator

Date: 5/9/2014

C:\QCdata\Physisorb\32-01-C-N-Sb-F-Al<sub>2</sub>O<sub>3</sub>.QPS

5/8/2014 12:25:36

Standard

60.0 C

77.3 K

30/0 sec (ads/des)

Instrument:

QuadraSorb Station 1

Equil timeout:

300/0 sec (ads/des)

## Multi-Point BET Plot

### Data Reduction Parameters

Adsorbate: Nitrogen

Molec. Wt.: 28.013 g

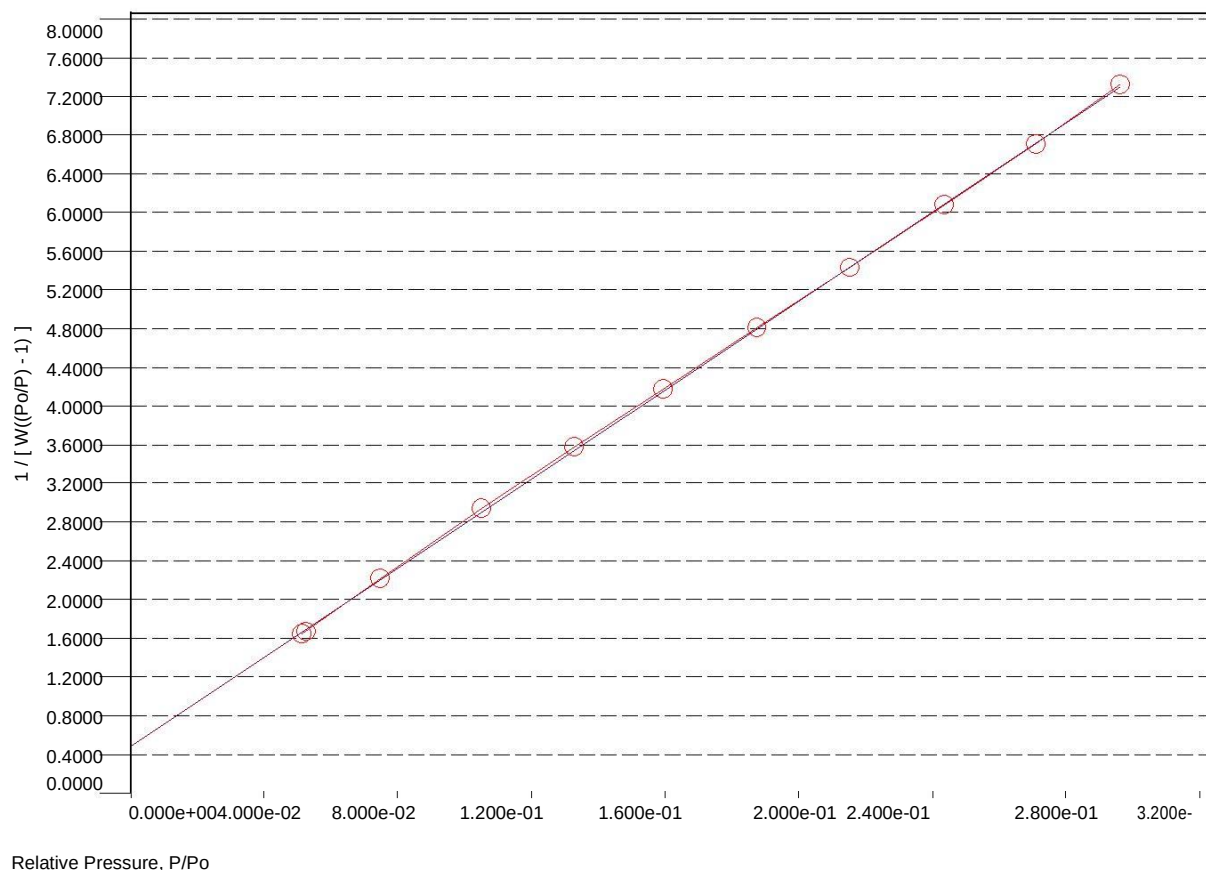
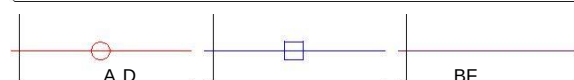
Temperature

77.350 K

Cross Section:

16.200 Å<sup>2</sup>

Liquid Density: 0.808 g/cc



Relative Pressure, P/P<sub>0</sub>

### BET summary

Slope = 23.025

Intercept = 4.877e-01

Correlation coefficient, r = 0.999939

C constant = 48.215

Surface Area = 148.110 m<sup>2</sup>/g

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Optimizing particle performance

### Analysis

Operator: operator Date: 5/8/2014

Sample ID: [BMIM][DBP]

Sample Desc: 32-02-C-N-P-Al<sub>2</sub>O<sub>3</sub>

Sample weight: 0.2532 g

Analysis Time: 779.5min

Void Vol.: He Mode. Cell: 9mm small bulb Run mode: Standard

Outgas Time: 4.0hrs

Analysis gas: Nitrogen

Press. Tolerance: 0.050/0.000 (ads/des)

Filename:

Comment:

End of run: 5/8/2014 11:04:48

OutgasTemp: 60.0 C

Bath Temp: 77.3 K

Equil time: 30/0 sec (ads/des)

### Report

Operator: operator

Date: 5/9/2014

C:\QCdata\Physisorb\32-02-C-N-P-Al<sub>2</sub>O<sub>3</sub>.QPS

Instrument: QuadraSorb Station 2

Equil timeout: 300/0 sec (ads/des)

## Multi-Point BET Plot

### Data Reduction Parameters

Adsorbate: Nitrogen

Molec. Wt.: 28.013 g

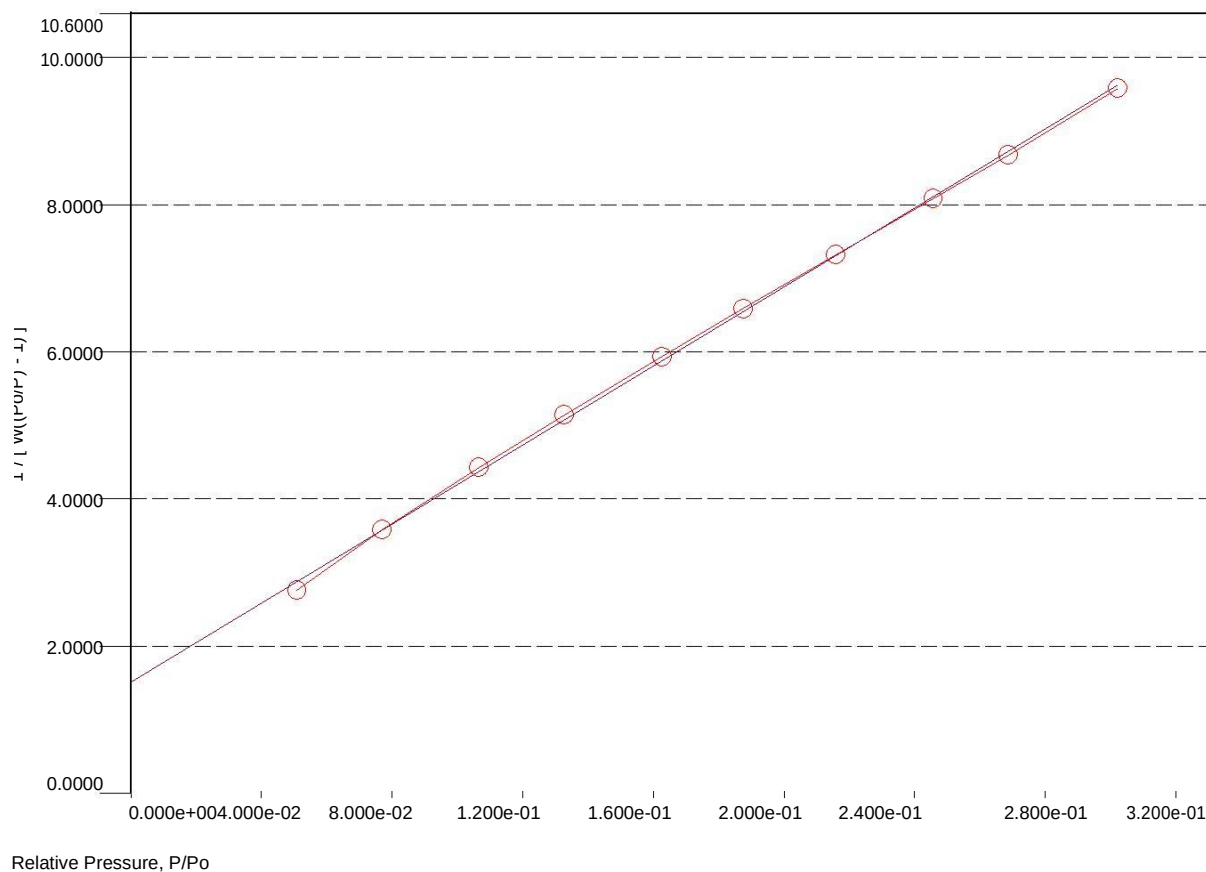
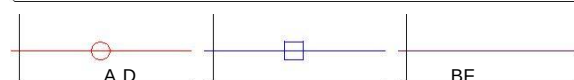
Temperature

77.350 K

Cross Section:

16.200 Å<sup>2</sup>

Liquid Density: 0.808 g/cc



Relative Pressure, P/Po

### BET summary

Slope = 26.852

Intercept = 1.506e+00

Correlation coefficient, r = 0.999668

C constant = 18.833

Surface Area = 122.805 m<sup>2</sup>/g

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### Analysis

Operator: operator Date: 5/8/2014

Sample ID: [BMIM][HSO<sub>4</sub>]

Sample Desc: 32-03-C-N-S-O-Al<sub>2</sub>O<sub>3</sub>

Sample weight: 0.1792 g

Analysis Time: 733.3min

Void Vol.: He Mode. Cell: 9mm small bulb

Outgas Time: 4.0hrs

Analysis gas: Nitrogen

Press. Tolerance: 0.050/0.000 (ads/des)

Filename:

Comment:

End of run: 5/8/2014 10:18:37

Run mode: Standard

Outgas Temp: 60.0 C

Bath Temp: 77.3 K

Equil time: 30/0 sec (ads/des)

### Report

Operator: operator

Date: 5/9/2014

C:\QCdata\Physisorb\32-03-C-N-S-O-Al<sub>2</sub>O<sub>3</sub>.QPS

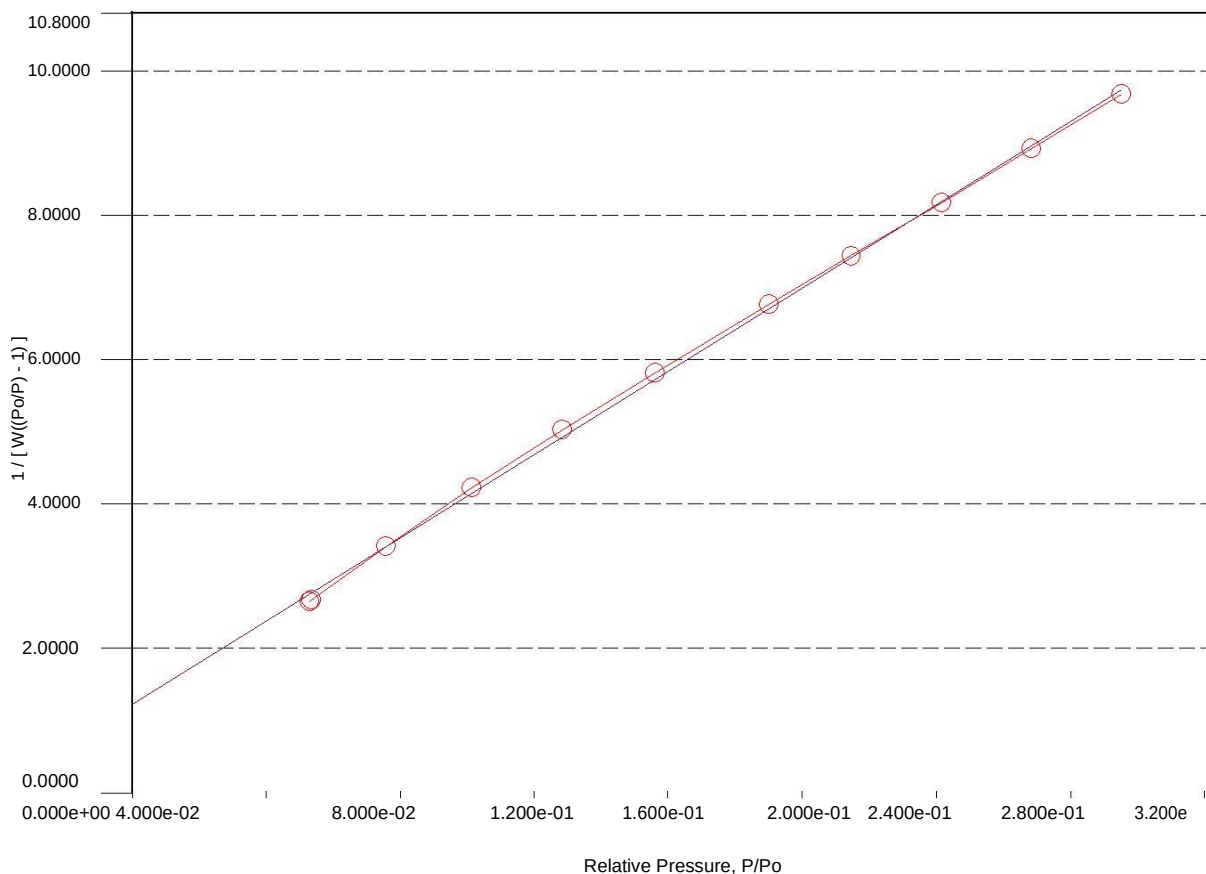
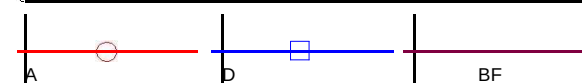
Instrument: QuadraSorb Station 3

Equil timeout: 300/0 sec (ads/des)

### Multi-Point BET Plot

#### Data Reduction Parameters

|                  |                             |                        |                       |
|------------------|-----------------------------|------------------------|-----------------------|
| <b>Adsorbate</b> | <b>Nitrogen</b>             | <b>Temperature</b>     | 77.350K               |
|                  | <b>Molec. Wt.:</b> 28.013 g | <b>Cross Section:</b>  | 16.200 Å <sup>2</sup> |
|                  |                             | <b>Liquid Density:</b> | 0.808 g/cc            |



Relative Pressure, P/Po

#### BET summary

Slope = 28.853  
Intercept = 1.221e+00  
Correlation coefficient, r = 0.999583  
C constant = 24.625  
Surface Area = 115.799 m<sup>2</sup>/g

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Optimizing particle performance

### Analysis

Operator: operator Date: 5/8/2014

Sample ID: [BMIM][BF<sub>4</sub>]

Sample Desc: 32-04-C-N-B-F-O-Al<sub>2</sub>O<sub>3</sub>

Sample weight: 0.1785 g

Analysis Time: 761.3min

Void Vol.: He Mode. Cell: 9mm small bulb

Outgas Time: 4.0hrs

Analysis gas: Nitrogen

Press. Tolerance: 0.050/0.000 (ads/des)

Filename:

Comment:

End of run: 5/8/2014 10:46:39

Run mode: Standard

Outgas Temp: 60.0 C

Bath Temp: 77.3 K

Equil time: 30/0 sec (ads/des)

### Report

Operator: operator

Date: 5/9/2014

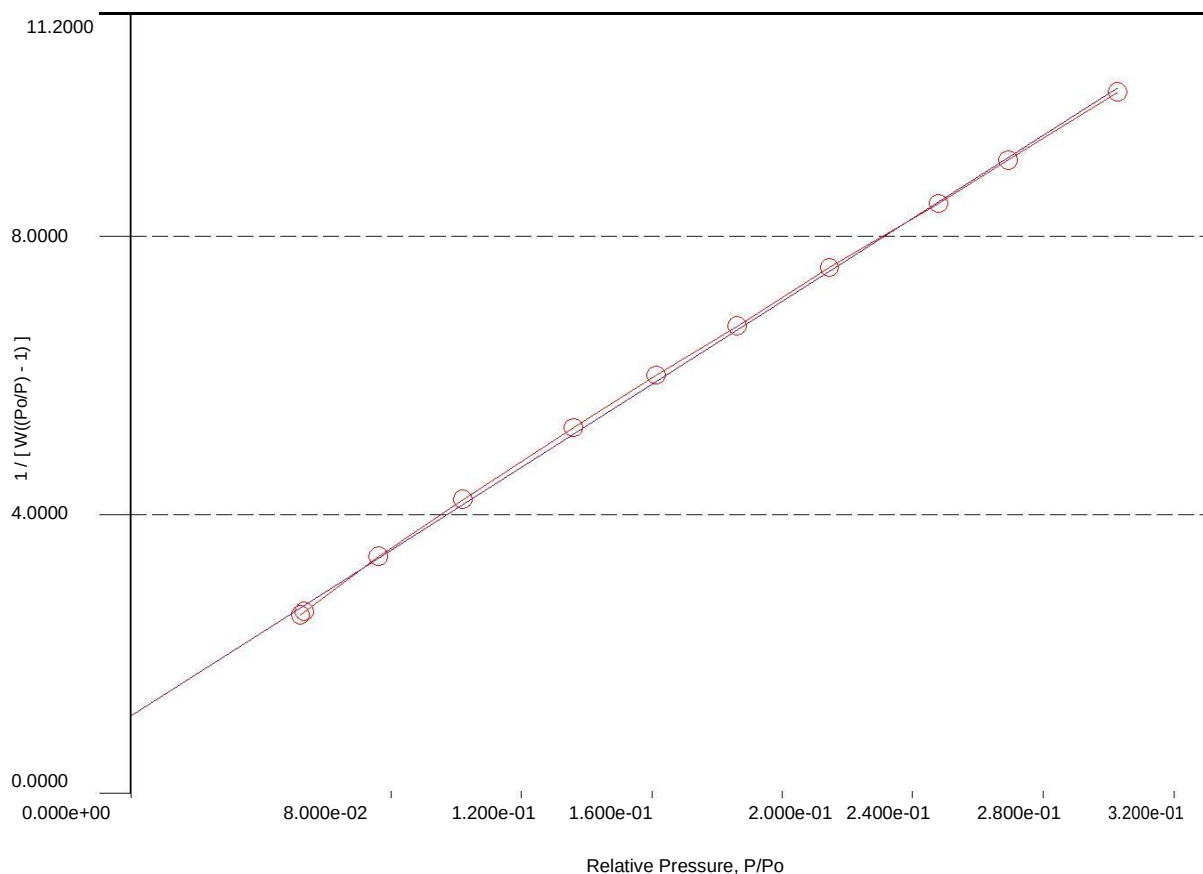
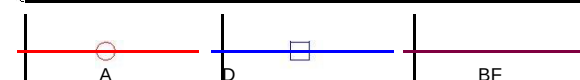
C:\QCdata\Physisorb\32-04-C-N-B-F-O-Al<sub>2</sub>O<sub>3</sub>.QPS

Instrument: QuadraSorb Station 4

Equil timeout: 300/0 sec (ads/des)

### Multi-Point BET Plot

| Data Reduction Parameters |                      |                 |                       |
|---------------------------|----------------------|-----------------|-----------------------|
| Adsorbate                 | Nitrogen             | Temperature     | 77.350K               |
|                           | Molec. Wt.: 28.013 g | Cross Section:  | 16.200 Å <sup>2</sup> |
|                           |                      | Liquid Density: | 0.808 g/cc            |



| BET summary                  |                           |
|------------------------------|---------------------------|
| Slope =                      | 29.862                    |
| Intercept =                  | 1.101e+00                 |
| Correlation coefficient, r = | 0.999629                  |
| C constant =                 | 28.121                    |
| Surface Area =               | 112.475 m <sup>2</sup> /g |

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Optimizing particle performance

### Analysis

Operator: operator Date: 5/9/2014

Sample ID: [BMIM][OS]

Sample Desc: 32-05-C-N-S-O-Al<sub>2</sub>O<sub>3</sub>

Sample weight: 0.2823 g

Analysis Time: 792.4min

Void Vol.: He Mode. Cell: 9mm small bulb Run mode: Standard

Outgas Time: 4.0hrs

Analysis gas: Nitrogen

Press. Tolerance: 0.050/0.000 (ads/des)

Filename:

Comment:

End of run: 5/9/2014 10:31:30

Outgas Temp: 60.0 C

Bath Temp: 77.3 K

Equil time: 30/0 sec (ads/des)

### Report

Operator: operator

Date: 5/9/2014

C:\QCdata\Physisorb\32-05-C-N-S-O-Al<sub>2</sub>O<sub>3</sub>.QPS

Instrument: QuadraSorb Station 1

Equil timeout: 300/0 sec (ads/des)

## Multi-Point BET Plot

### Data Reduction Parameters

Adsorbate: Nitrogen

Molec. Wt.: 28.013 g

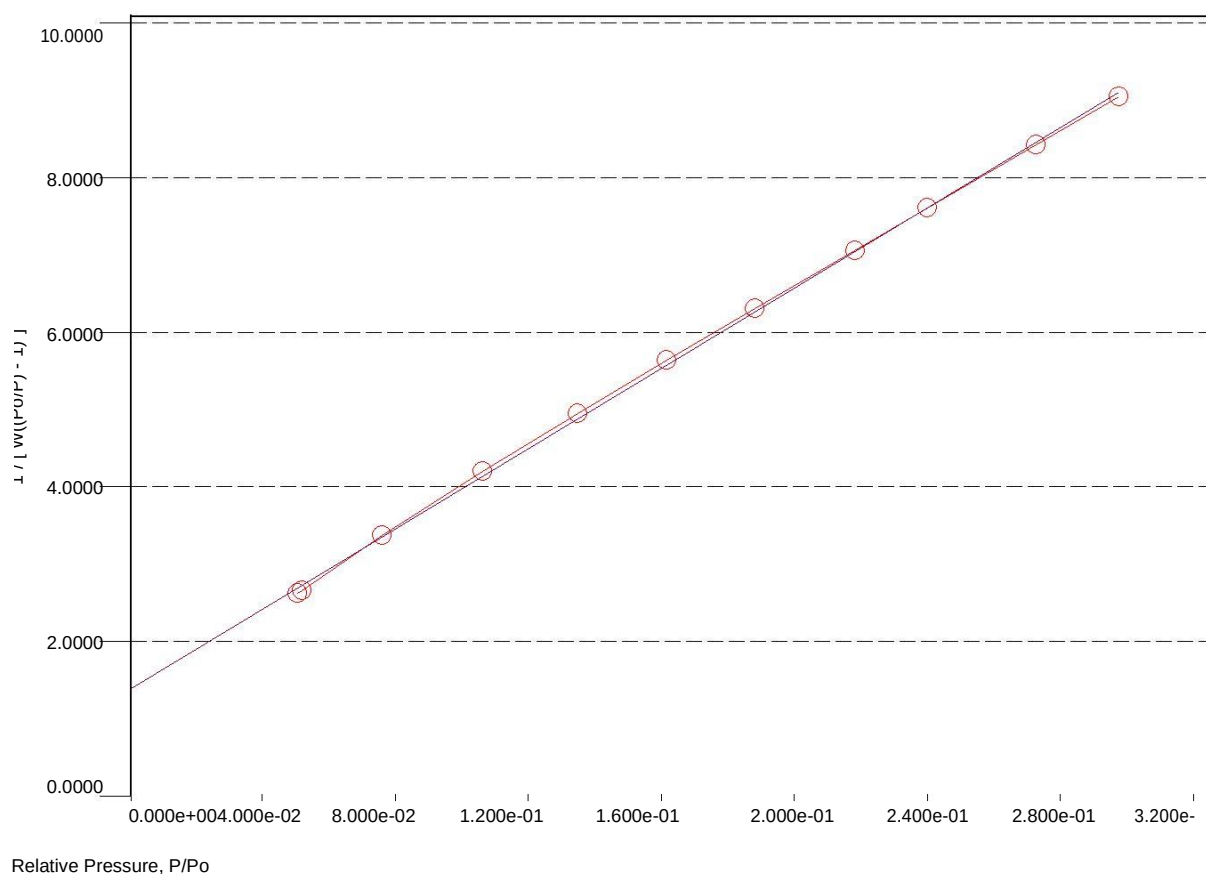
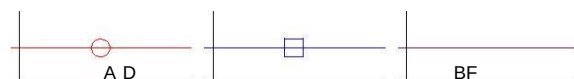
Temperature

77.350 K

Cross Section:

16.200 Å<sup>2</sup>

Liquid Density: 0.808 g/cc



Relative Pressure, P/Po

### BET summary

Slope = 25.942

Intercept = 1.397e+00

Correlation coefficient, r = 0.999718

C constant = 19.569

Surface Area = 127.385 m<sup>2</sup>/g

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Optimizing particle performance

### Analysis

Operator: operator Date: 5/9/2014

Sample ID: [BMIM][TOS]

Sample Desc: 32-06-C-N-S-O-Al<sub>2</sub>O<sub>3</sub>

Sample weight: 0.2975 g

Analysis Time: 844.5min

Void Vol.: He Mode. Cell: 9mm small bulb

Outgas Time: 4.0hrs

Analysis gas: Nitrogen

Press. Tolerance: 0.050/0.000 (ads/des)

Filename:

Comment:

End of run: 5/9/2014 11:23:40

Run mode: Standard

Outgas Temp: 60.0 C

Bath Temp: 77.3 K

Equil time: 30/0 sec (ads/des)

### Report

Operator: operator

Date: 5/9/2014

C:\QCdata\Physisorb\32-06-C-N-S-O-Al<sub>2</sub>O<sub>3</sub>.QPS

Instrument: QuadraSorb Station 2

Equil timeout: 300/0 sec (ads/des)

## Multi-Point BET Plot

### Data Reduction Parameters

Adsorbate: Nitrogen

Molec. Wt.: 28.013 g

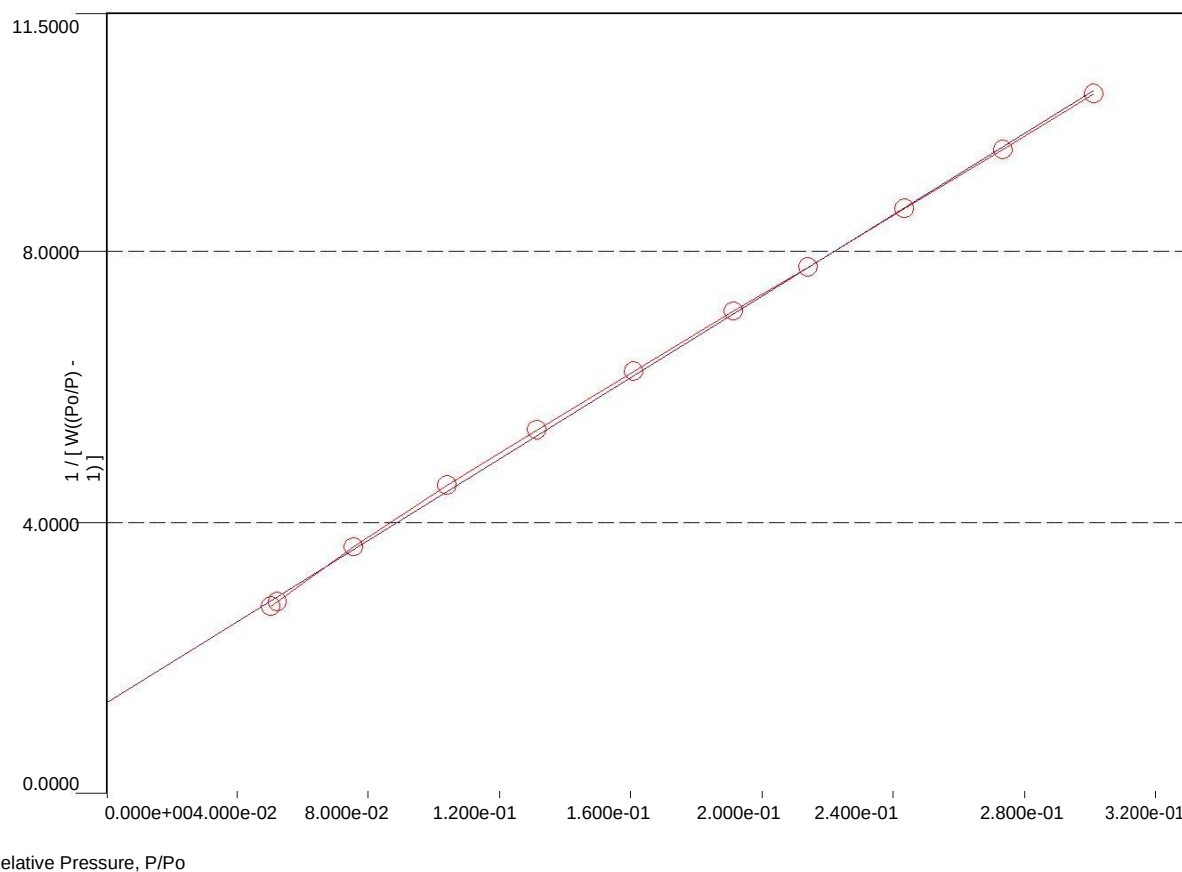
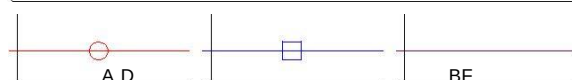
Temperature

77.350K

Cross Section:

16.200 Å<sup>2</sup>

Liquid Density: 0.808 g/cc



Relative Pressure, P/Po

### BET summary

Slope = 29.977

Intercept = 1.343e+00

Correlation coefficient, r = 0.999728

C constant = 23.313

Surface Area = 111.190 m<sup>2</sup>/g

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Optimizing particle performance

### Analysis

Operator: operator Date: 5/9/2014

Sample ID: [BMIM][NTf<sub>2</sub>]

Sample Desc: 32-07-C-N-F-S-O-Al<sub>2</sub>O<sub>3</sub>

Sample weight: 0.2685 g

Analysis Time: 825.0 min

Void Vol.: He Mode. Cell: 9mm small bulb

Outgas Time: 4.0 hrs

Analysis gas: Nitrogen

Press. Tolerance: 0.050/0.000 (ads/des)

Filename:

Comment:

End of run: 5/9/2014 11:04:11

Run mode: Standard

Outgas Temp: 60.0 C

Bath Temp: 77.3 K

Equil time: 30/0 sec (ads/des)

### Report

Operator: operator

Date: 5/9/2014

C:\QCdata\Physisorb\32-07-C-N-F-S-O-Al<sub>2</sub>O<sub>3</sub>.QPS

Instrument: QuadraSorb Station 3

Equil timeout: 300/0 sec (ads/des)

## Multi-Point BET Plot

### Data Reduction Parameters

Adsorbate: Nitrogen

Molec. Wt.: 28.013 g

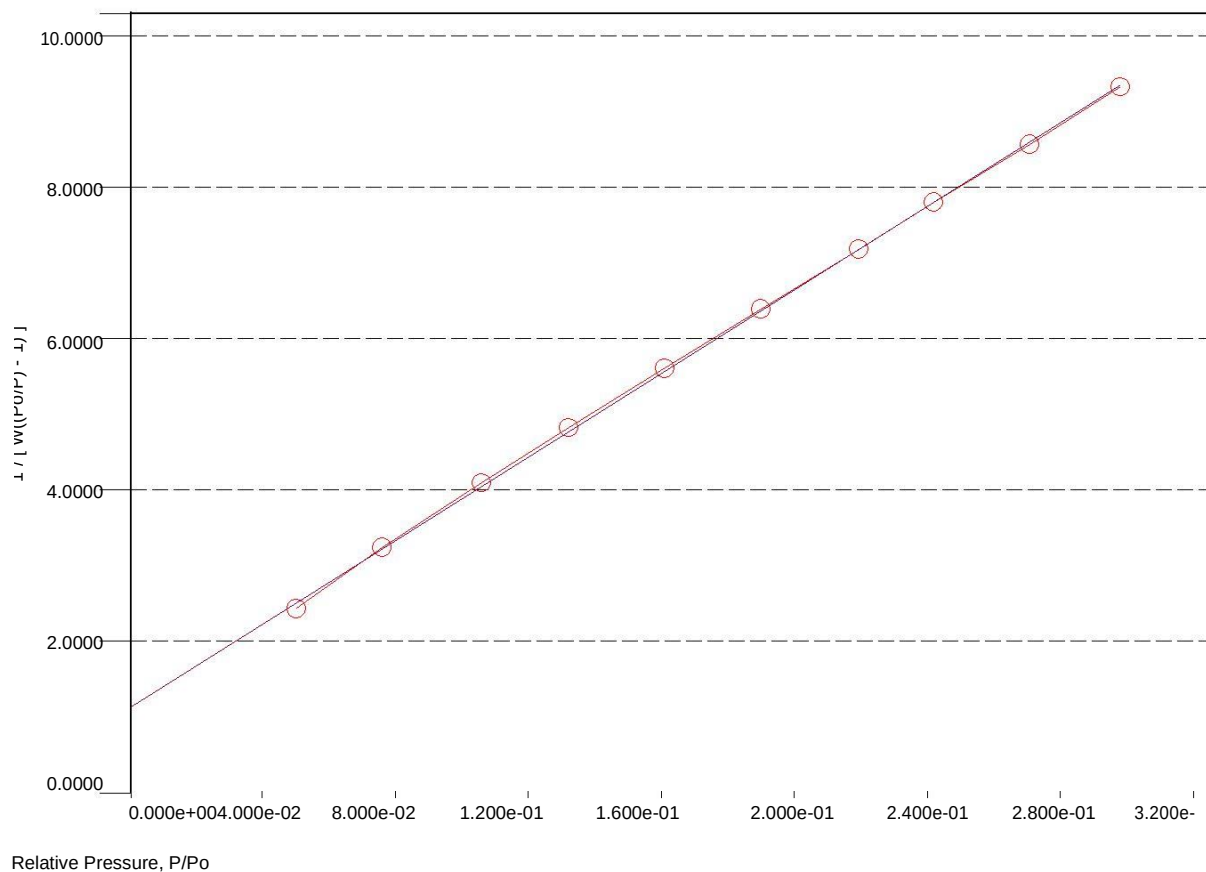
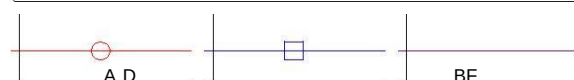
Temperature

77.350 K

Cross Section:

16.200 Å<sup>2</sup>

Liquid Density: 0.808 g/cc



Relative Pressure, P/Po

### BET summary

Slope = 27.555

Intercept = 1.138e+00

Correlation coefficient, r = 0.999840

C constant = 25.204

Surface Area = 121.368 m<sup>2</sup>/g

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Optimizing particle performance

### Analysis

Operator: operator Date: 5/9/2014

Sample ID: [BMIM][TfO]

Sample Desc: 32-08-C-N-S-O-F-Al<sub>2</sub>O<sub>3</sub>

Sample weight: 0.2885 g

Analysis Time: 868.8 min

Void Vol.: He Mode. Cell: 9mm small bulb

Outgas Time: 4.0 hrs

Analysis gas: Nitrogen

Press. Tolerance: 0.050/0.000 (ads/des)

Filename:

Comment:

End of run:

Outgas Temp:

Bath Temp:

Equil time:

### Report

Operator: operator

Date: 5/9/2014

C:\QCdata\Physisorb\32-08-C-N-S-O-F-Al<sub>2</sub>O<sub>3</sub>.QPS

5/9/2014 11:47:57

Instrument:

QuadraSorb Station 4

Standard

60.0 C

77.3 K

30/0 sec (ads/des)

Equil timeout:

300/0 sec (ads/des)

## Multi-Point BET Plot

### Data Reduction Parameters

Adsorbate: Nitrogen

Molec. Wt.: 28.013 g

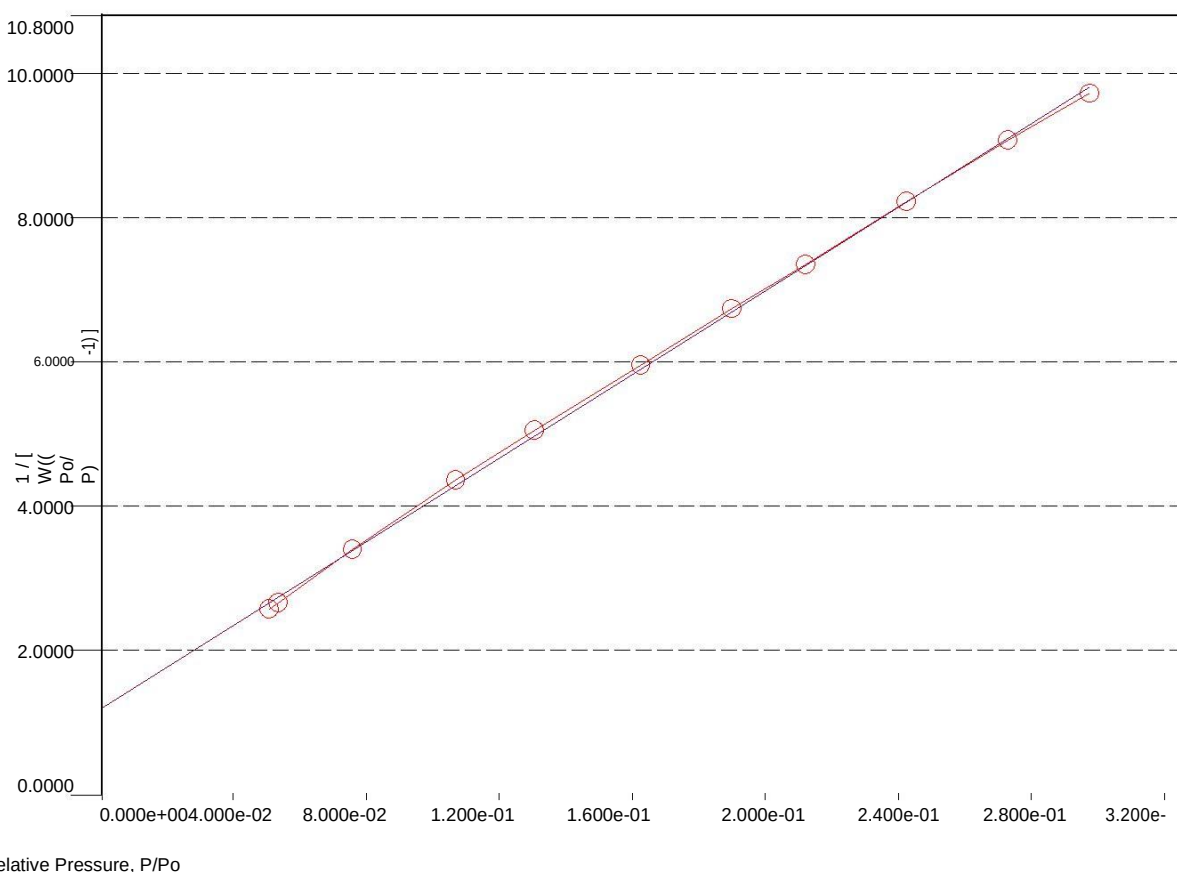
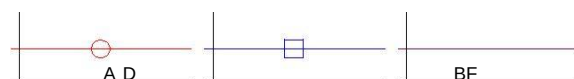
Temperature

77.350 K

Cross Section:

16.200 Å<sup>2</sup>

Liquid Density: 0.808 g/cc



Relative Pressure, P/P<sub>0</sub>

### BET summary

Slope = 28.892

Intercept = 1.202e+00

Correlation coefficient, r = 0.999691

C constant = 25.030

Surface Area = 115.720 m<sup>2</sup>/g

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Optimizing particle performance

#### Analysis

Operator:operator Date:5/10/2014

Sample ID: [BMIM][OAc]

Sample Desc: 32-09-C-N-O-Al2O3

Sample weight: 0.2647 g

Analysis Time: 426.9min

Void Vol.: He Mode.Cell: 9mm small bulbRun mode Standard

Outgas Time: 4.0hrs

Analysis gas: Nitrogen

Press. Tolerance: 0.050/0.000 (ads/des)

Filename:

Comment:

End of run: 5/10/2014 4:27:32

OutgasTemp: 60.0 C

Bath Temp: 77.3 K

Equil time: 30/0 sec (ads/des)

#### Report

Operator:operator

Date:5/12/2014

C:\QCdata\Physisorb\32-09-C-N-O-Al2O3.QPS

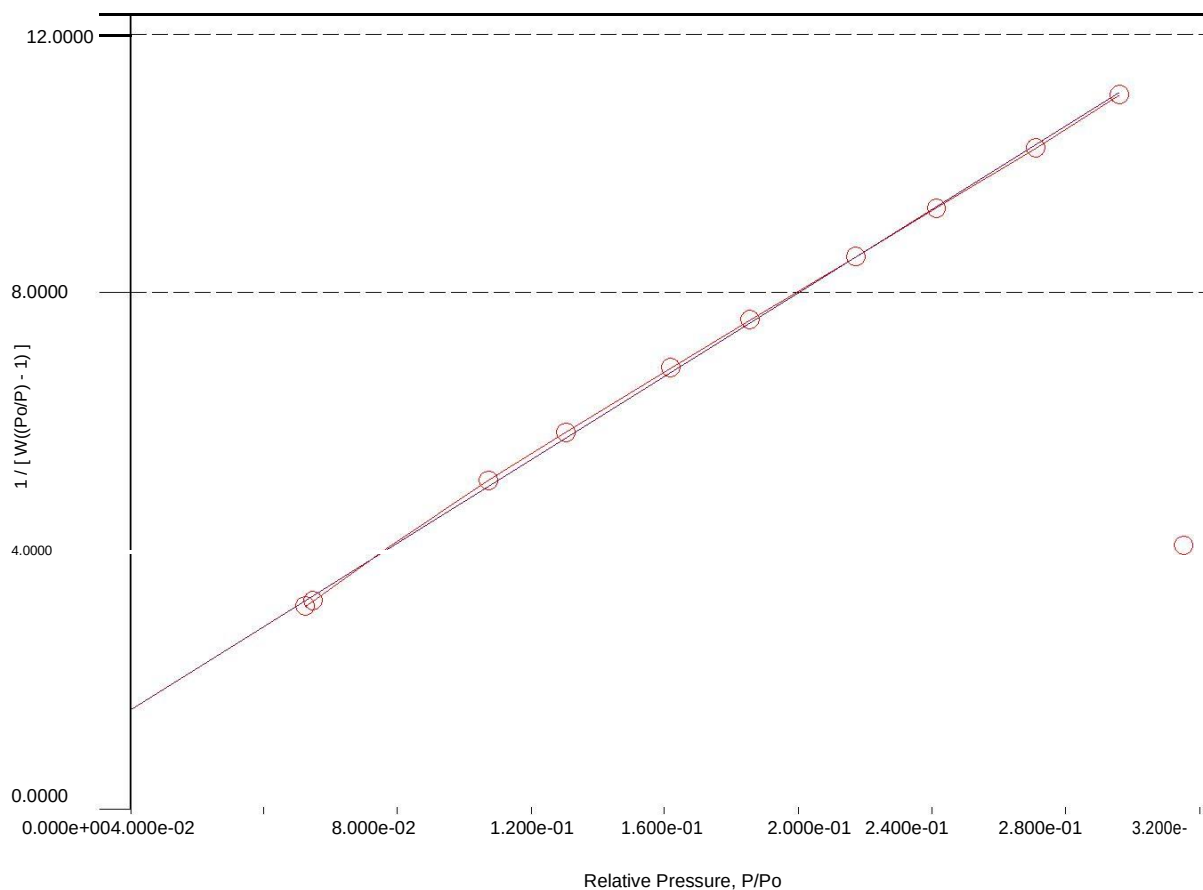
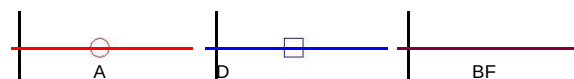
Instrument: QuadraSorb Station 1

Equil timeout: 300/0 sec (ads/des)

### Multi-Point BET Plot

#### Data Reduction Parameters

|                  |                             |                       |                       |                        |            |
|------------------|-----------------------------|-----------------------|-----------------------|------------------------|------------|
| <b>Adsorbate</b> | <b>Nitrogen</b>             | <b>Temperature</b>    | 77.350K               | <b>Liquid Density:</b> | 0.808 g/cc |
|                  | <b>Molec. Wt.:</b> 28.013 g | <b>Cross Section:</b> | 16.200 Å <sup>2</sup> |                        |            |



#### BET summary

Slope = 32.255  
Intercept = 1.544e+00  
Correlation coefficient, r = 0.999752  
C constant = 21.886  
Surface Area = 103.036 m<sup>2</sup>/g

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Optimizing particle performance

### Analysis

Operator: operator Date: 5/10/2014

Sample ID:  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

Sample Desc: 32-10-Al<sub>2</sub>O<sub>3</sub>

Sample weight: 0.1459 g

Analysis Time: 513.8min

Void Vol.: He Mode. Cell: 9mm small bulb

Outgas Time: 4.0hrs

Analysis gas: Nitrogen

Press. Tolerance: 0.050/0.000 (ads/des)

Filename:

Comment:

End of run: 5/10/2014 5:54:28

Run mode: Standard

Outgas Temp: 60.0 C

Bath Temp: 77.3 K

Equil time: 30/0 sec (ads/des)

### Report

Operator: operator Date: 5/12/2014

C:\QCdata\Physisorb\32-10-Al2O3.QPS

Instrument: QuadraSorb Station 2

Equil timeout: 300/0 sec (ads/des)

## Multi-Point BET Plot

### Data Reduction Parameters

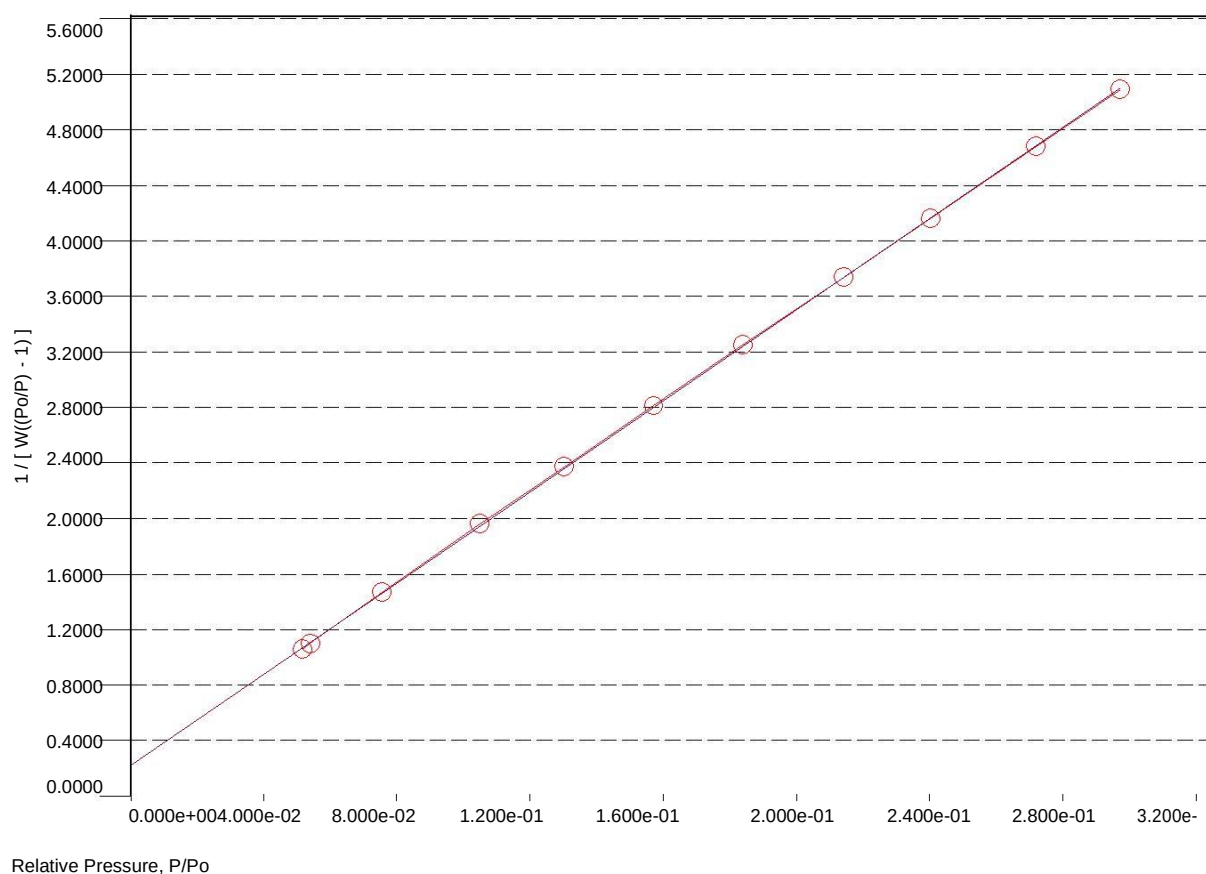
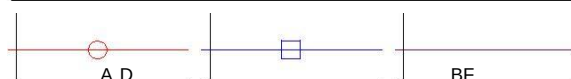
Adsorbate: Nitrogen

Molec. Wt.: 28.013 g

Temperature: 77.350 K

Cross Section: 16.200 Å<sup>2</sup>

Liquid Density: 0.808 g/cc



### BET summary

Slope = 16.416

Intercept = 2.247e-01

Correlation coefficient, r = 0.999971

C constant = 74.064

Surface Area = 209.276 m<sup>2</sup>/g

### Thermal Stability Analysis by TGA

Approximately 15 mg of samples were placed in platinum pans and purged with nitrogen for one hr. For the removal of water adsorbed by support material or IL, a pretreatment period for each IL was performed at 80 °C for one hr. Following the pretreatment period, TGA measurements (TA Instruments TGA Q500 model) were performed at a heating rate of 10 °C/min in flowing nitrogen within a temperature range of 24 to 500 °C for bulk ILs and a range of 24-800 °C for ILs coated on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Since the decomposition of bulk ILs may contaminate the instrument, decomposition range for these ILs kept at lower temperatures compared to the ILs on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

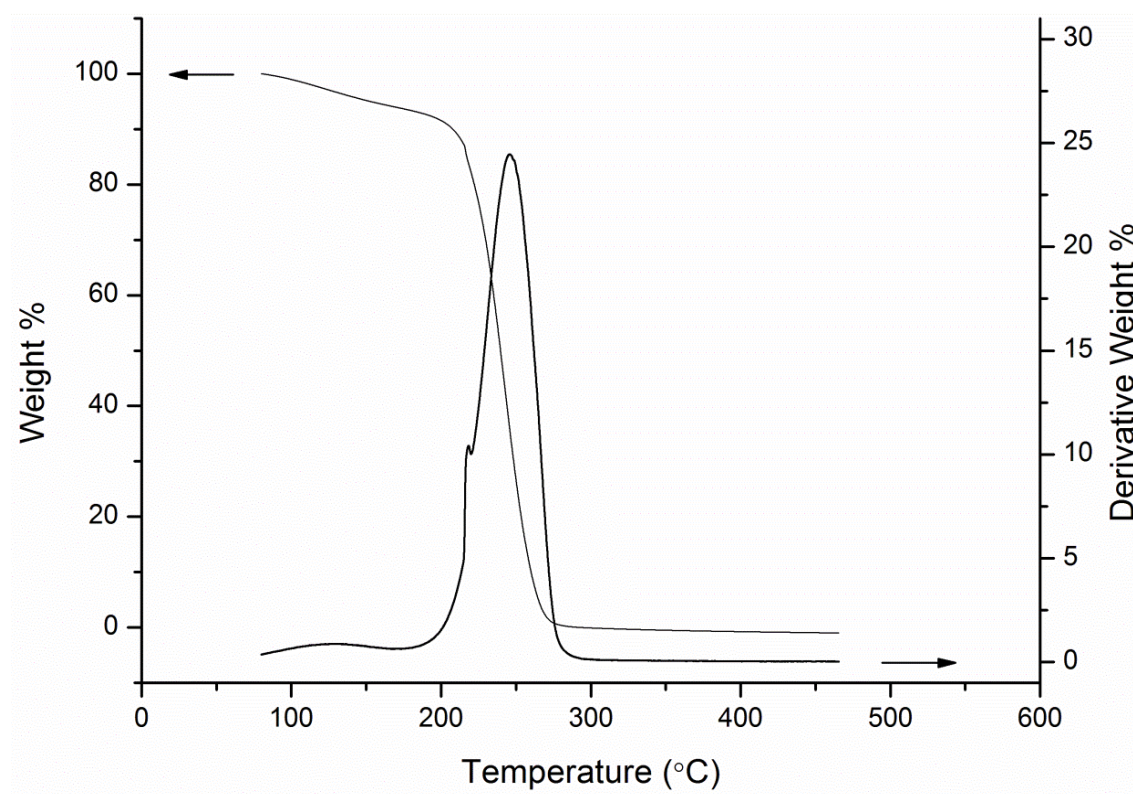


**Figure 3A-1** TG/DTG curve of bulk [BMIM][OAc].

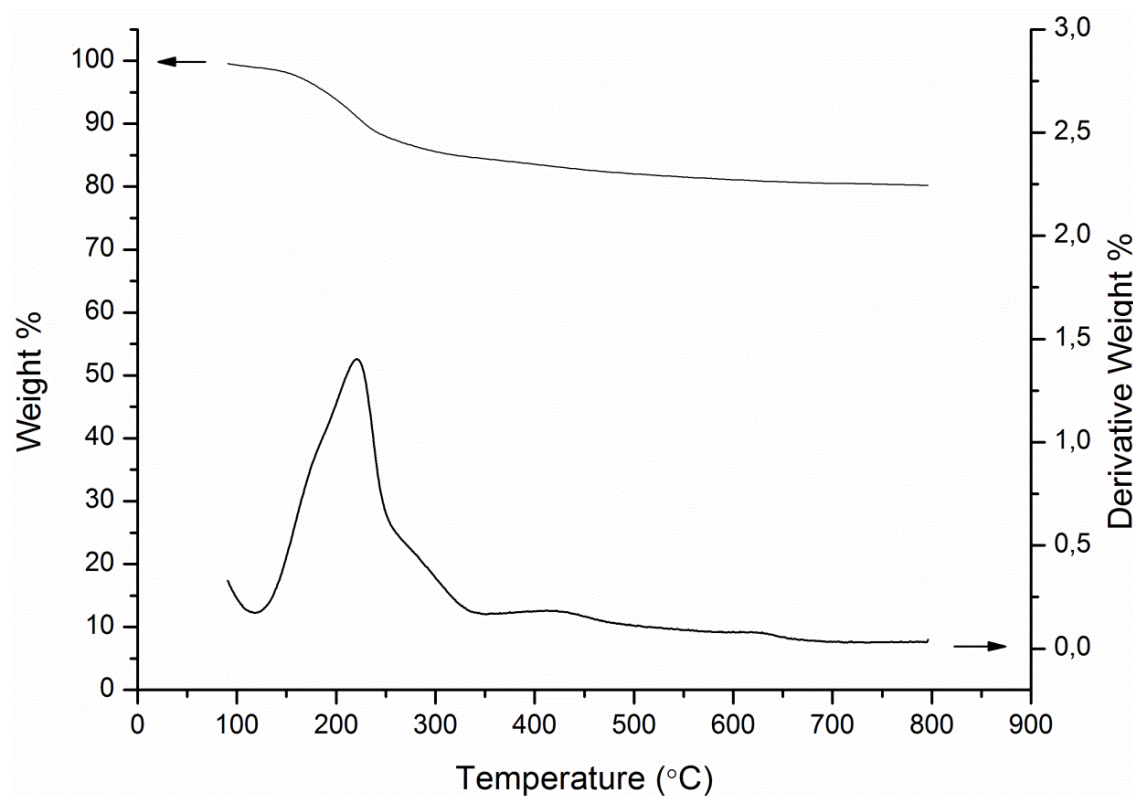


**Figure 3A-2** TG/DTG curve of [BMIM][OAc] on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

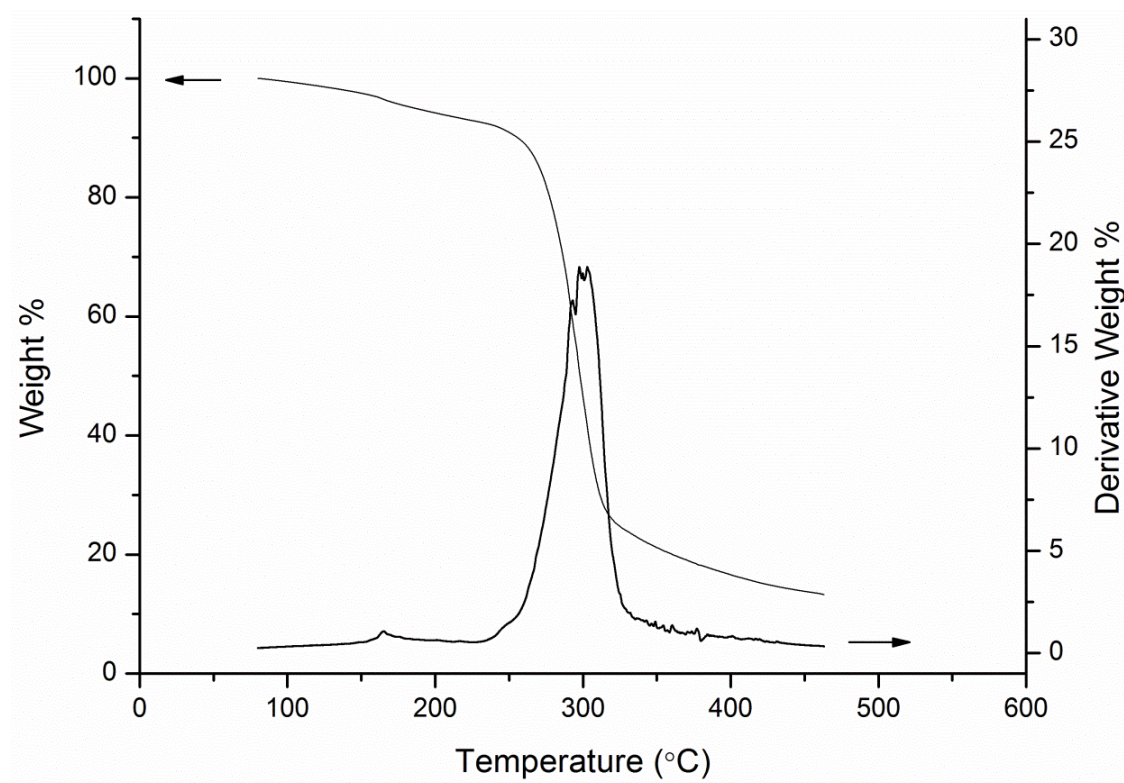


**Figure 3A-3** TG/DTG curve of bulk [BMIM][DBP].

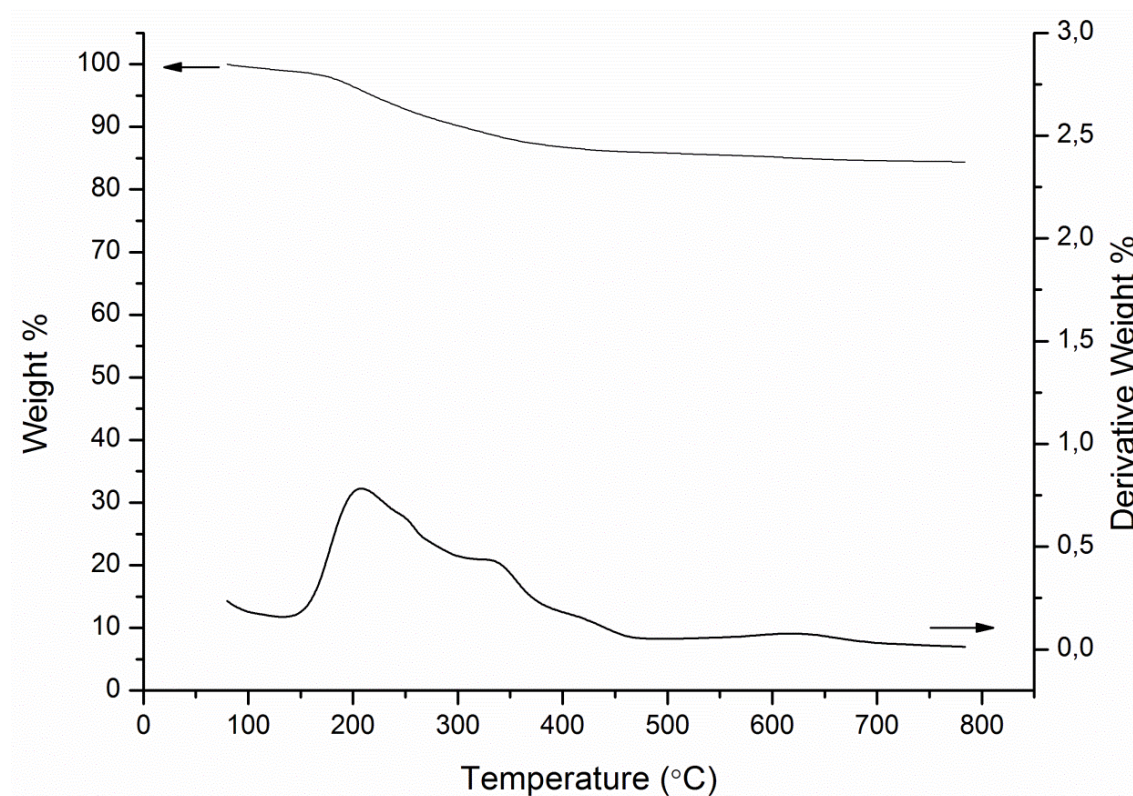


**Figure 3A-4** TG/DTG curve of [BMIM][DBP] on  $\gamma$ - $\text{Al}_2\text{O}_3$ .

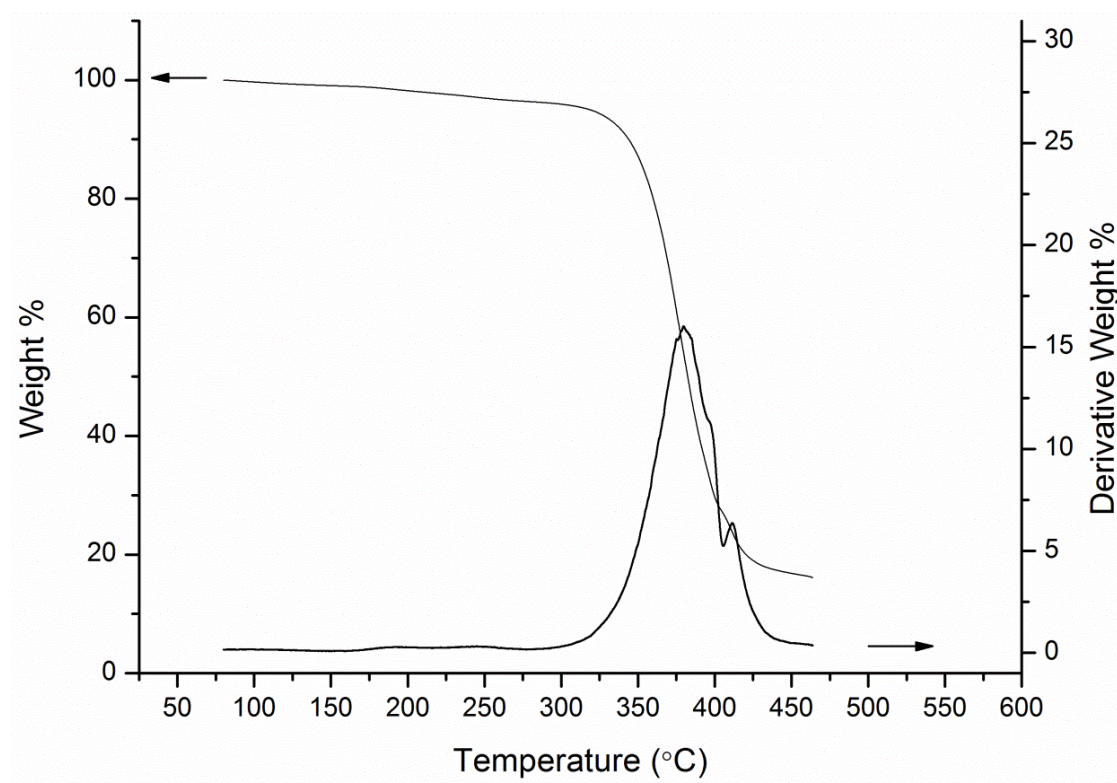


**Figure 3A-5** TG/DTG curve of bulk [BMIM][TOS].

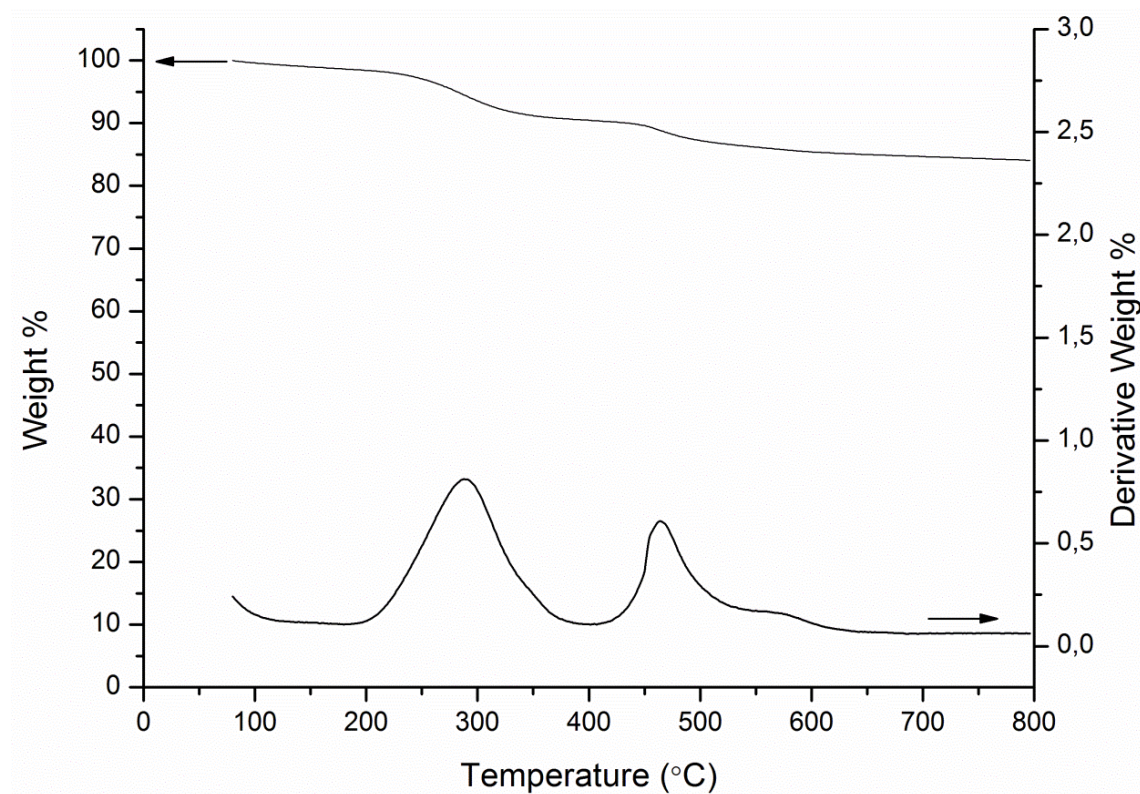


**Figure 3A-6** TG/DTG curve of [BMIM][TOS] on  $\gamma$ - $\text{Al}_2\text{O}_3$ .

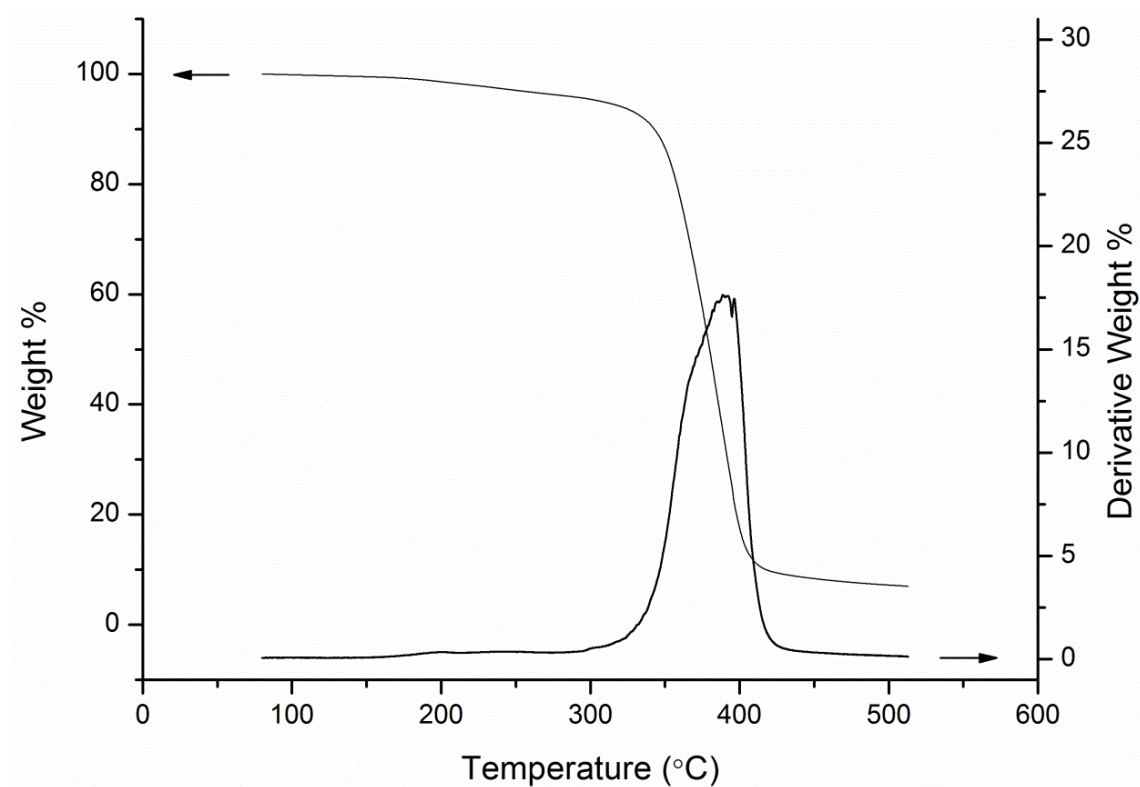


**Figure 3A-7** TG/DTG curve of bulk [BMIM][HSO<sub>4</sub>].

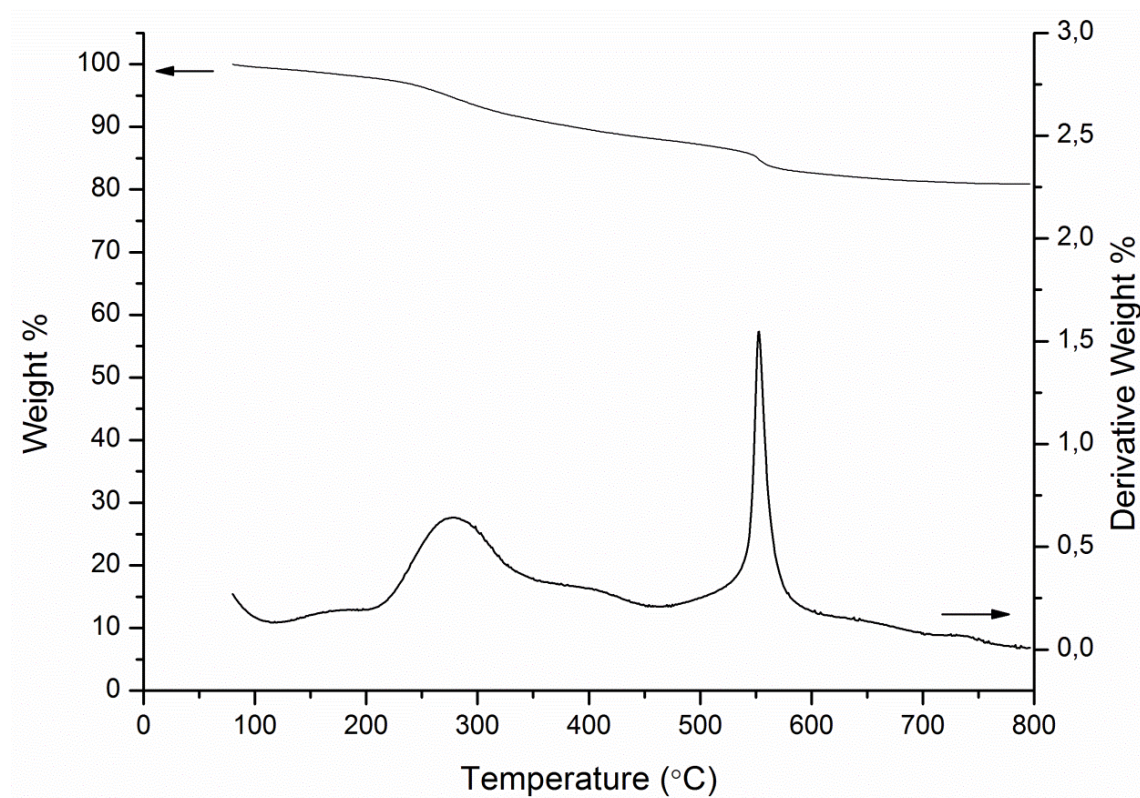


**Figure 3A-8** TG/DTG curve of [BMIM][HSO<sub>4</sub>] on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

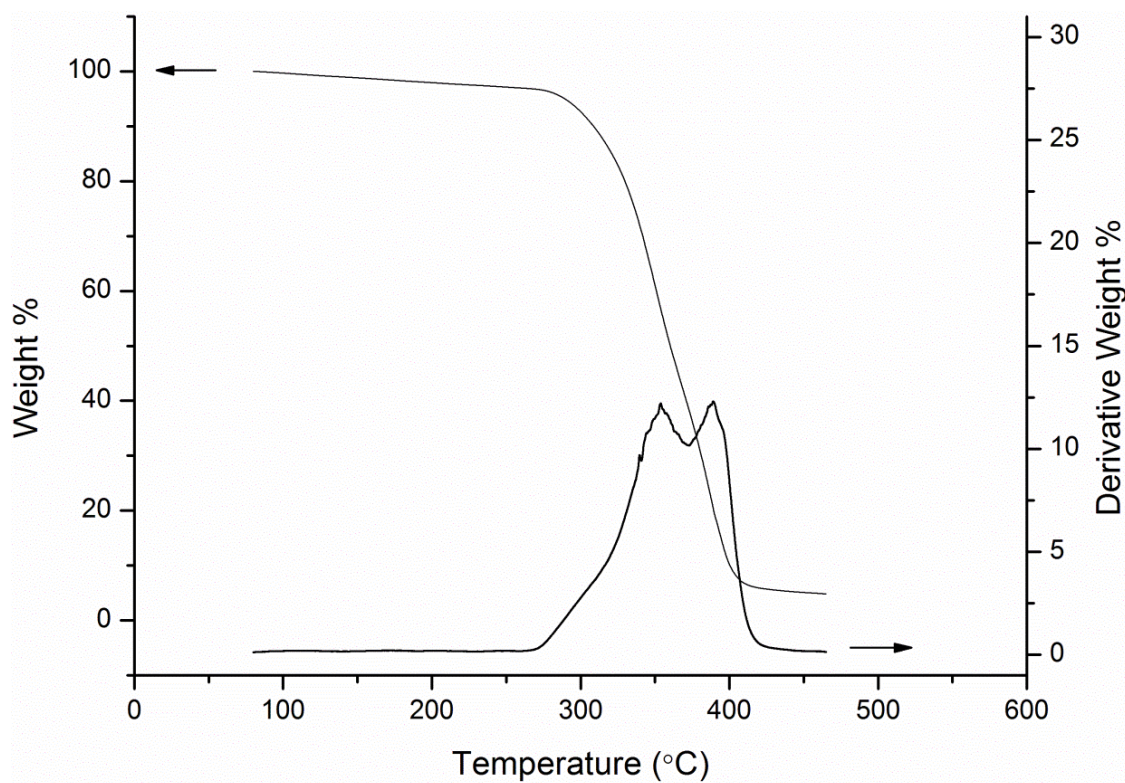


**Figure 3A-9** TG/DTG curve of bulk [BMIM][OS].

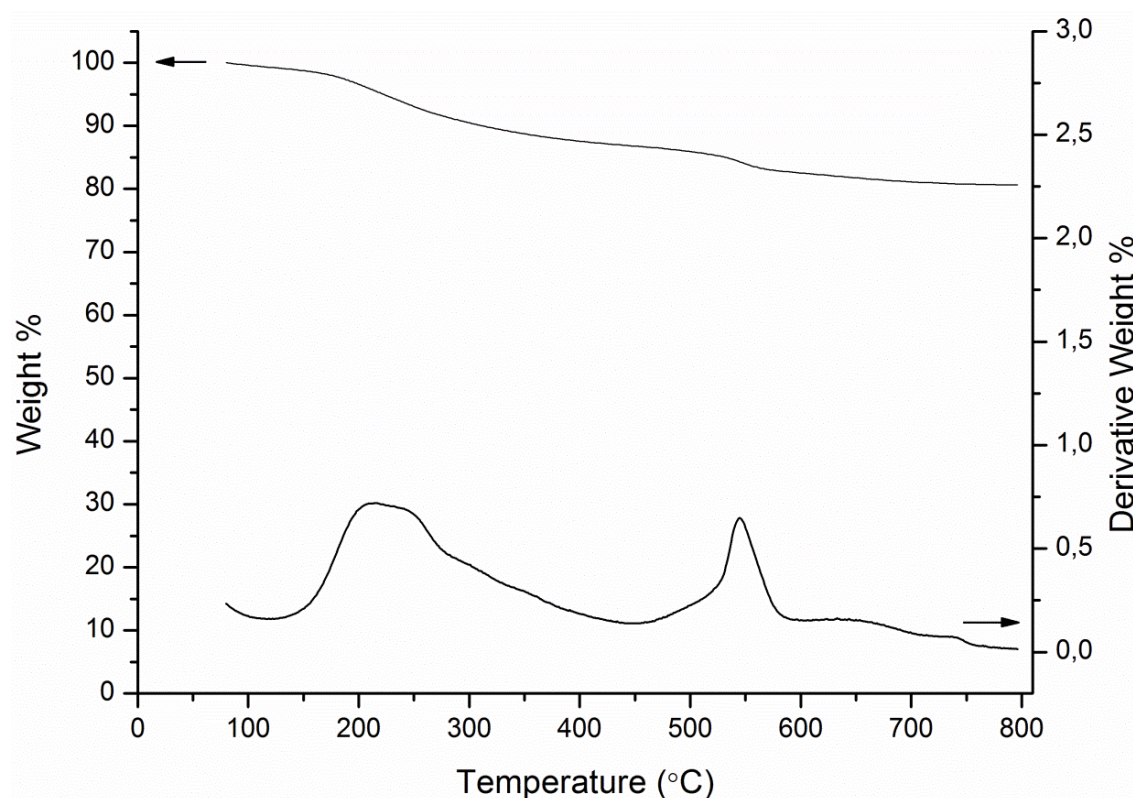


**Figure 3A-10** TG/DTG curve of [BMIM][OS] on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

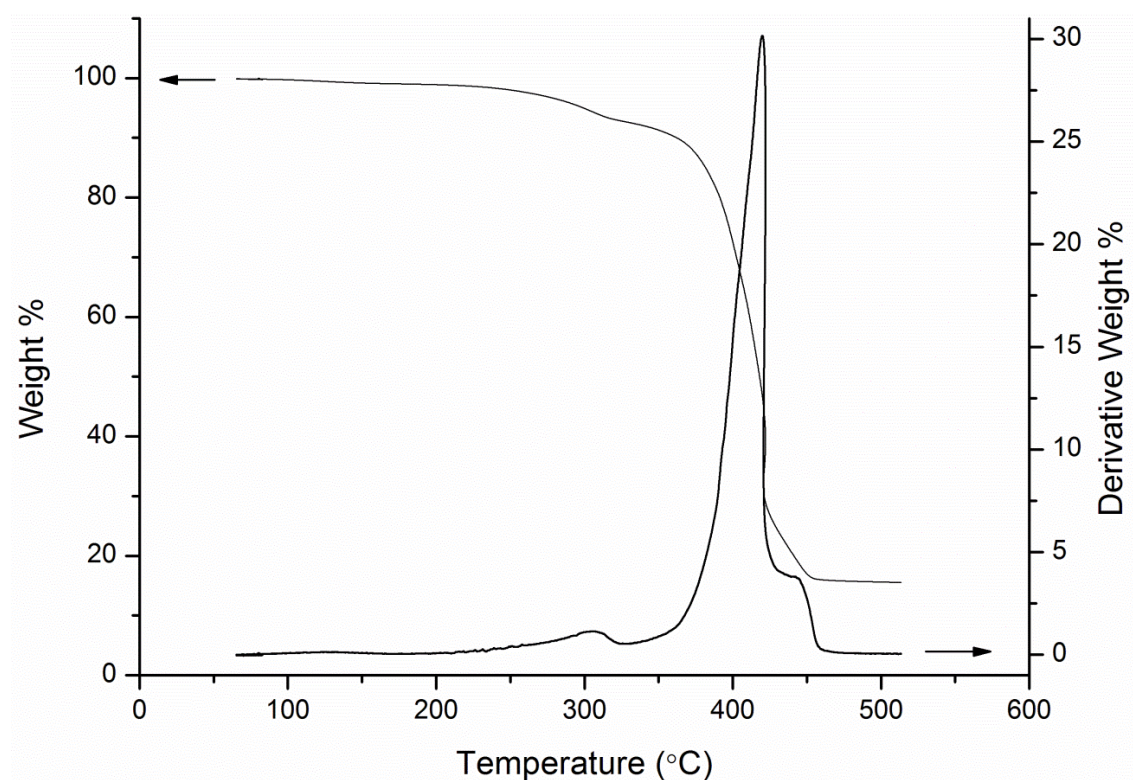


**Figure 3A-11** TG/DTG curve of bulk [BMIM][TfO].

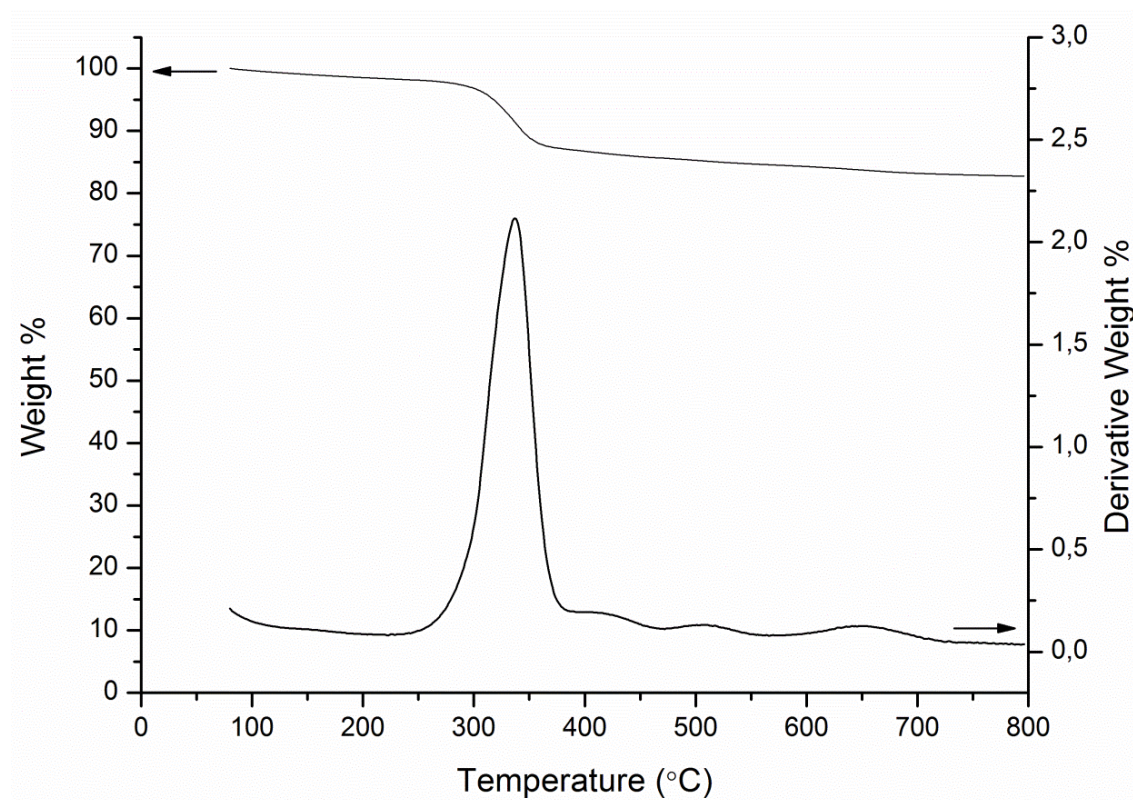


**Figure 3A-12** TG/DTG curve of [BMIM][TfO] on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

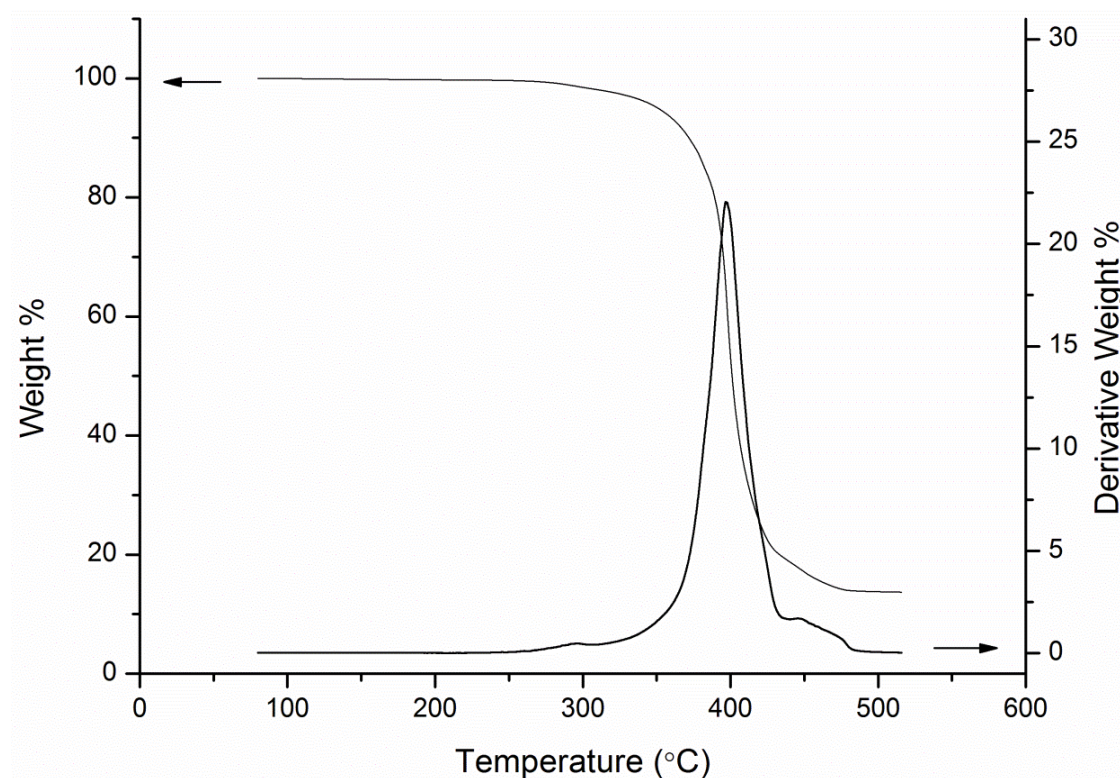


**Figure 3A-13** TG/DTG curve of bulk [BMIM][BF<sub>4</sub>].

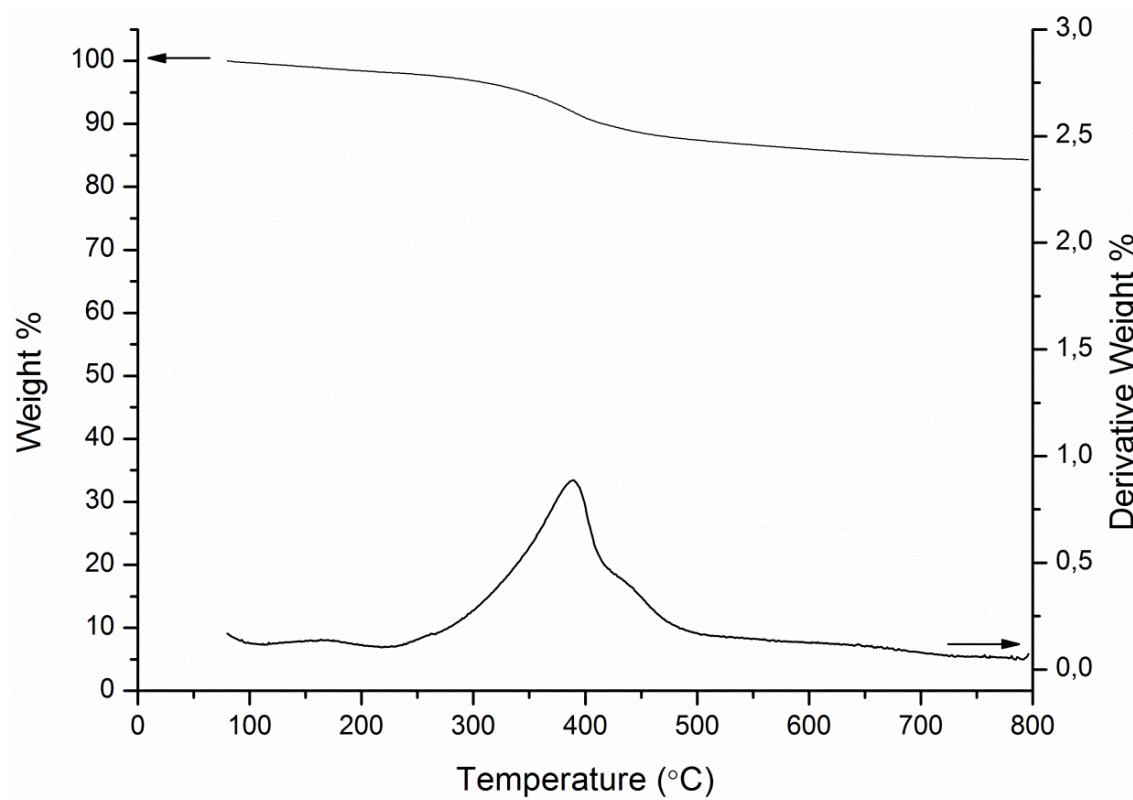


**Figure 3A-14** TG/DTG curve of [BMIM][BF<sub>4</sub>] on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

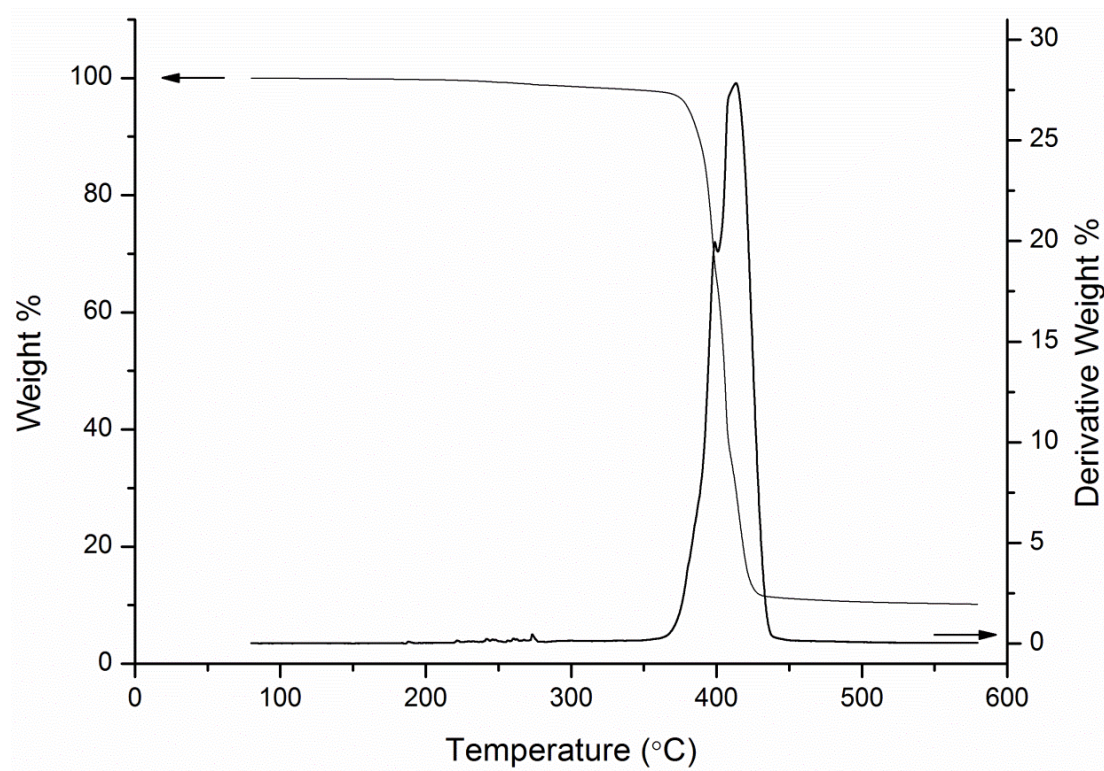


**Figure 3A-15** TG/DTG curve of bulk [BMIM][SbF<sub>6</sub>].

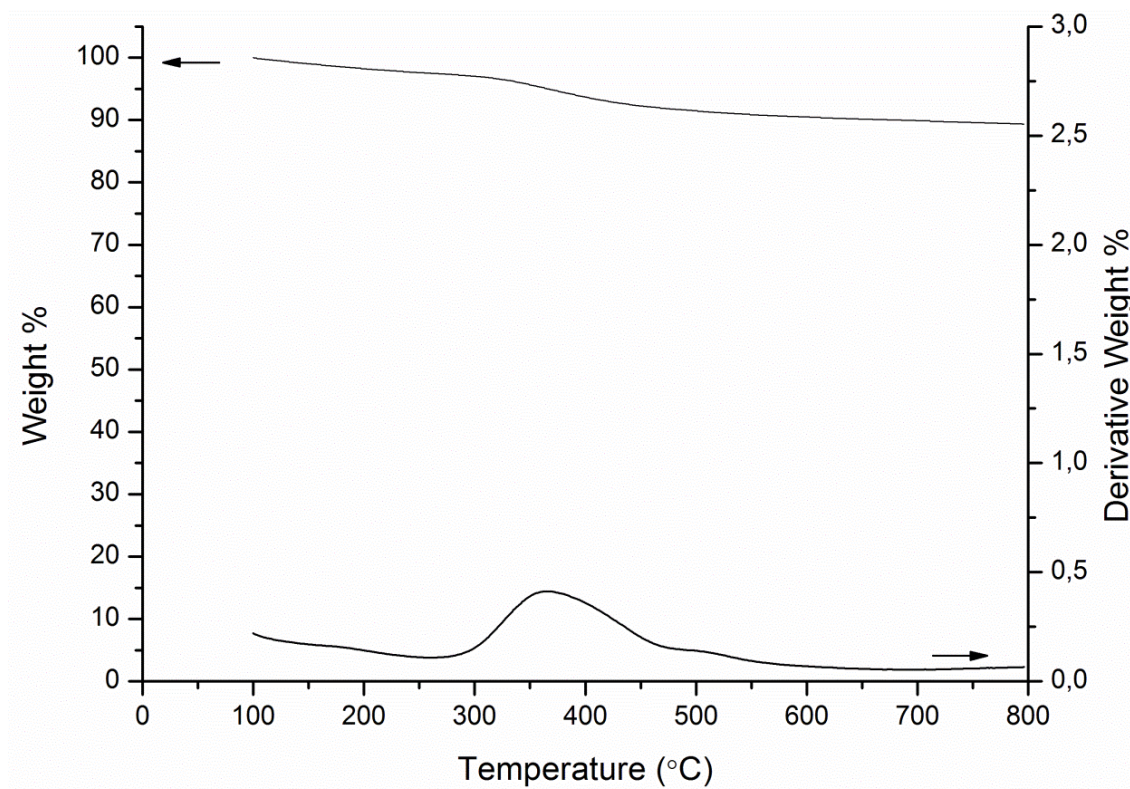


**Figure 3A-16** TG/DTG curve of [BMIM][SbF<sub>6</sub>] on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

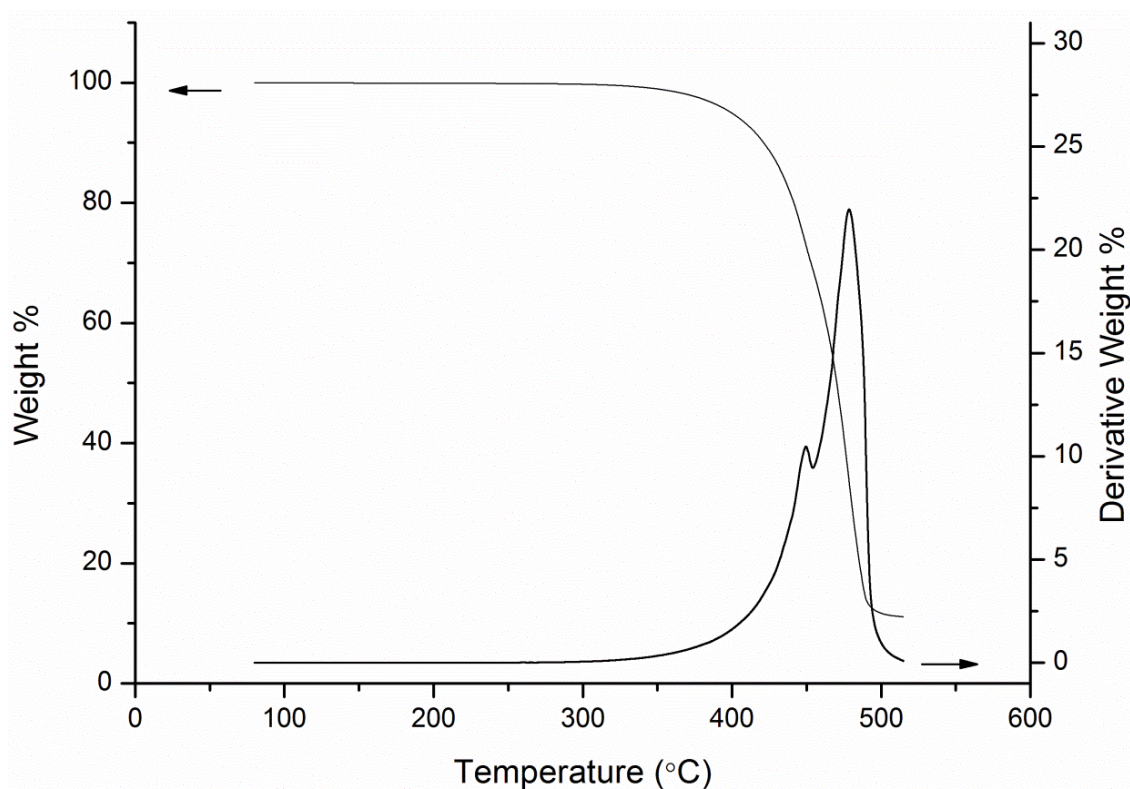


**Figure 3A-17** TG/DTG curve of bulk [BMIM][NTf<sub>2</sub>].

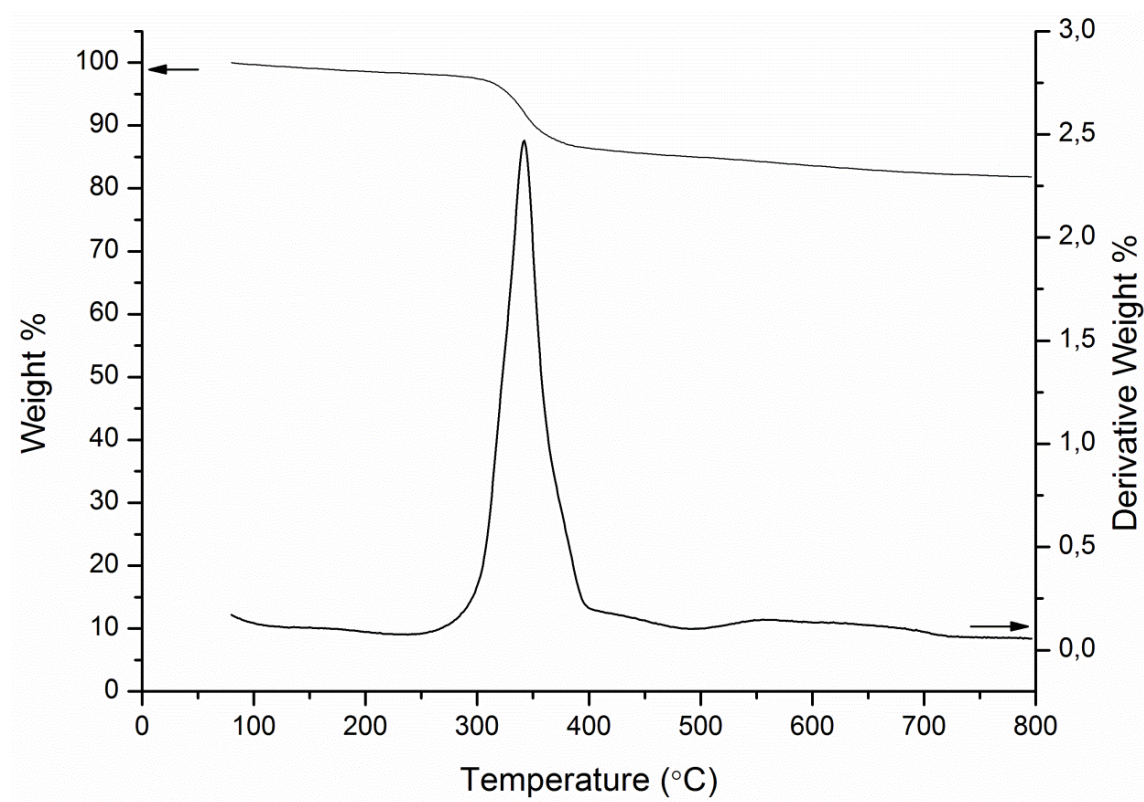


**Figure 3A-18** TG/DTG curve of [BMIM][NTf<sub>2</sub>] on γ-Al<sub>2</sub>O<sub>3</sub>.

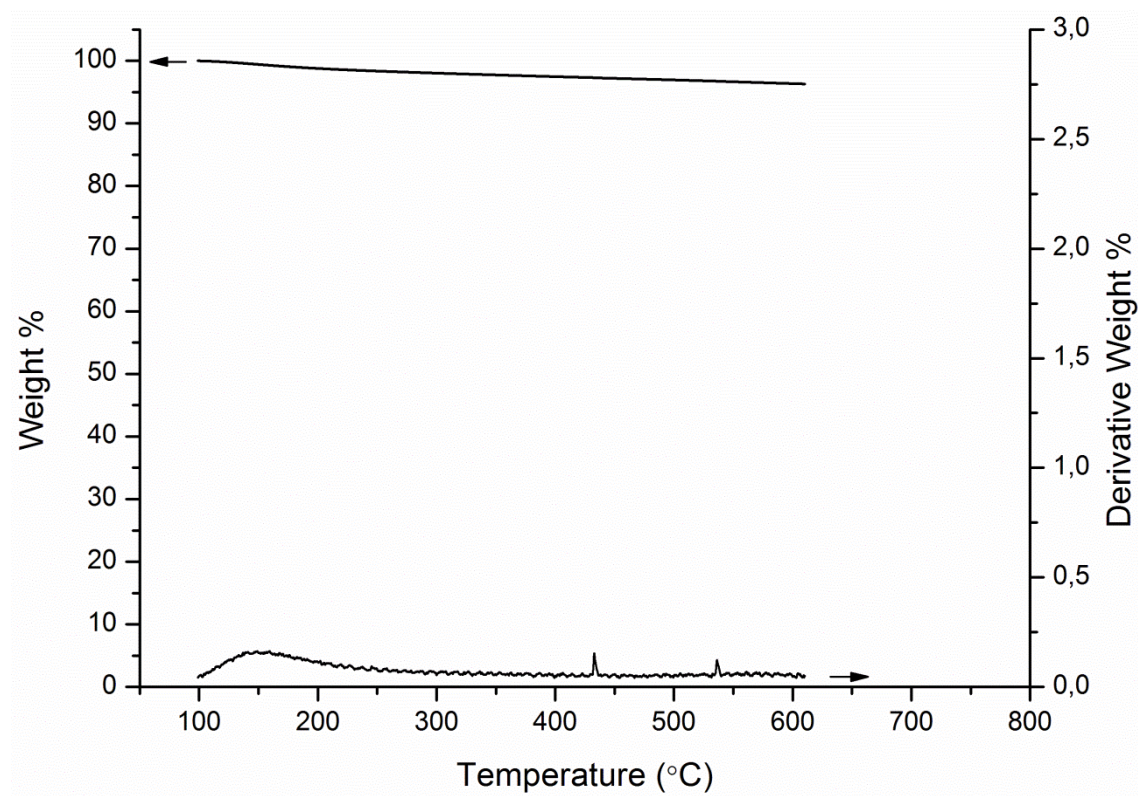


**Figure 3A-19** TG/DTG curve of γ-Al<sub>2</sub>O<sub>3</sub> as reference.

**References**

1. Kroon, M. C.; Buijs, W.; Peters, C. J.; Witkamp, G. J., Quantum chemical aided prediction of the thermal decomposition mechanisms and temperatures of ionic liquids, *Thermochim. Acta* **2007**, 465, 40–47.

## **Chapter 4**

### **APPENDIX 4A**

#### **A Model to Predict Maximum Operating Temperatures of Metal-Oxide-Supported [BMIM]<sup>+</sup>-Based Ionic Liquids**

##### **Thermal Stability Analysis by TGA**

Approximately 15 mg of supported samples were placed in platinum pans and purged with nitrogen for 1 h. Following the pretreatment period, TGA measurements (TA Instruments TGA Q500 model) were performed at a heating rate of 2 and 10 °C/min under flowing nitrogen within a temperature range of 24 to 500 °C for bulk ILs and a range of 24-600 °C for supported ILs.

TGA and DTGA profile shapes of each IL change significantly when they are coated on support materials. The profiles suggest at least a two-step decomposition mechanism; however, data is not sufficient to elucidate complete mechanisms for the decomposition reaction in each of the individual samples considered here.

Figure S1 illustrates a comparison of TGA measurements performed on a representative metal-oxide supported IL sample at heating rates of 2 and 10 °C/min. Data confirm that the heating rate does not have any significant effect on  $T'_{\text{onset}}$  (it is 360 °C at 10 °C/min and 358 °C at 2 °C/min). However,  $T_{\text{onset}}$  is approximately 15 °C lower when

the heating rate was 2 °C/min ( $T_{\text{onset}} = 364$  °C) than that measured when the heating rate was 10 °C/min ( $T_{\text{onset}} = 378$  °C). This difference in  $T_{\text{onset}}$  measured at different heating rates further justifies the consideration of  $T'_{\text{onset}}$  over  $T_{\text{onset}}$  values, as  $T'_{\text{onset}}$  values do not reflect any effect of heating rate.

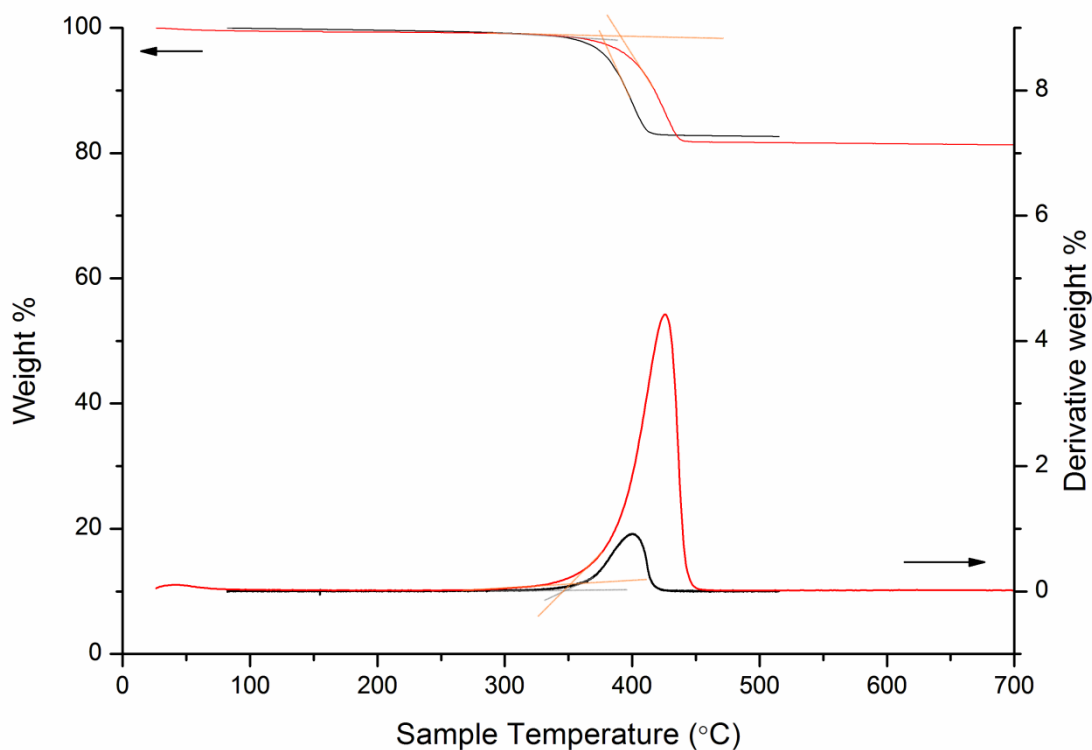


**Figure 4A-1.** Effect of heating rate on the measured  $T'_{\text{onset}}$  and  $T_{\text{onset}}$  values for a representative metal-oxide supported IL, [BMIM][NTf<sub>2</sub>] on SiO<sub>2</sub>. Heating rates: 10 °C/min (red lines); 2 °C/min (black lines).

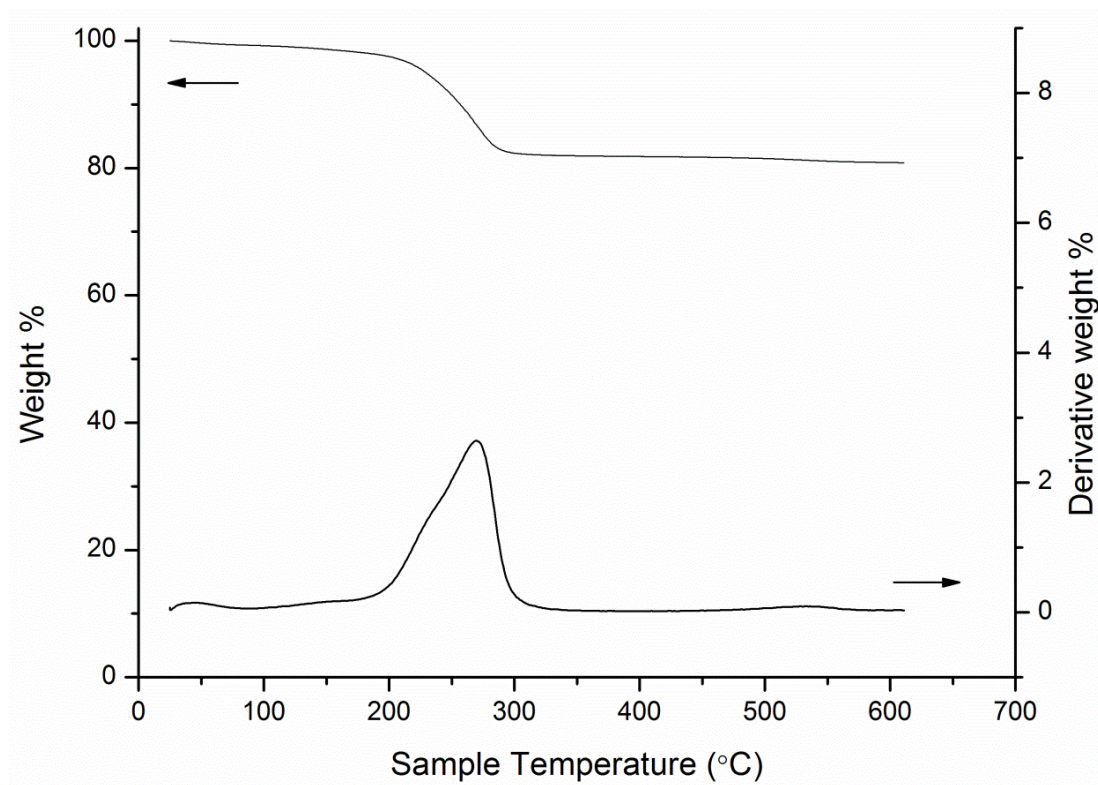


**Figure 4A-2** TG/DTG curve of [BMIM][OAc] on SiO<sub>2</sub>.

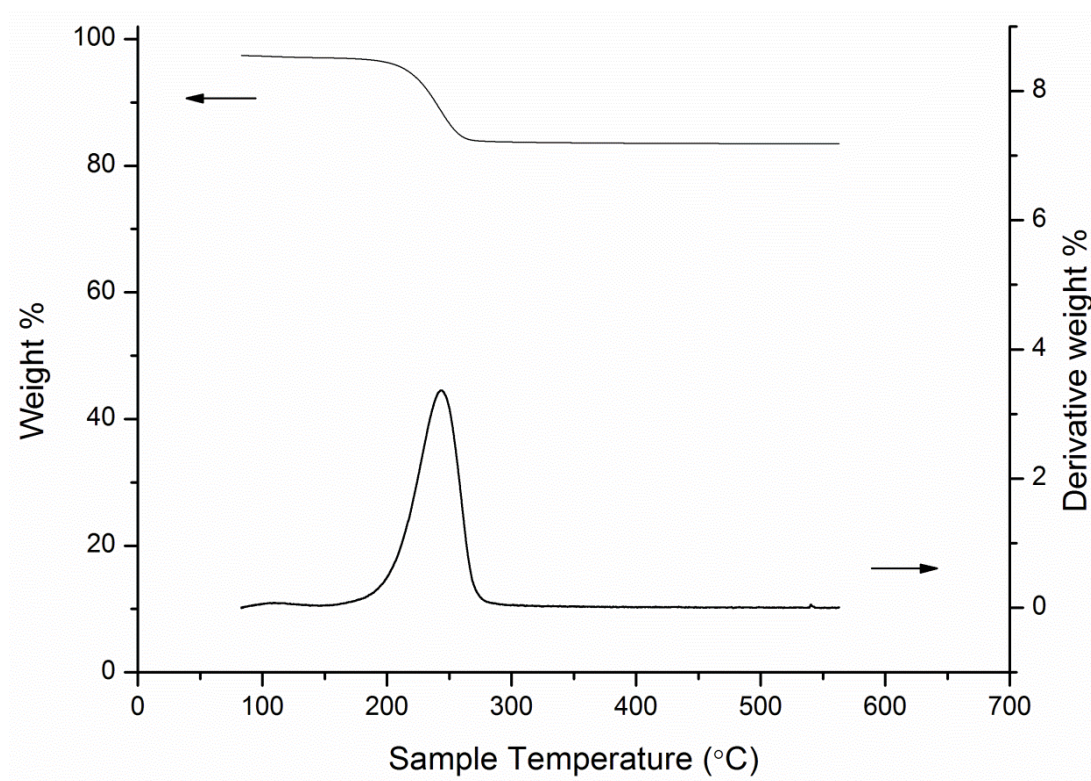


**Figure 4A-3** TG/DTG curve of [BMIM][OAc] on TiO<sub>2</sub>.

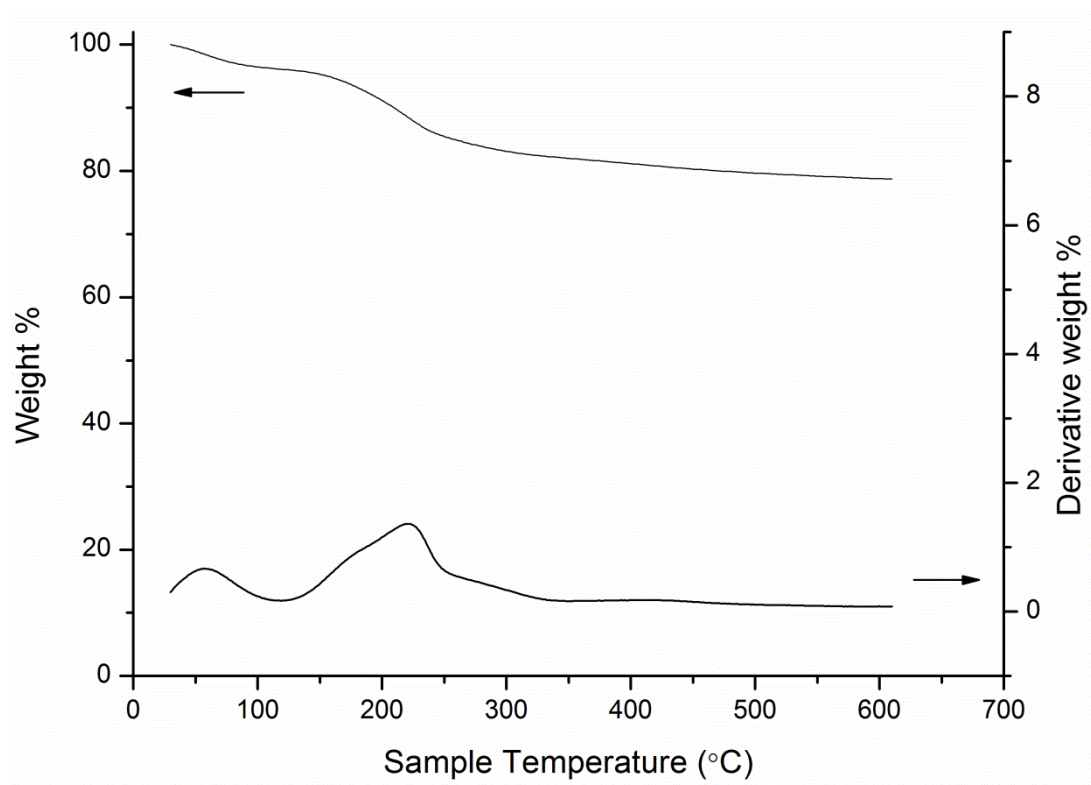


**Figure 4A-4** TG/DTG curve of [BMIM][OAc] on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

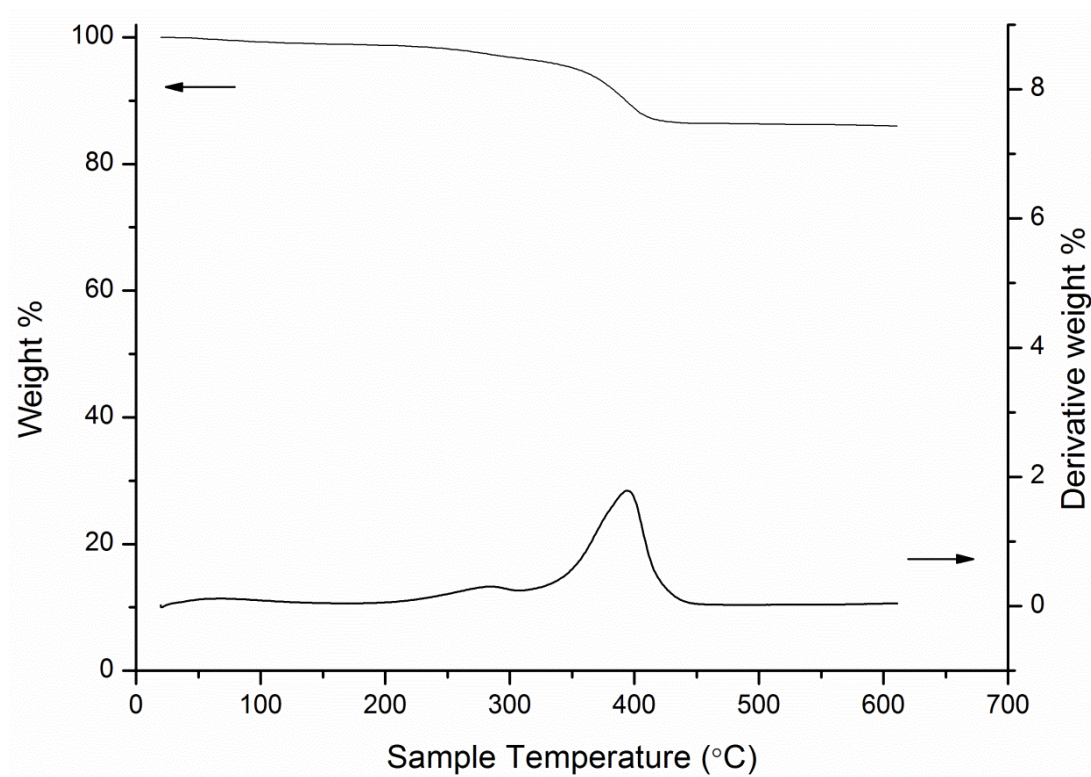


**Figure 4A-5** TG/DTG curve of [BMIM][OAc] on MgO.

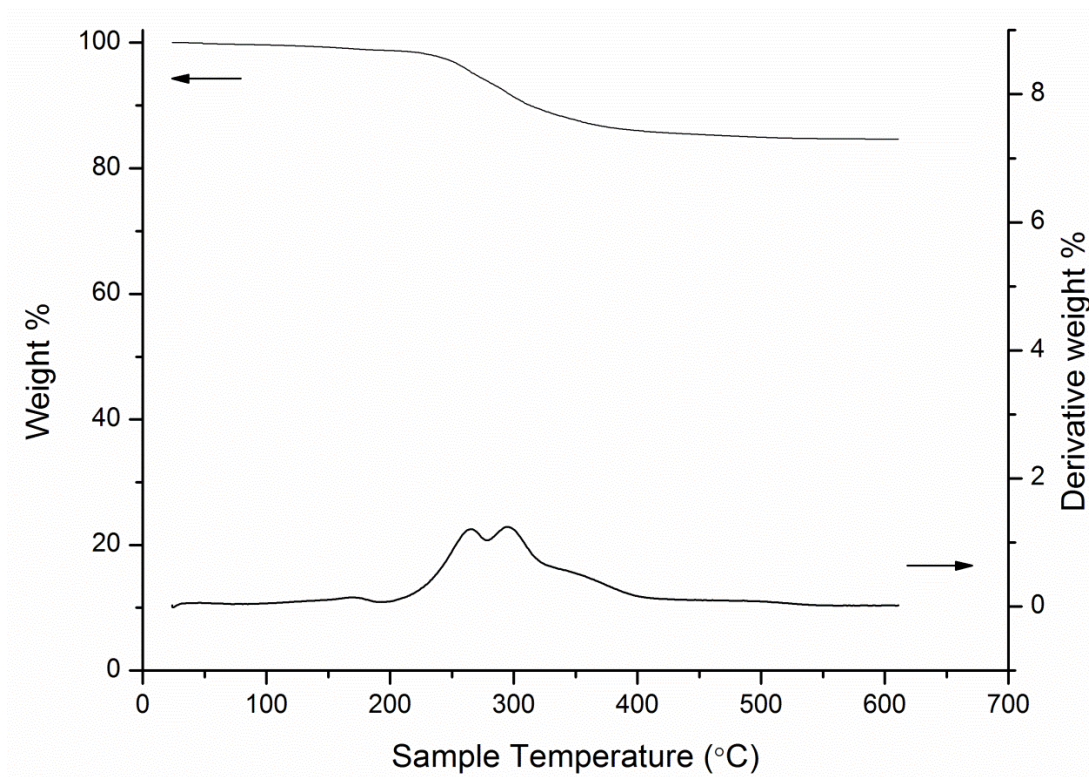


**Figure 4A-6** TG/DTG curve of [BMIM][DBP] on SiO<sub>2</sub>.

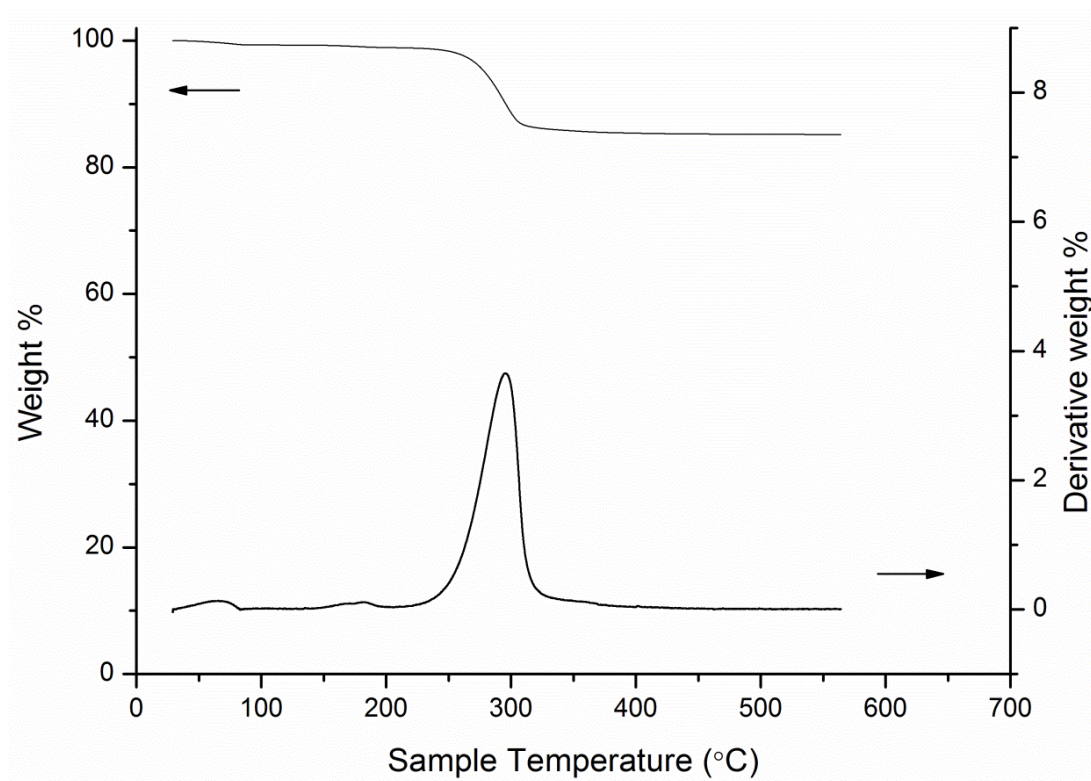


**Figure 4A-7** TG/DTG curve of [BMIM][DBP] on  $\text{TiO}_2$ .

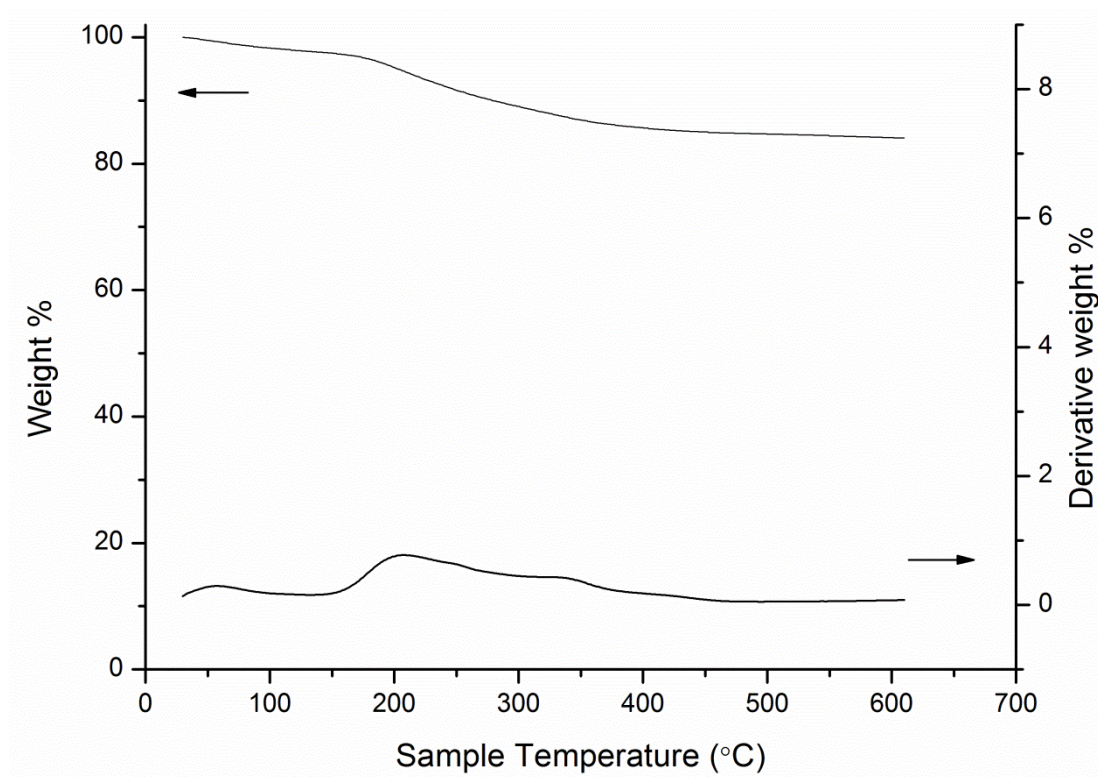


**Figure 4A-8** TG/DTG curve of [BMIM][DBP] on  $\gamma$ - $\text{Al}_2\text{O}_3$ .

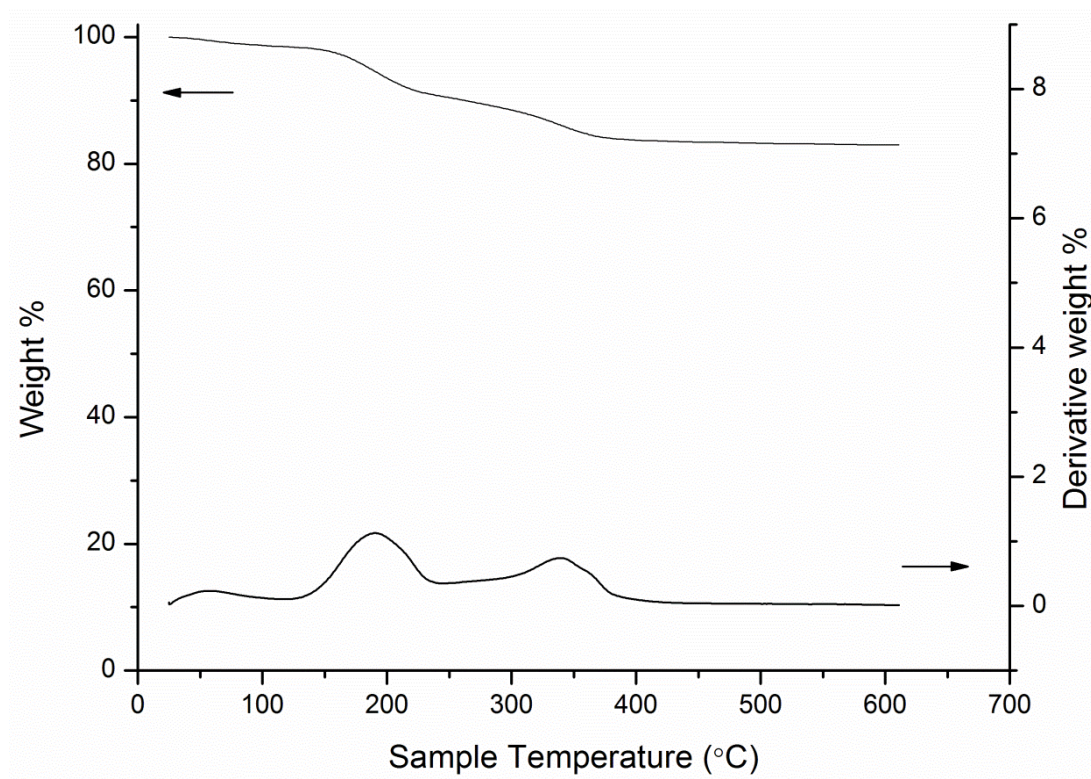


**Figure 4A-9** TG/DTG curve of [BMIM][DBP] on MgO.

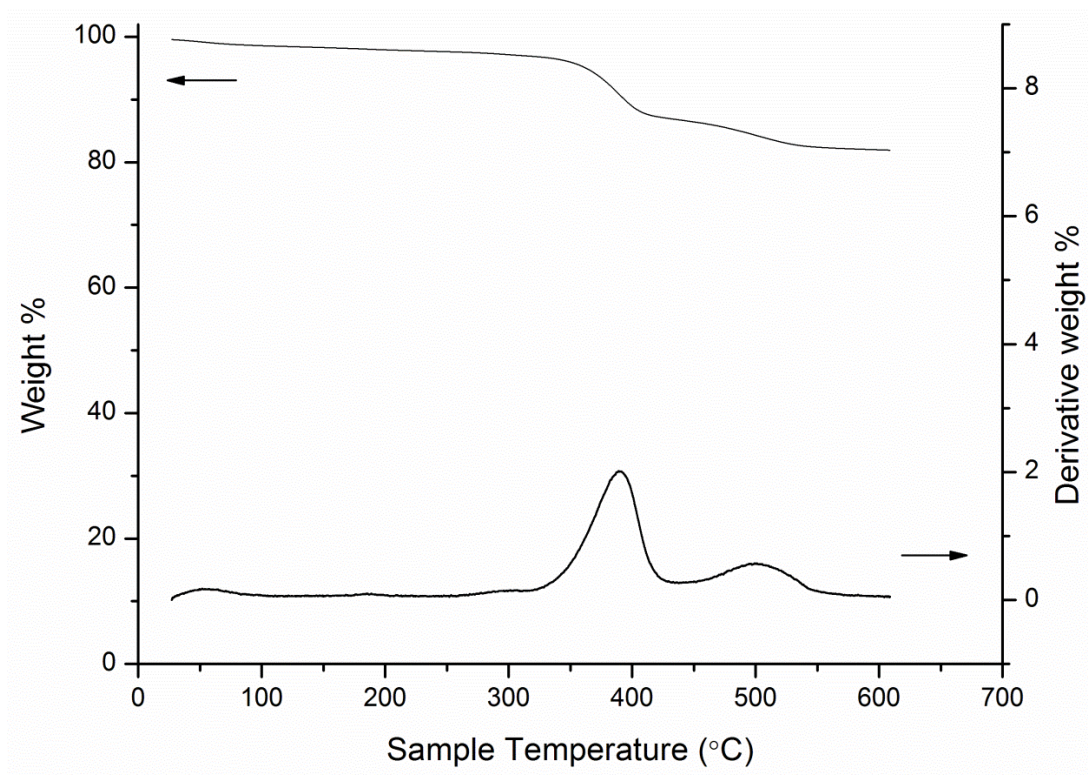


**Figure 4A-10** TG/DTG curve of [BMIM][TOS] on SiO<sub>2</sub>.

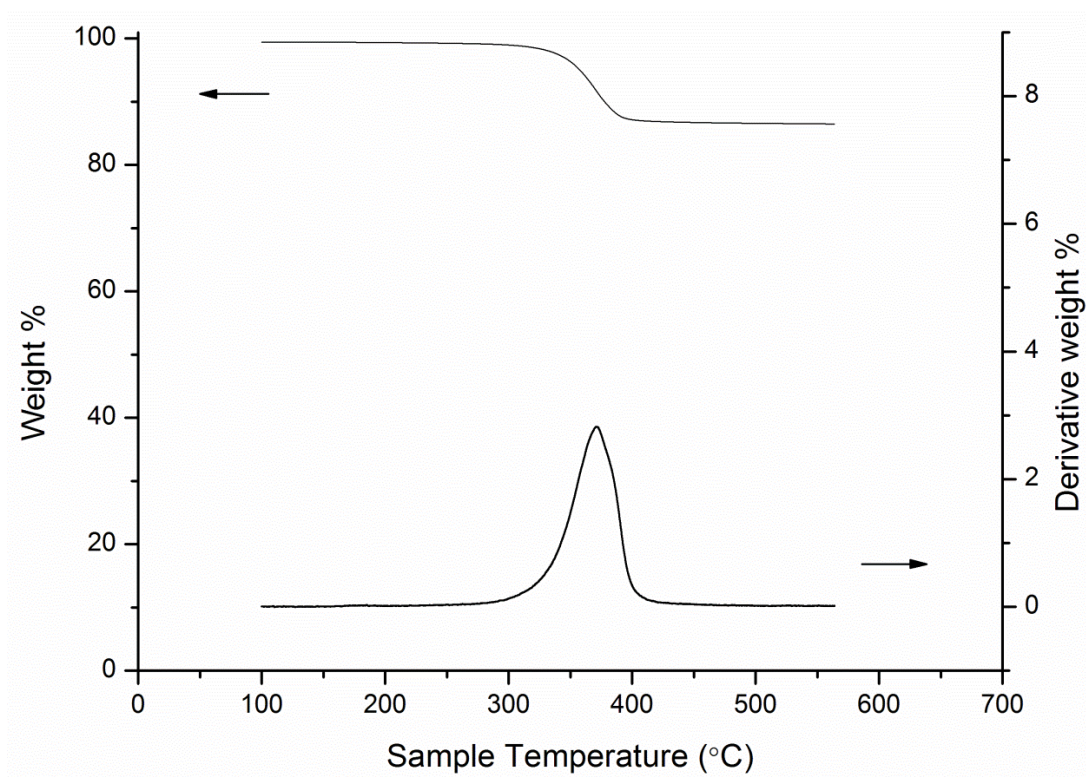


**Figure 4A-11** TG/DTG curve of [BMIMTOS] on TiO<sub>2</sub>.

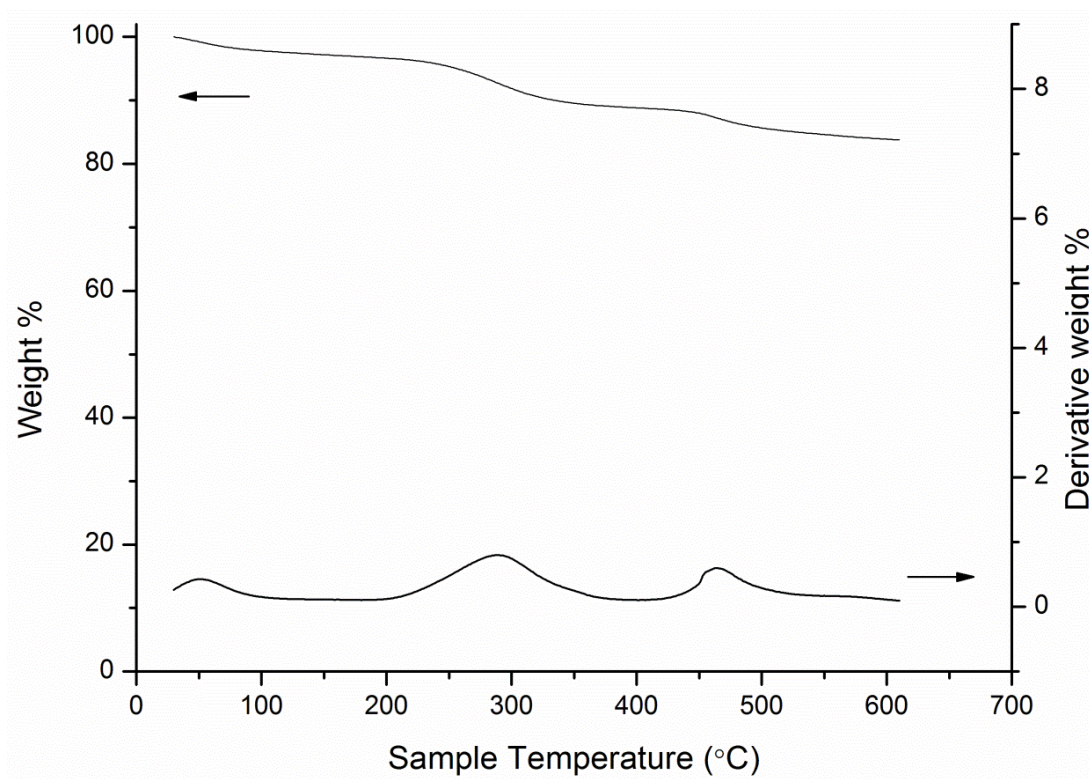


**Figure 4A-12** TG/DTG curve of [BMIMTOS] on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

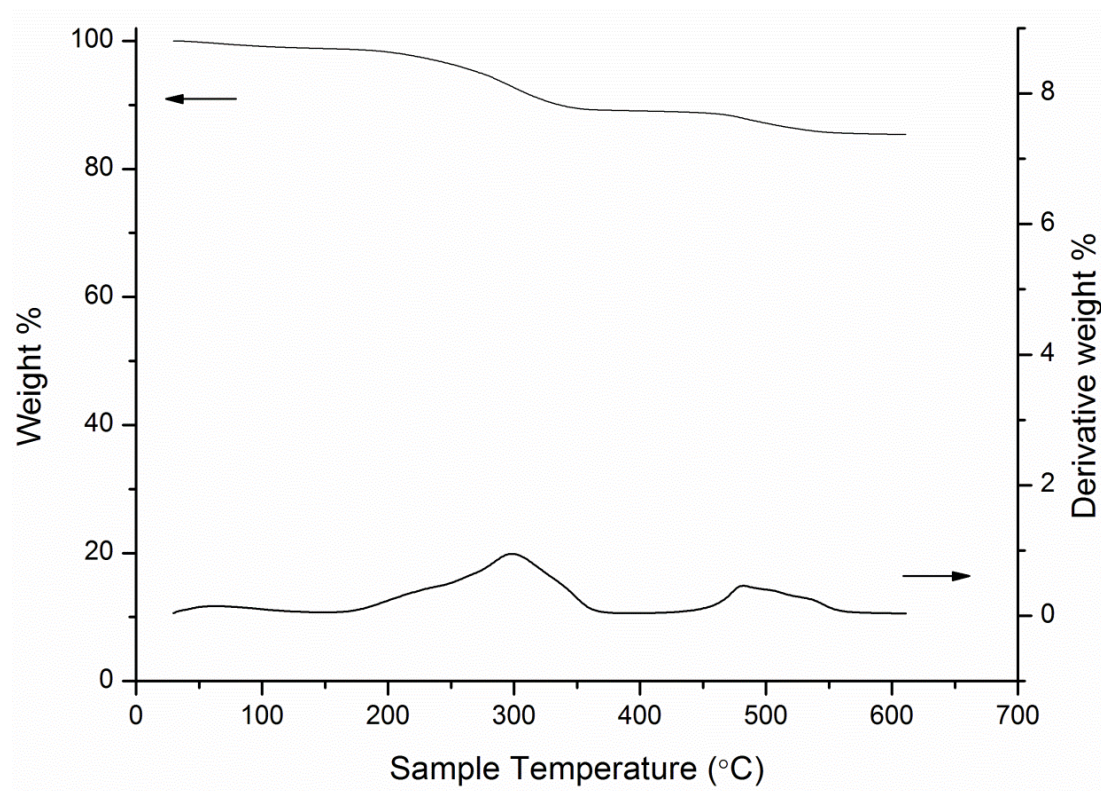


**Figure 4A-13** TG/DTG curve of [BMIMTOS] on MgO.

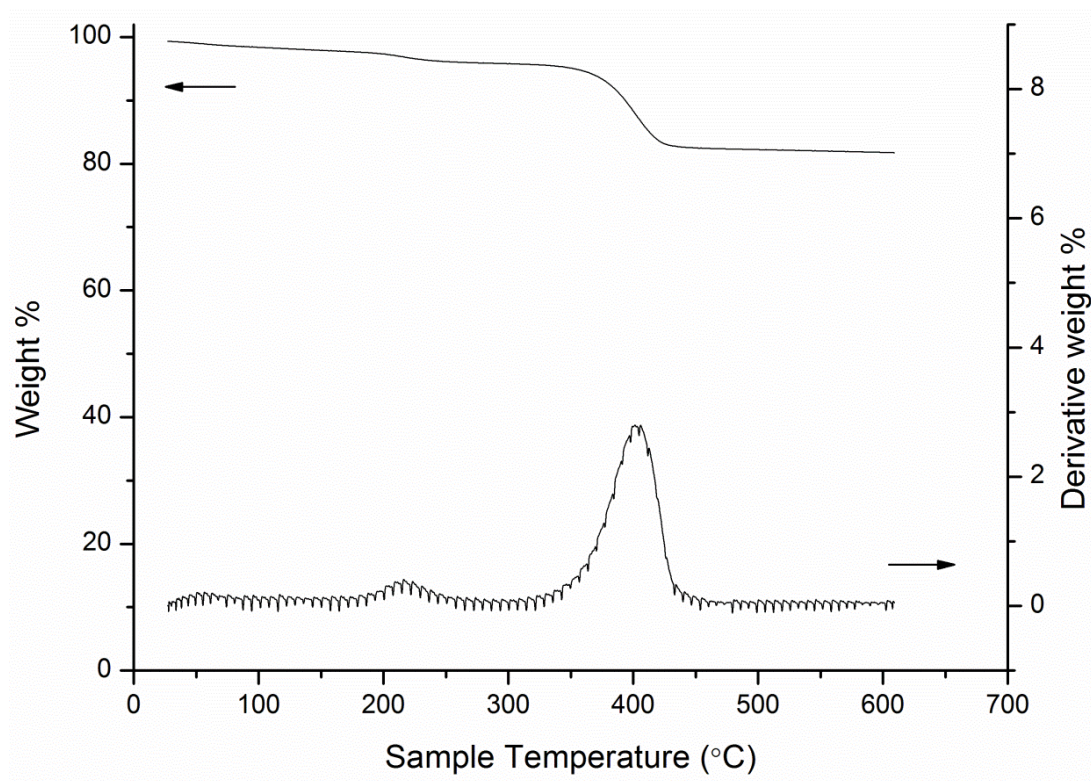


**Figure 4A-14** TG/DTG curve of [BMIM][HSO<sub>4</sub>] on SiO<sub>2</sub>.

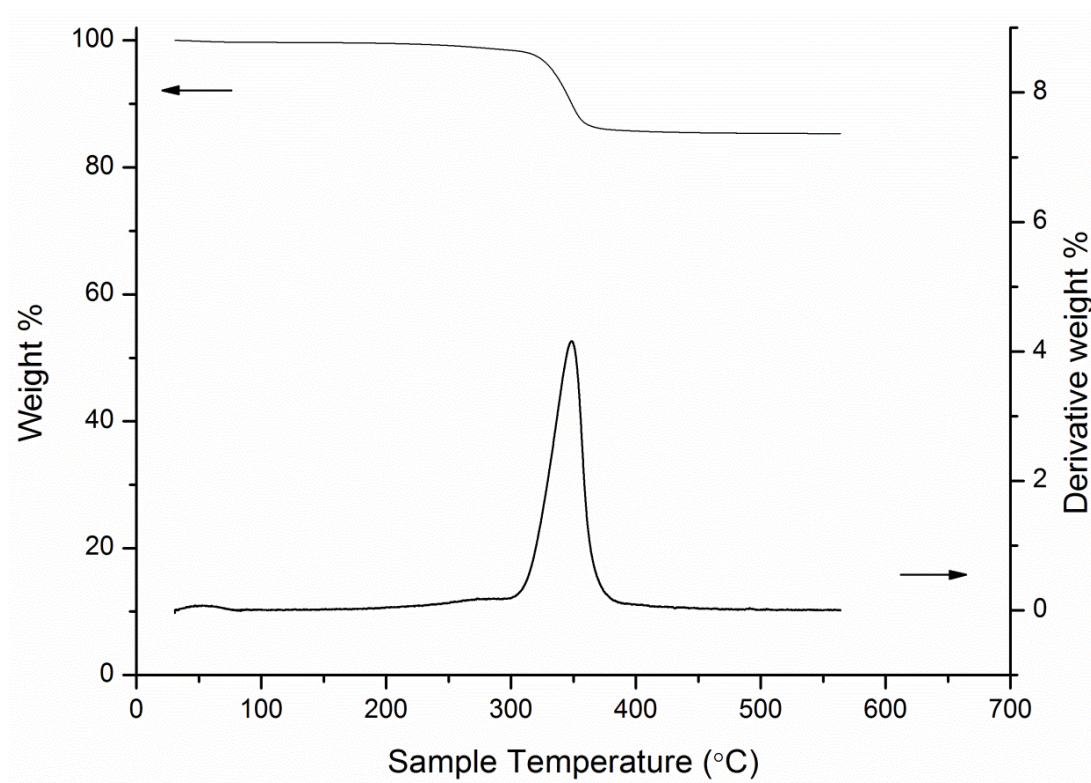


**Figure 4A-15** TG/DTG curve of [BMIM][HSO<sub>4</sub>] on TiO<sub>2</sub>.

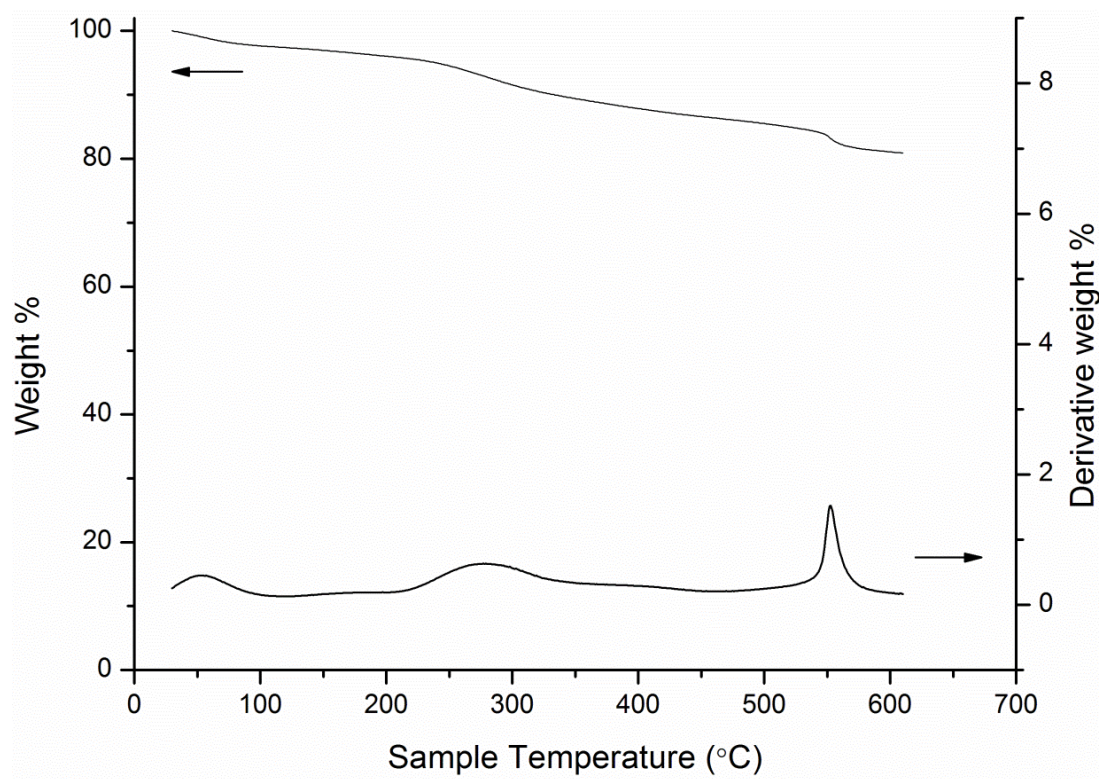


**Figure 4A-16** TG/DTG curve of [BMIM][HSO<sub>4</sub>] on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

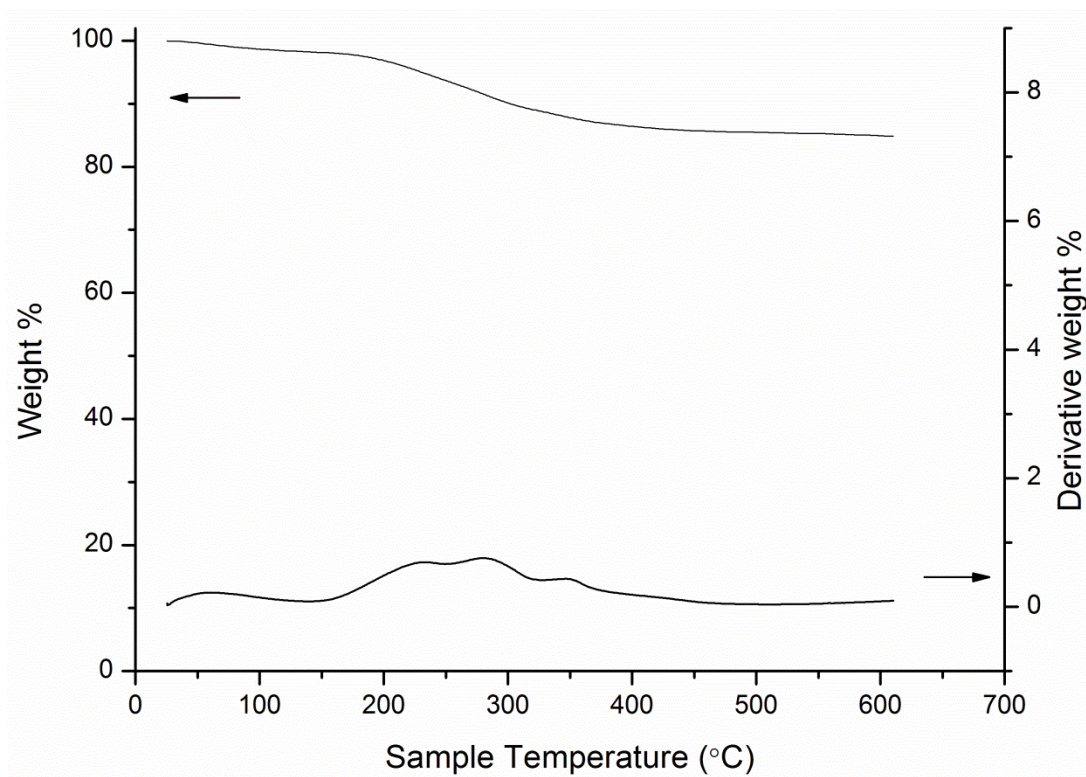


**Figure 4A-17** TG/DTG curve of [BMIM][HSO<sub>4</sub>] on MgO.

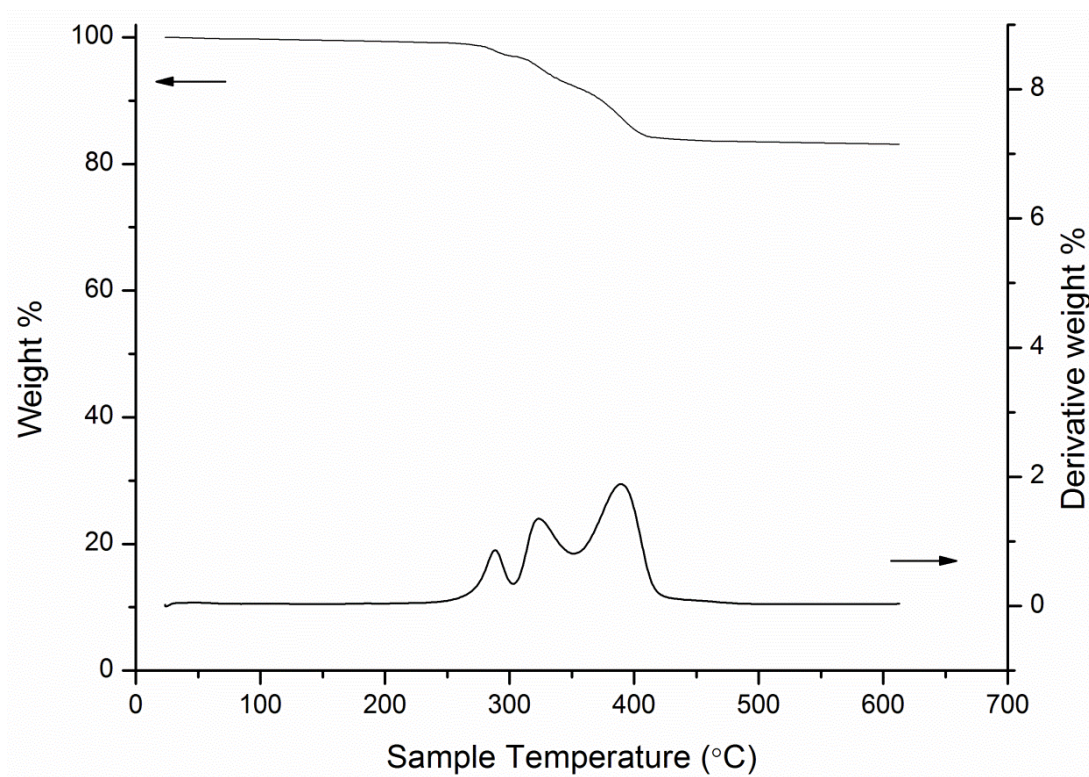


**Figure 4A-18** TG/DTG curve of [BMIM][OS] on SiO<sub>2</sub>.

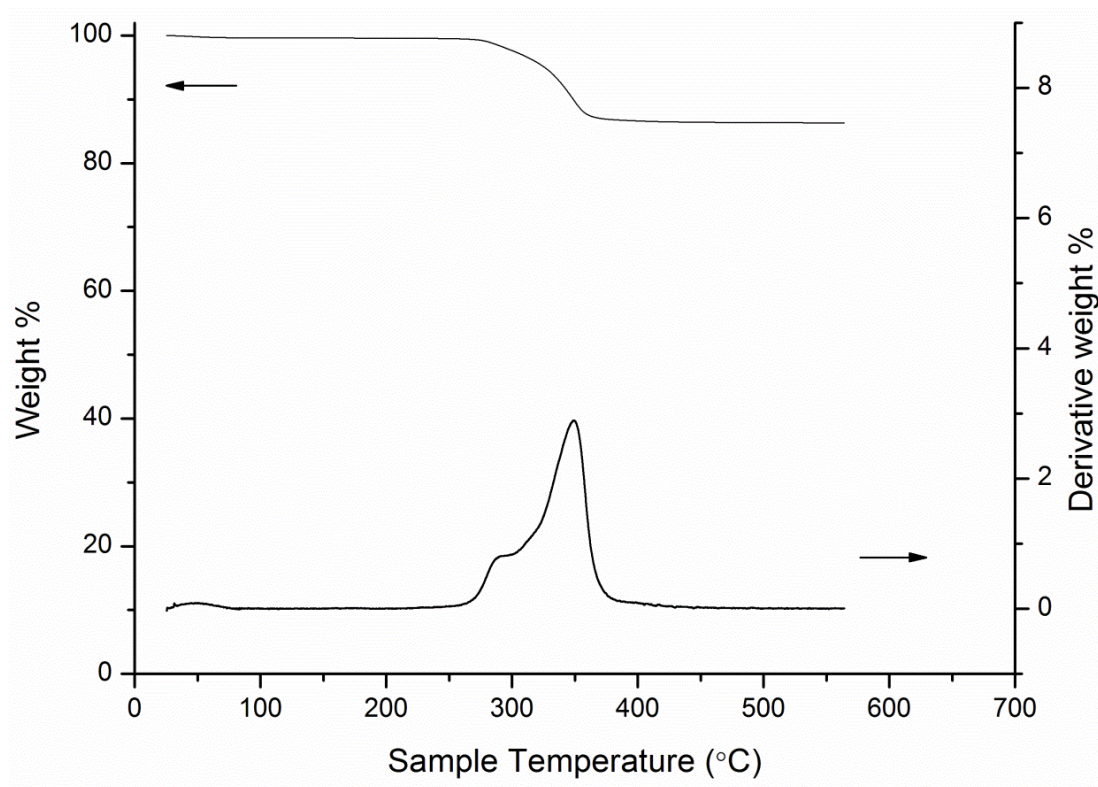


**Figure 4A-19** TG/DTG curve of [BMIM][OS] on TiO<sub>2</sub>.

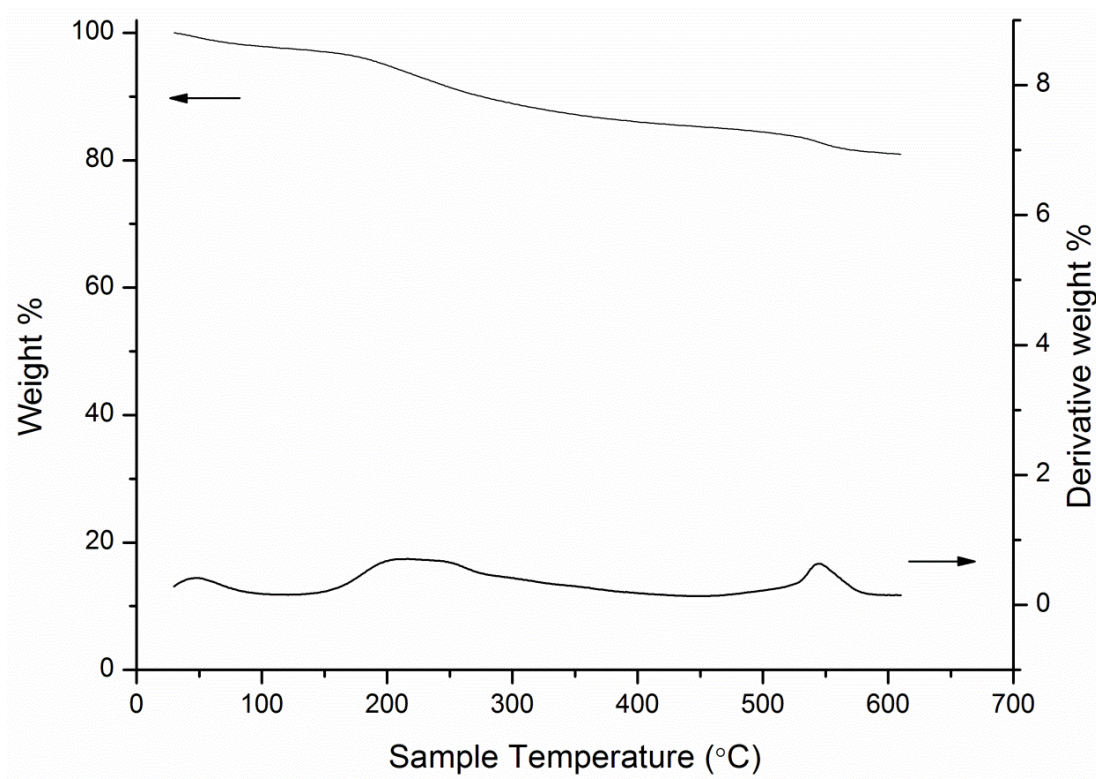


**Figure 4A-20** TG/DTG curve of [BMIM][OS] on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

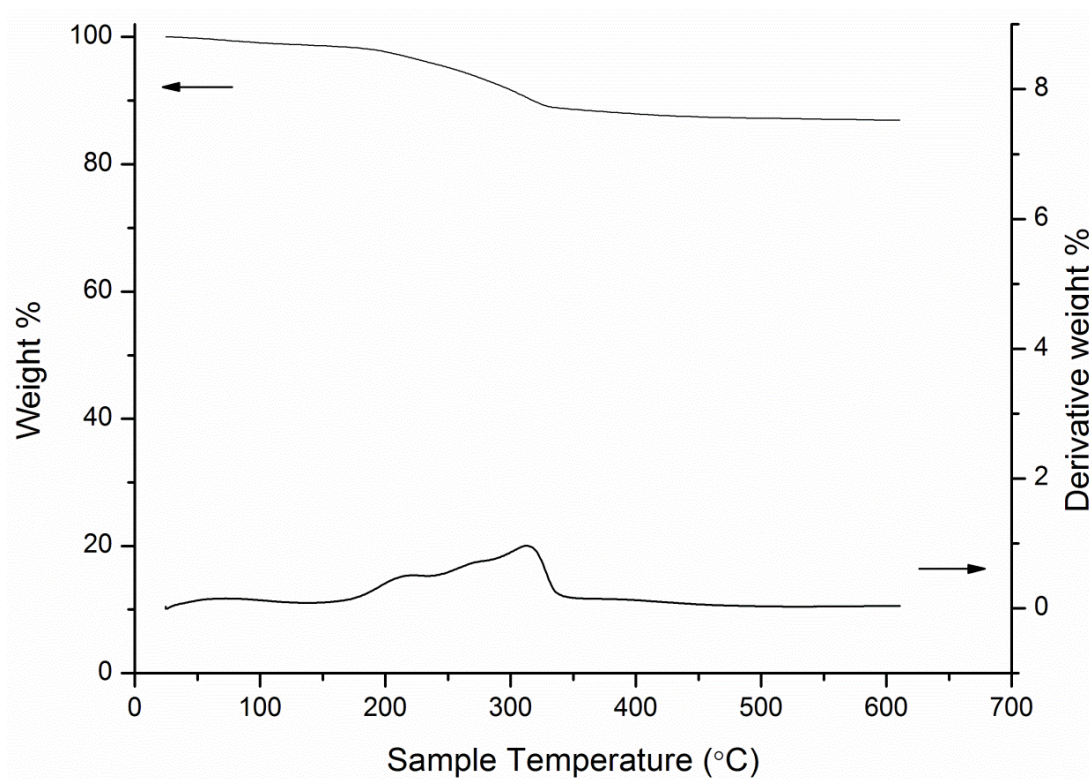


**Figure 4A-21** TG/DTG curve of [BMIM][OS] on MgO.

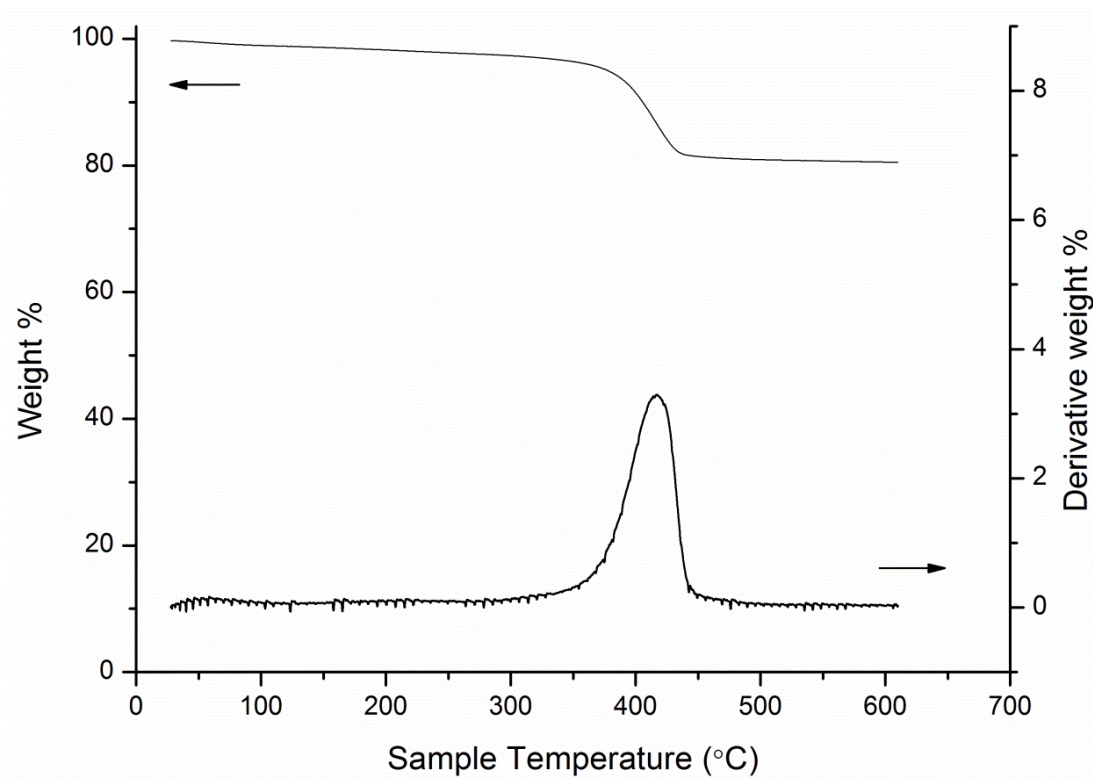


**Figure 4A-22** TG/DTG curve of [BMIM][TfO] on SiO<sub>2</sub>.

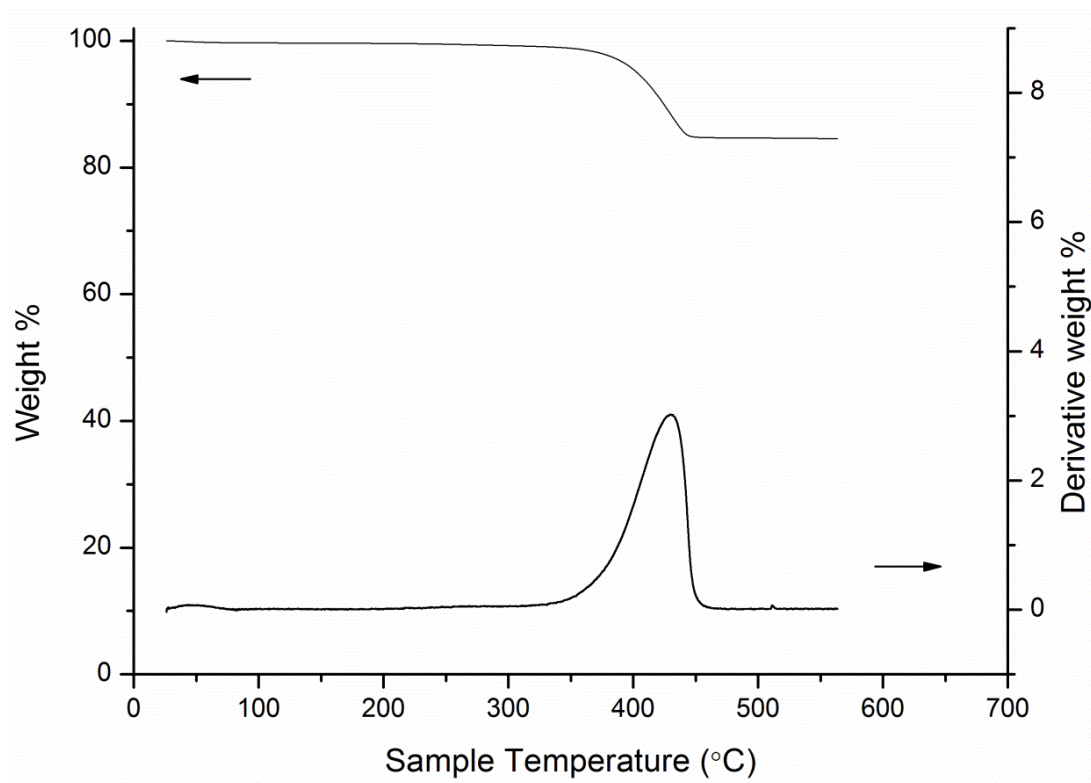


**Figure 4A-23** TG/DTG curve of [BMIM][TfO] on TiO<sub>2</sub>.

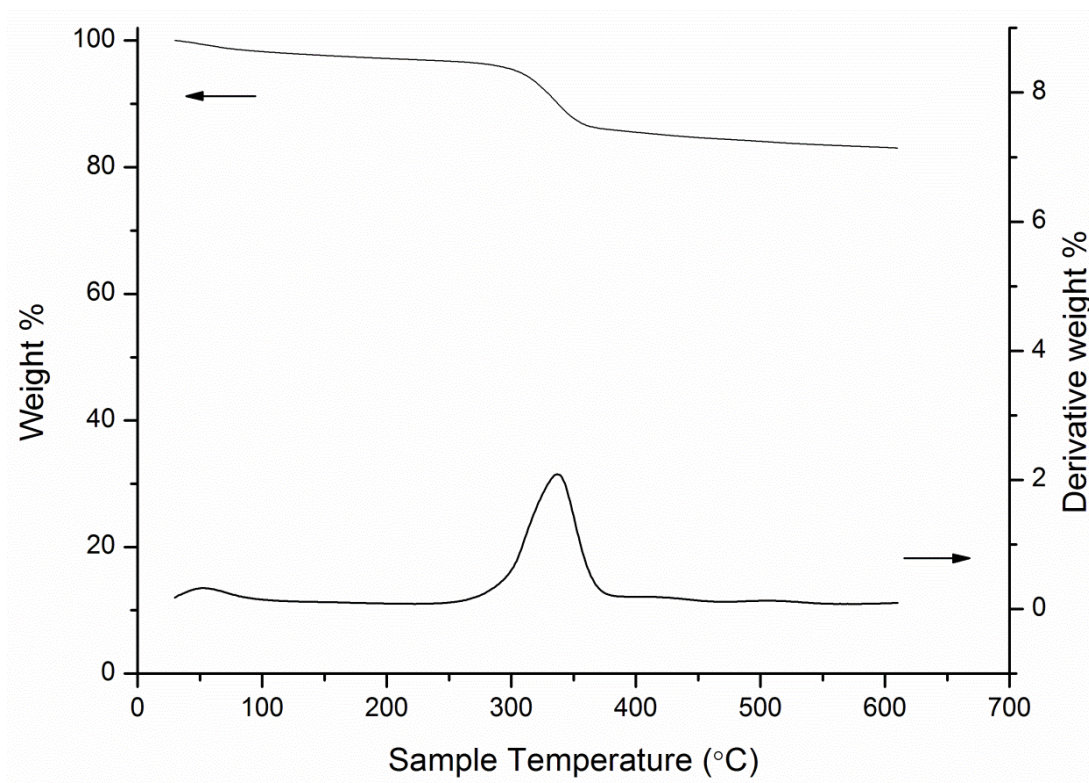


**Figure 4A-24** TG/DTG curve of [BMIM][TfO] on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

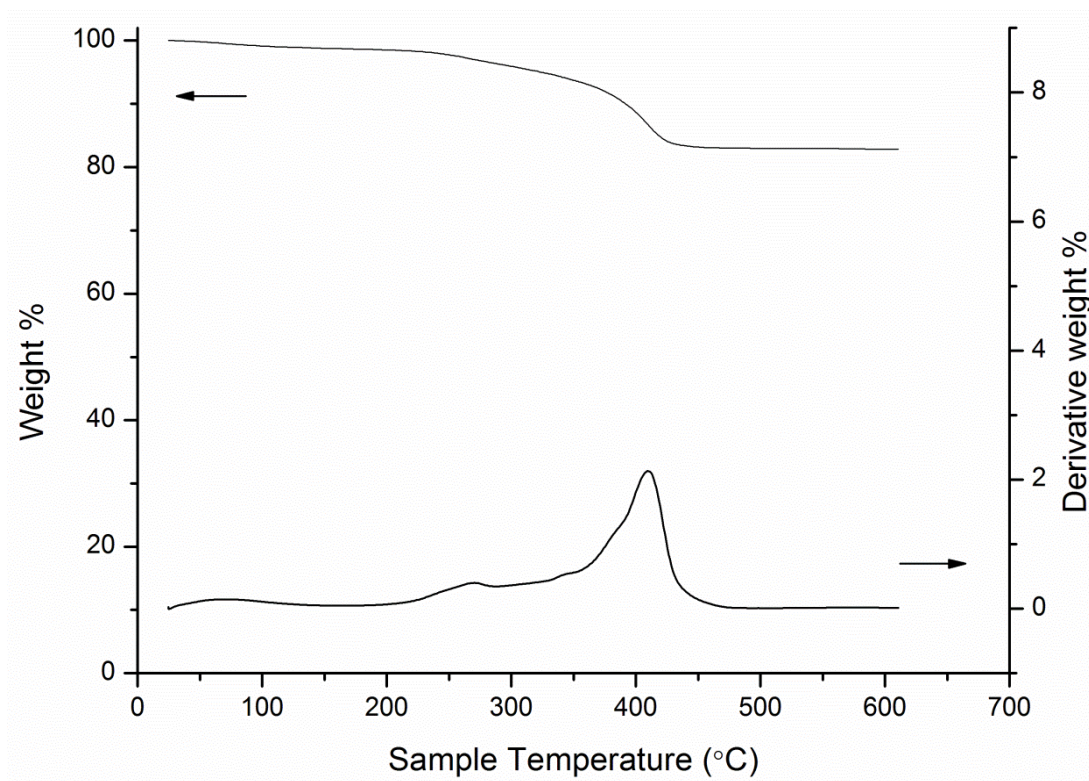


**Figure 4A-25** TG/DTG curve of [BMIM][TfO] on MgO.

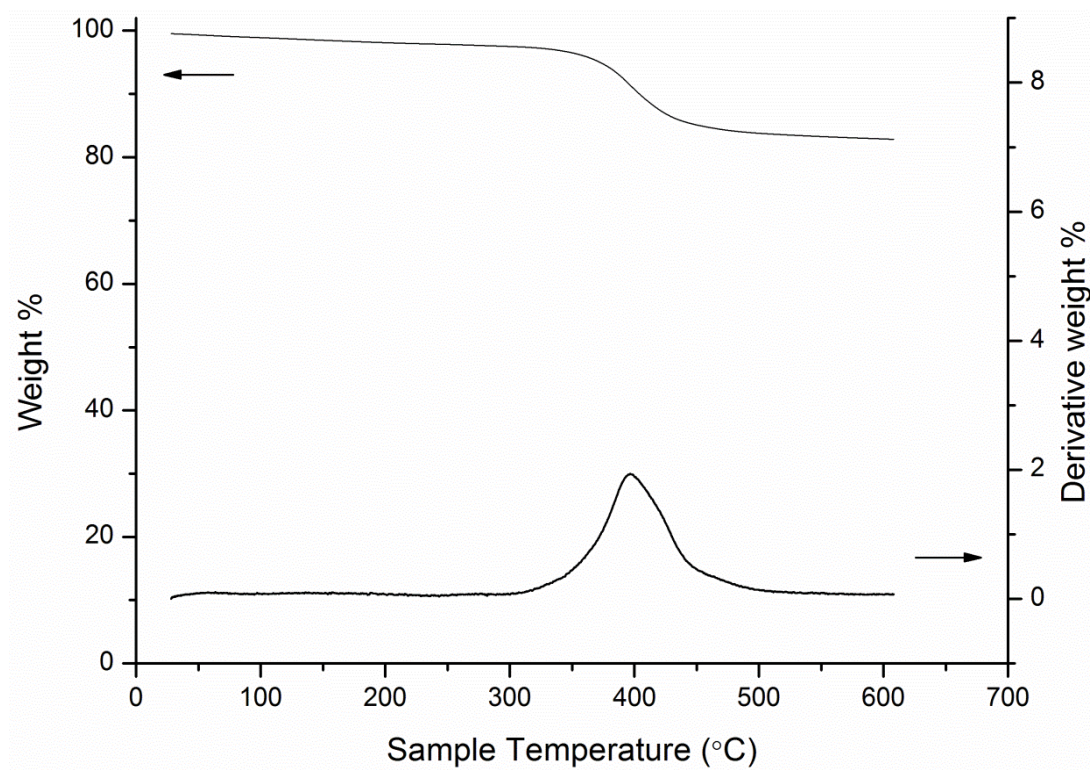


**Figure 4A-26** TG/DTG curve of [BMIM][BF<sub>4</sub>] on SiO<sub>2</sub>.

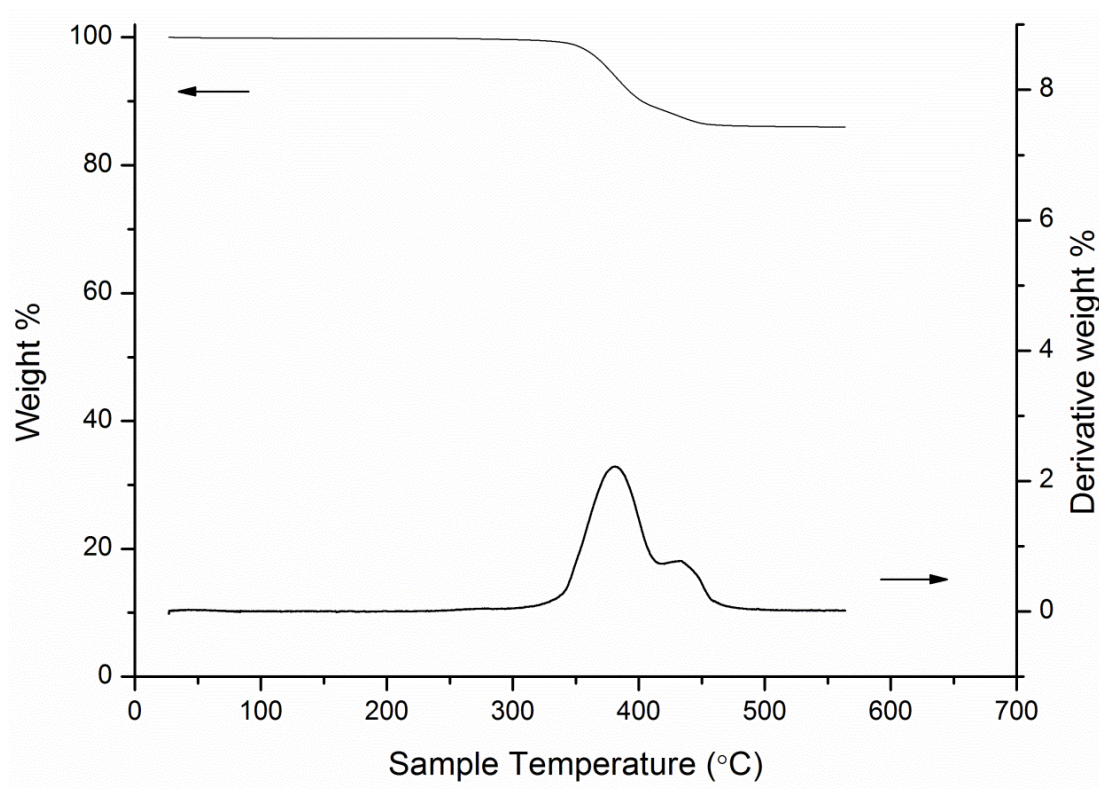


**Figure 4A-27** TG/DTG curve of [BMIM][BF<sub>4</sub>] on TiO<sub>2</sub>.

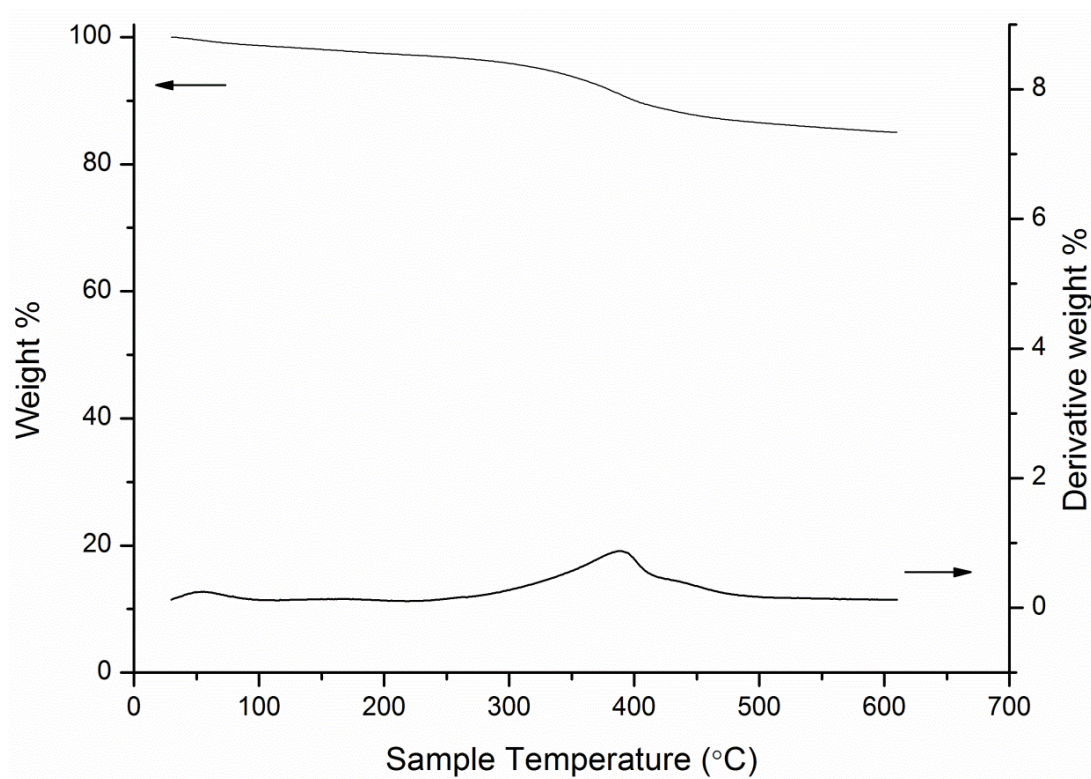


**Figure 4A-28** TG/DTG curve of [BMIM][BF<sub>4</sub>] on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

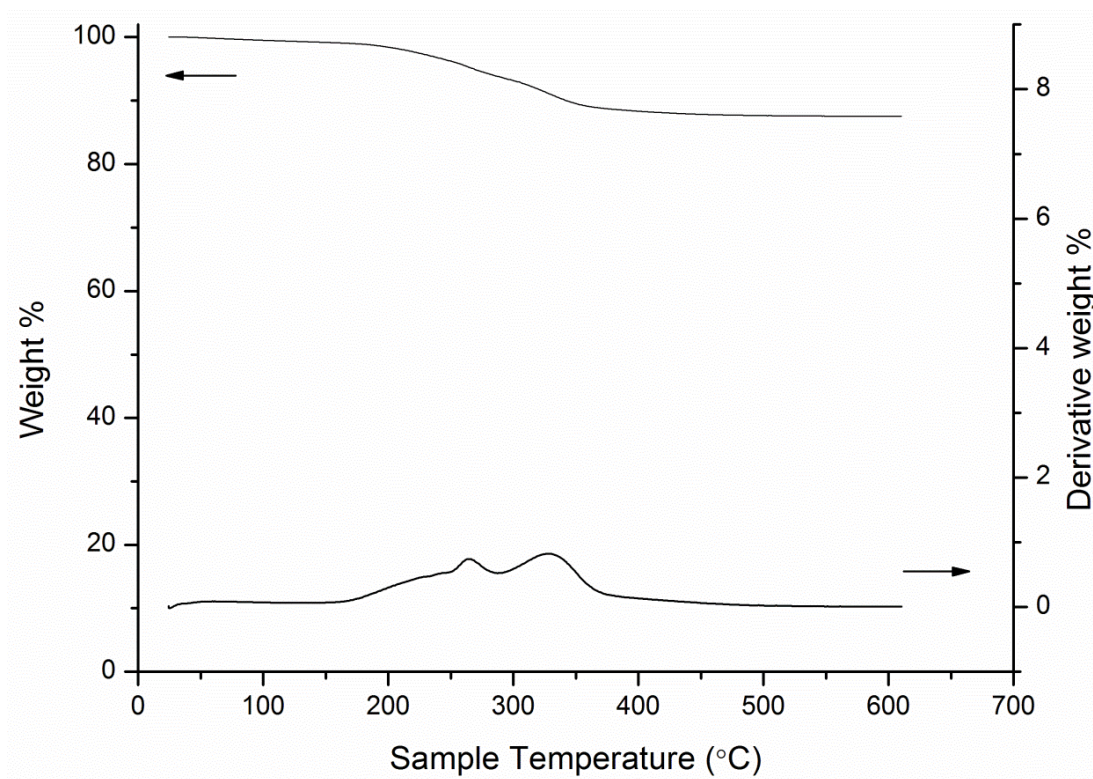


**Figure 4A-29** TG/DTG curve of [BMIM][BF<sub>4</sub>] on MgO.

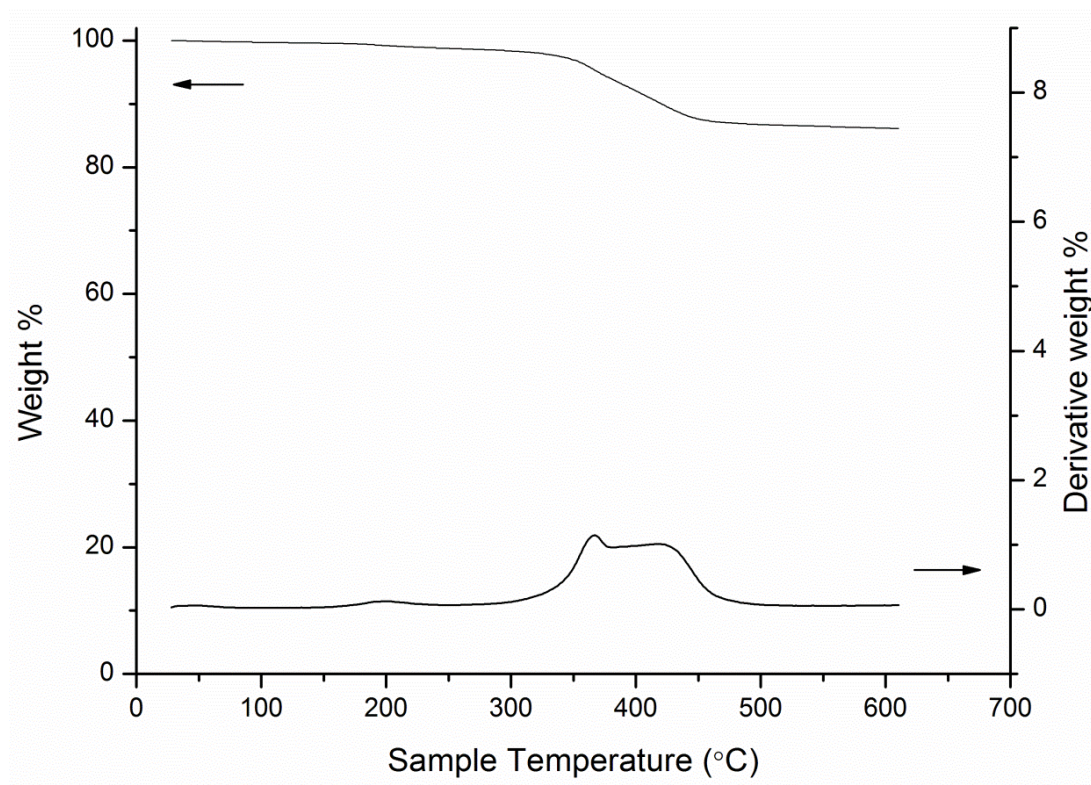


**Figure 4A-30** TG/DTG curve of [BMIM][SbF<sub>6</sub>] on SiO<sub>2</sub>.

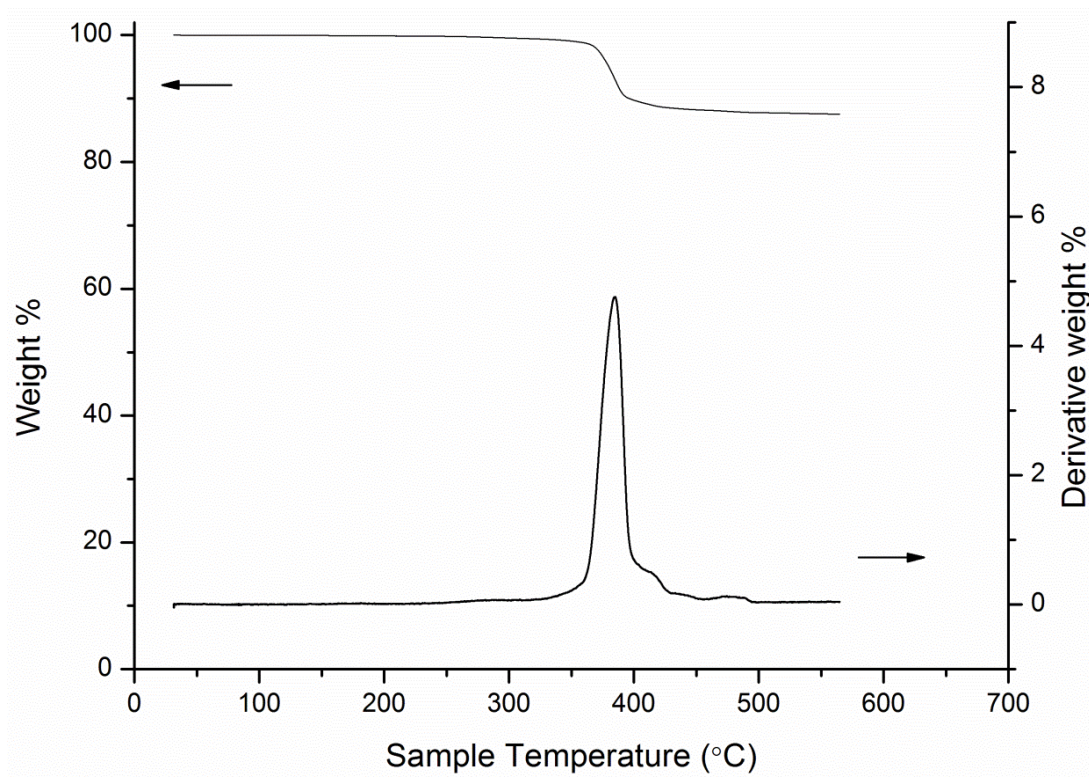


**Figure 4A-31** TG/DTG curve of [BMIM][SbF<sub>6</sub>] on TiO<sub>2</sub>.

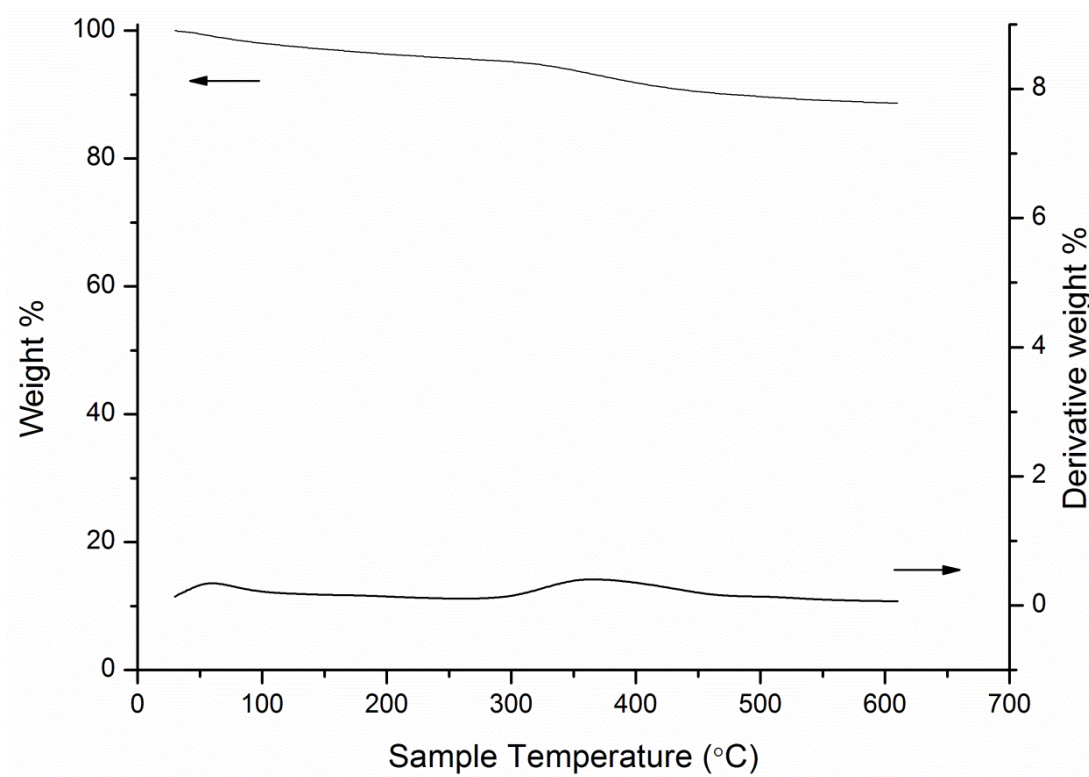


**Figure 4A-32** TG/DTG curve of [BMIM][SbF<sub>6</sub>] on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

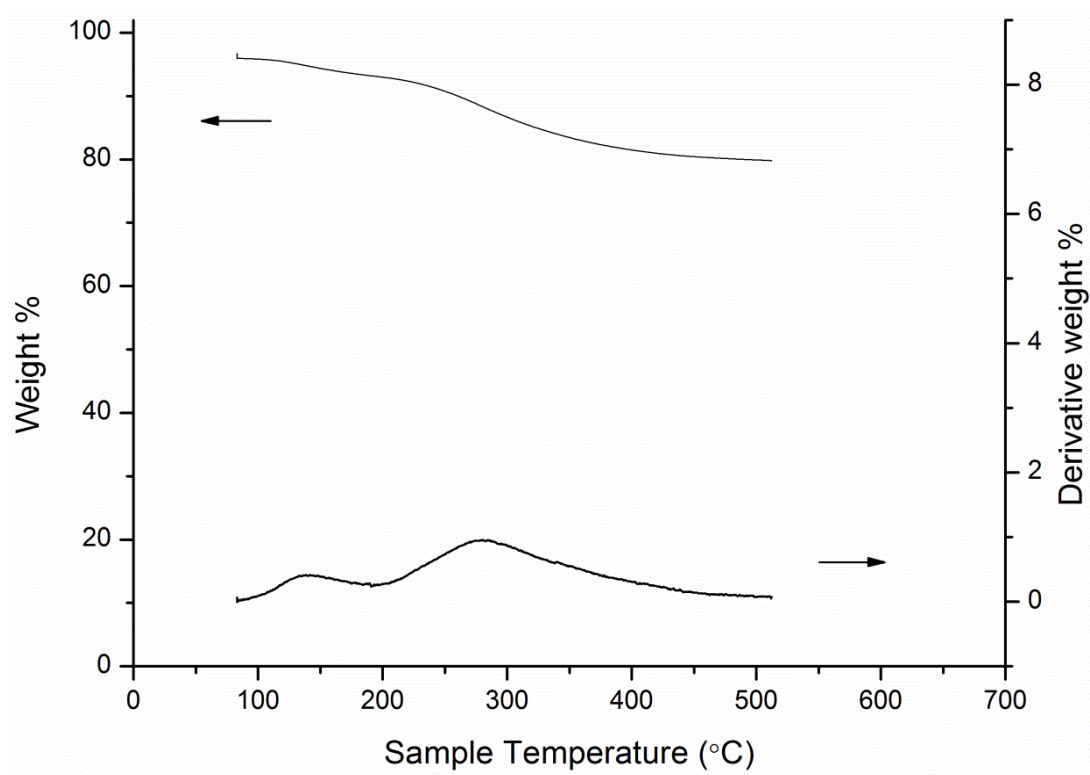


**Figure 4A-33** TG/DTG curve of [BMIM][SbF<sub>6</sub>] on MgO.

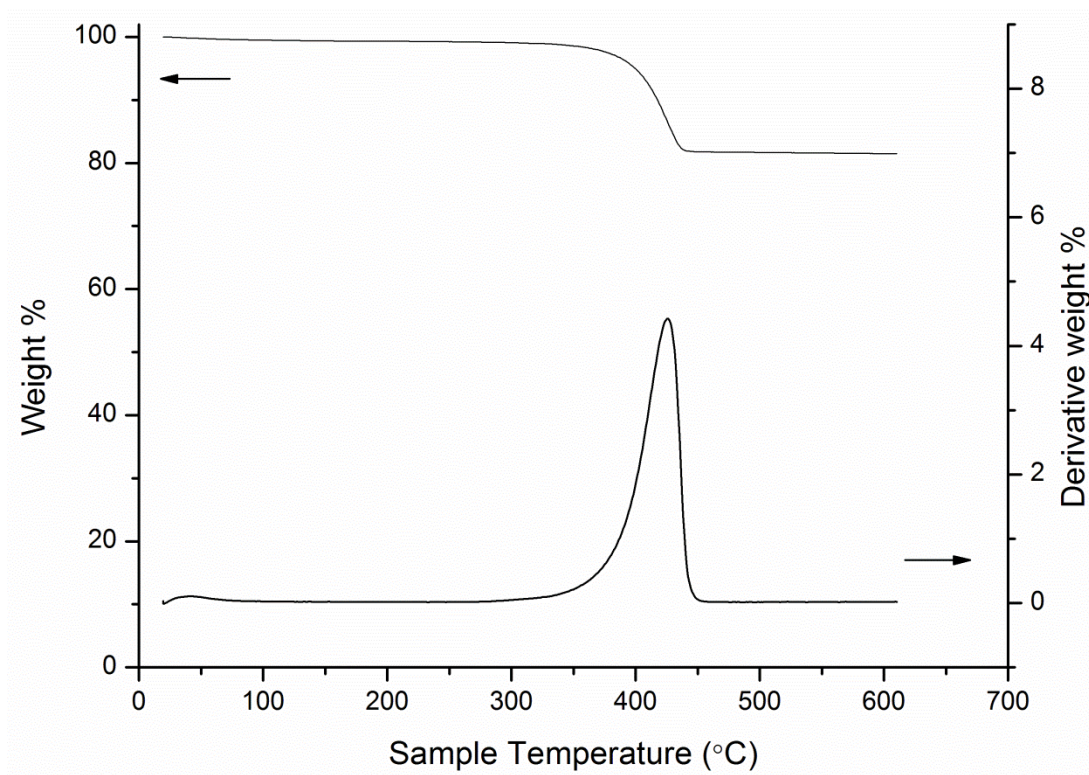


**Figure 4A-34** TG/DTG curve of [BMIM][NTf<sub>2</sub>] on SiO<sub>2</sub>.

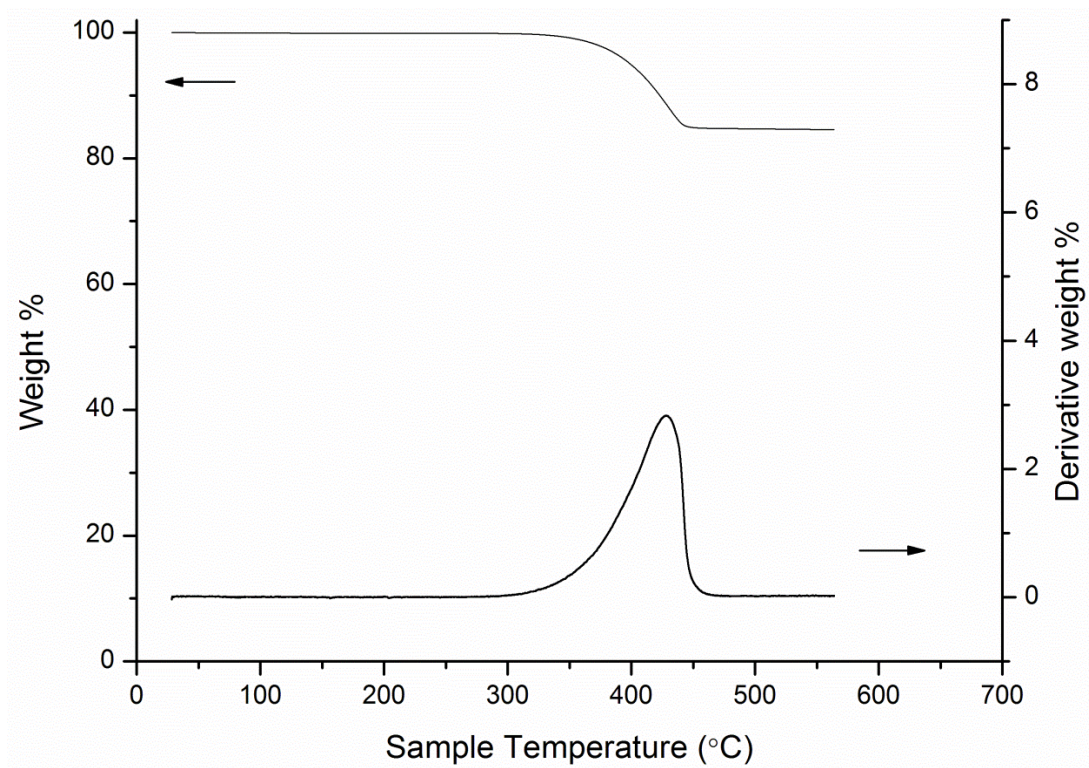


**Figure 4A-35** TG/DTG curve of [BMIM][NTf<sub>2</sub>] on TiO<sub>2</sub>.

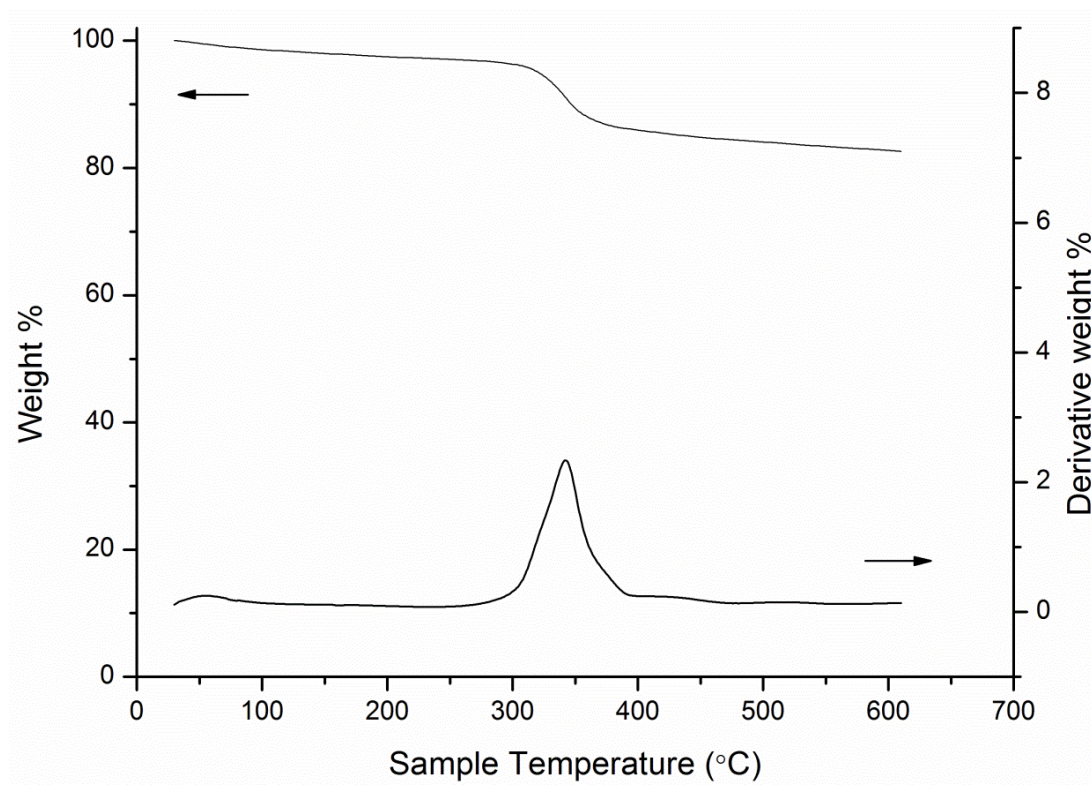


**Figure 4A-36** TG/DTG curve of [BMIM][NTf<sub>2</sub>] on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

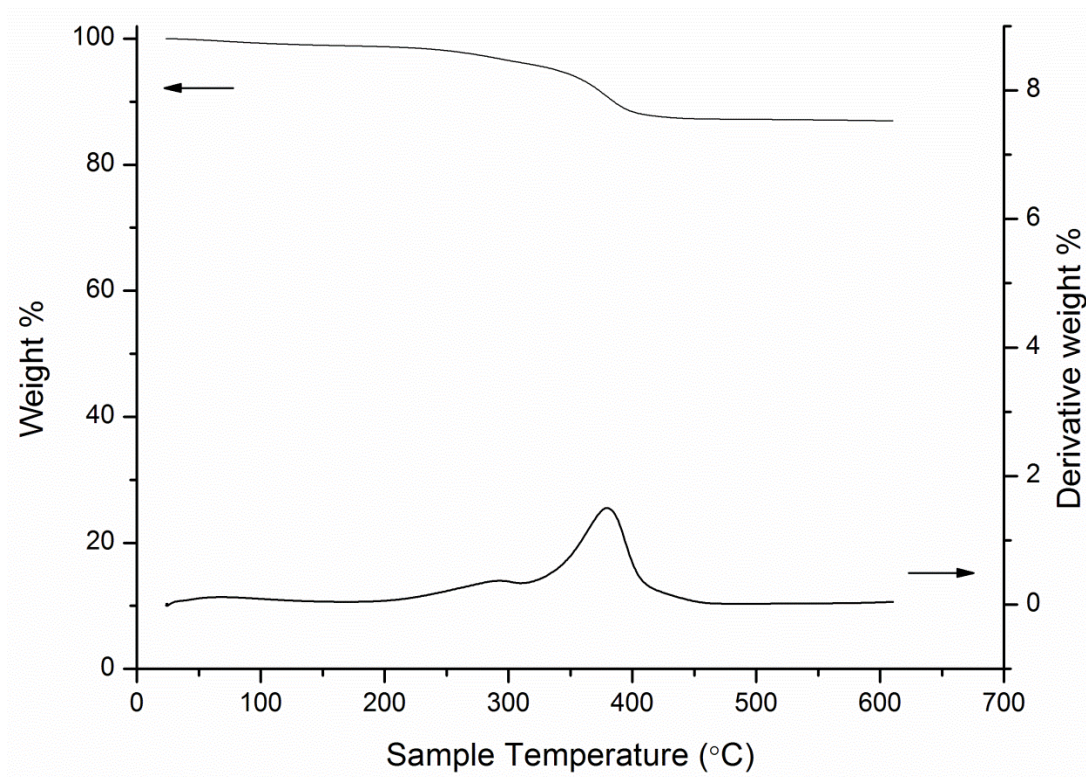


**Figure 4A-37** TG/DTG curve of [BMIM][NTf<sub>2</sub>] on MgO.

*Thermal Stability Limits on metal-oxide Fe<sub>2</sub>O<sub>3</sub>;*

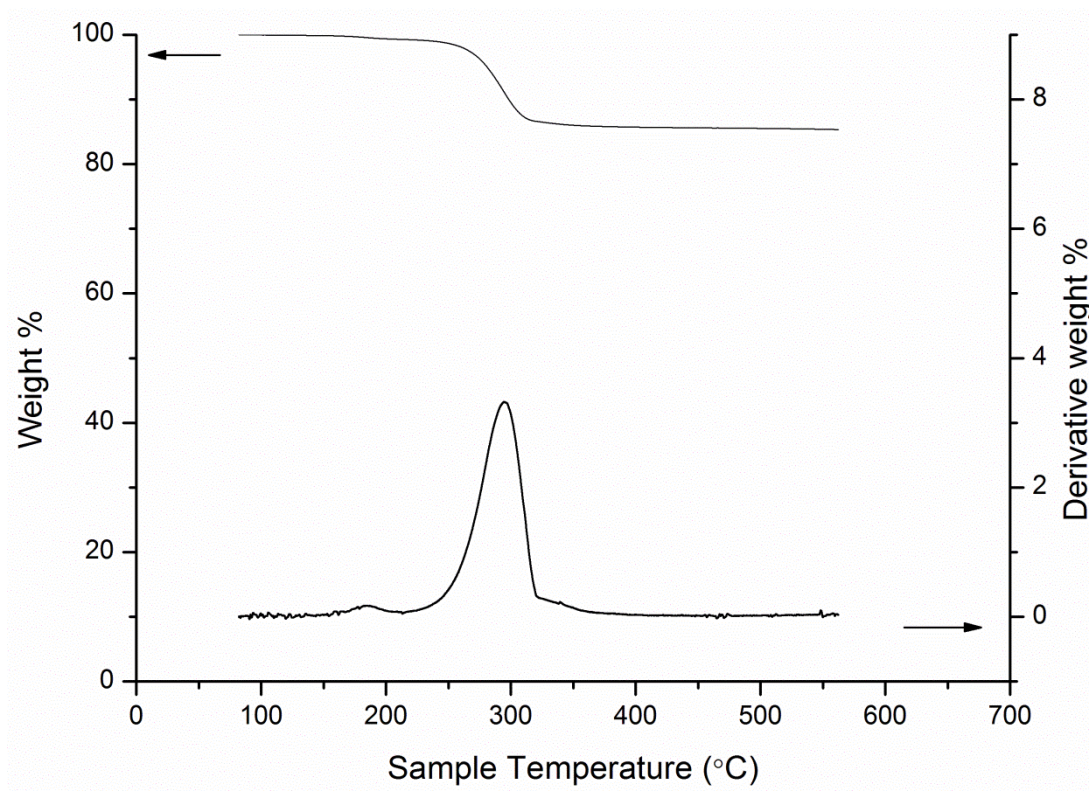


**Figure 4A-38** TG/DTG curve of [BMIM][DBP] on  $\text{Fe}_2\text{O}_3$ .

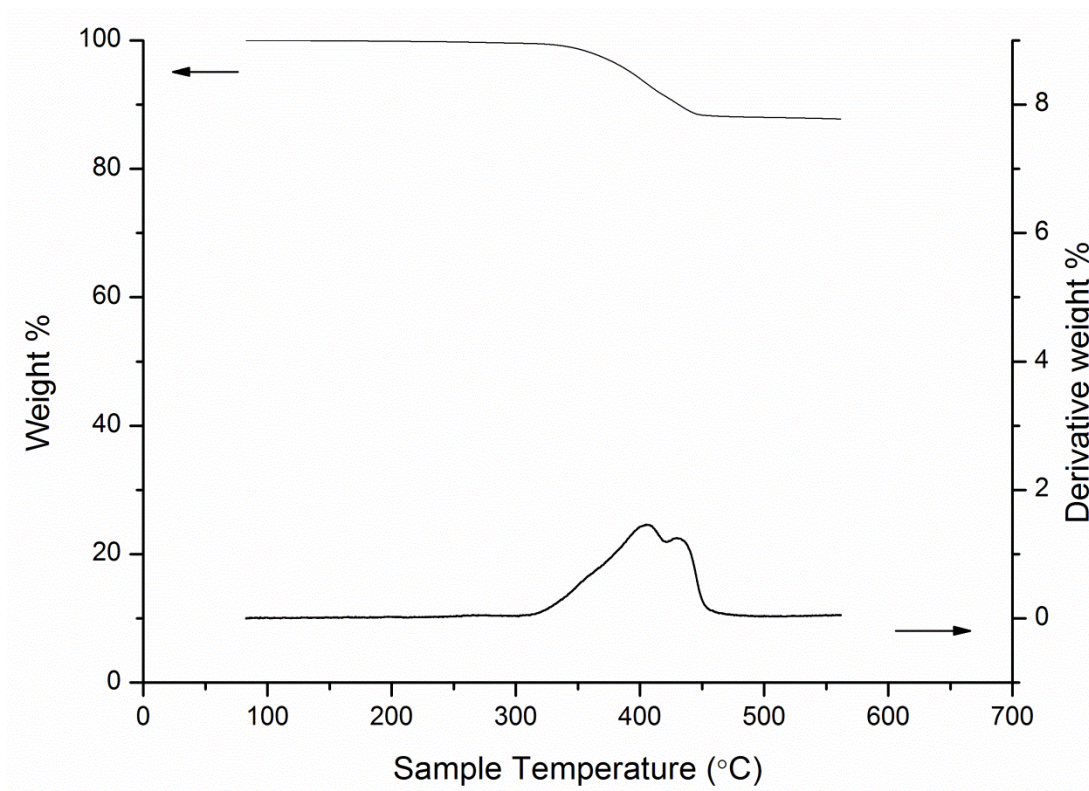


**Figure 4A-39** TG/DTG curve of [BMIM][BF<sub>4</sub>] on Fe<sub>2</sub>O<sub>3</sub>.

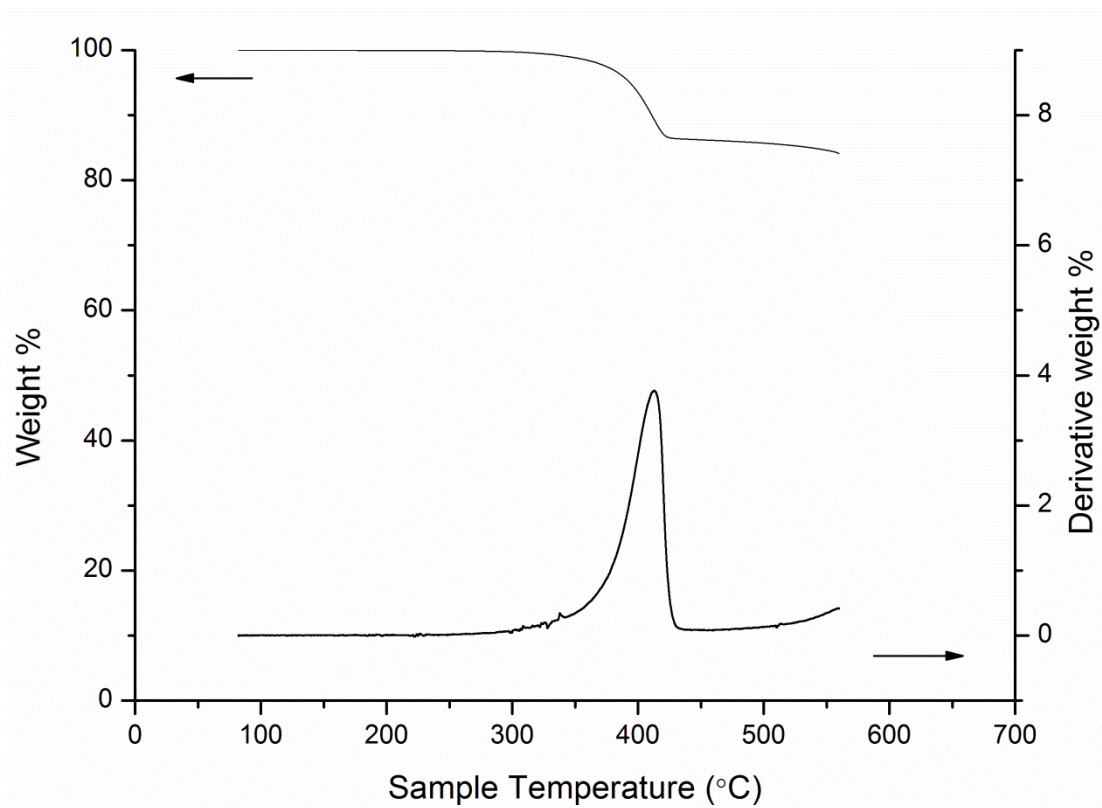


**Figure 4A-40** TG/DTG curve of [BMIM][NTf<sub>2</sub>] on La<sub>2</sub>O<sub>3</sub>.

*Thermal Stability Limits on metal-oxide CeO<sub>2</sub>;*

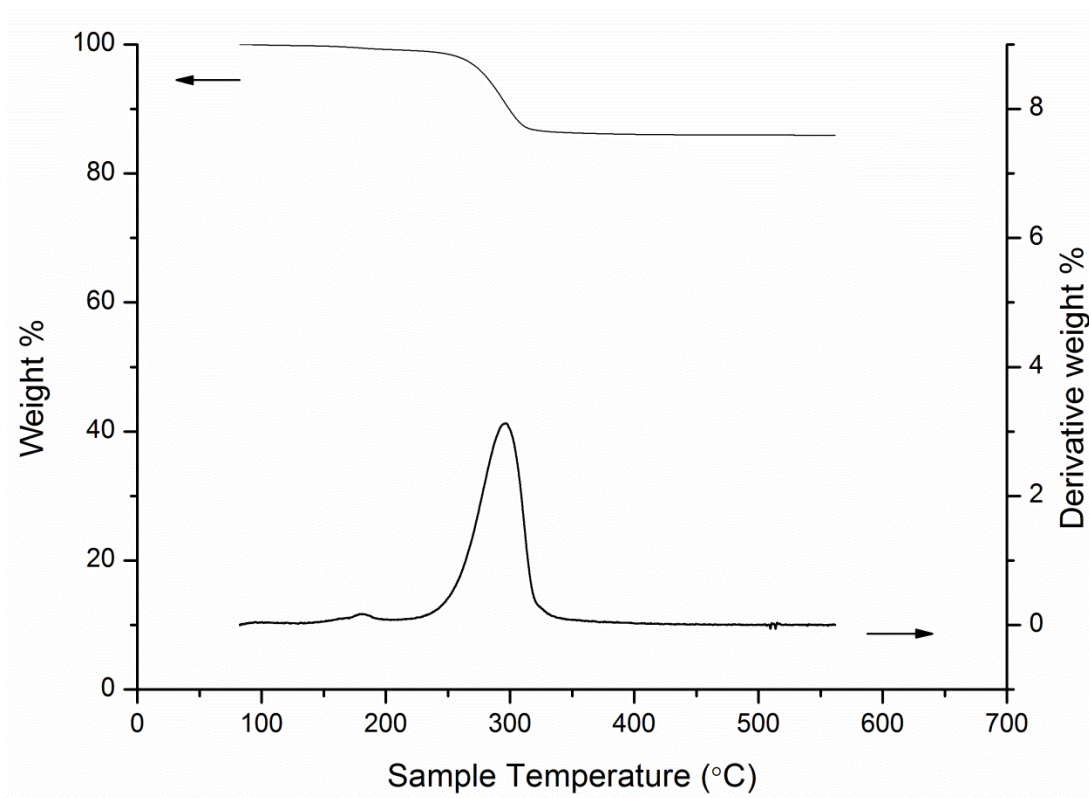


**Figure 4A-41** TG/DTG curve of [BMIM][DBP] on CeO<sub>2</sub>.

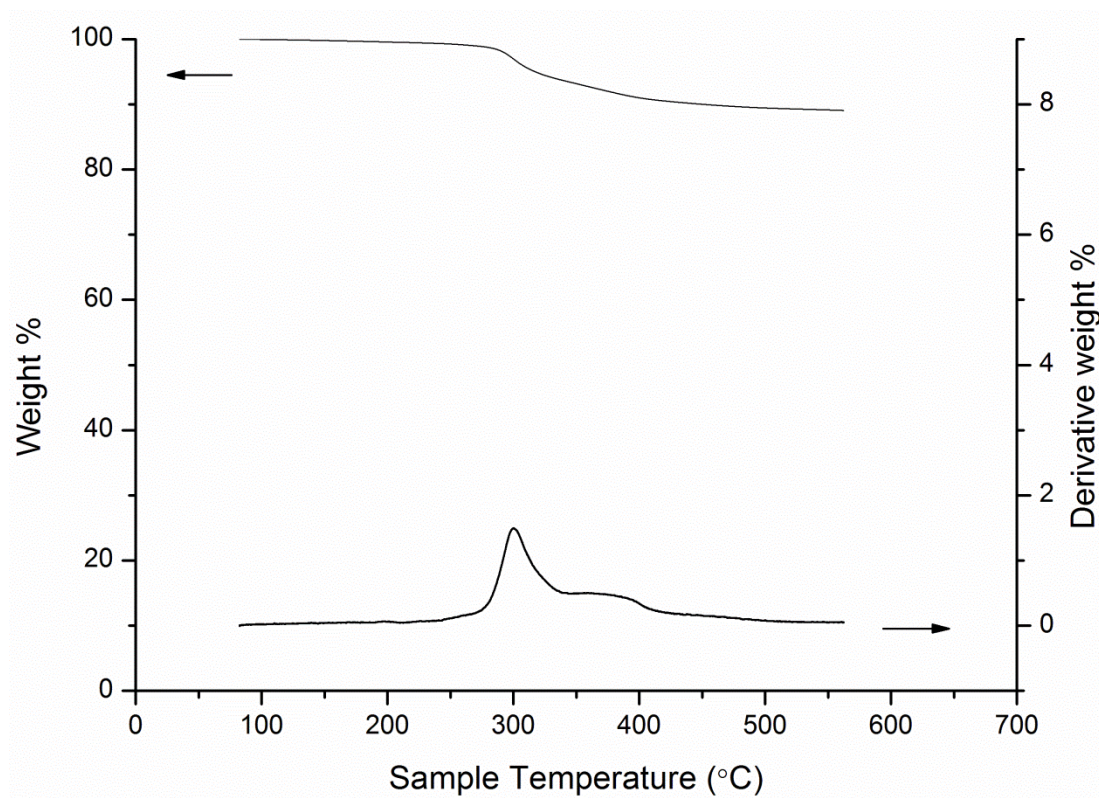


**Figure 4A-42** TG/DTG curve of [BMIM][BF<sub>4</sub>] on CeO<sub>2</sub>.

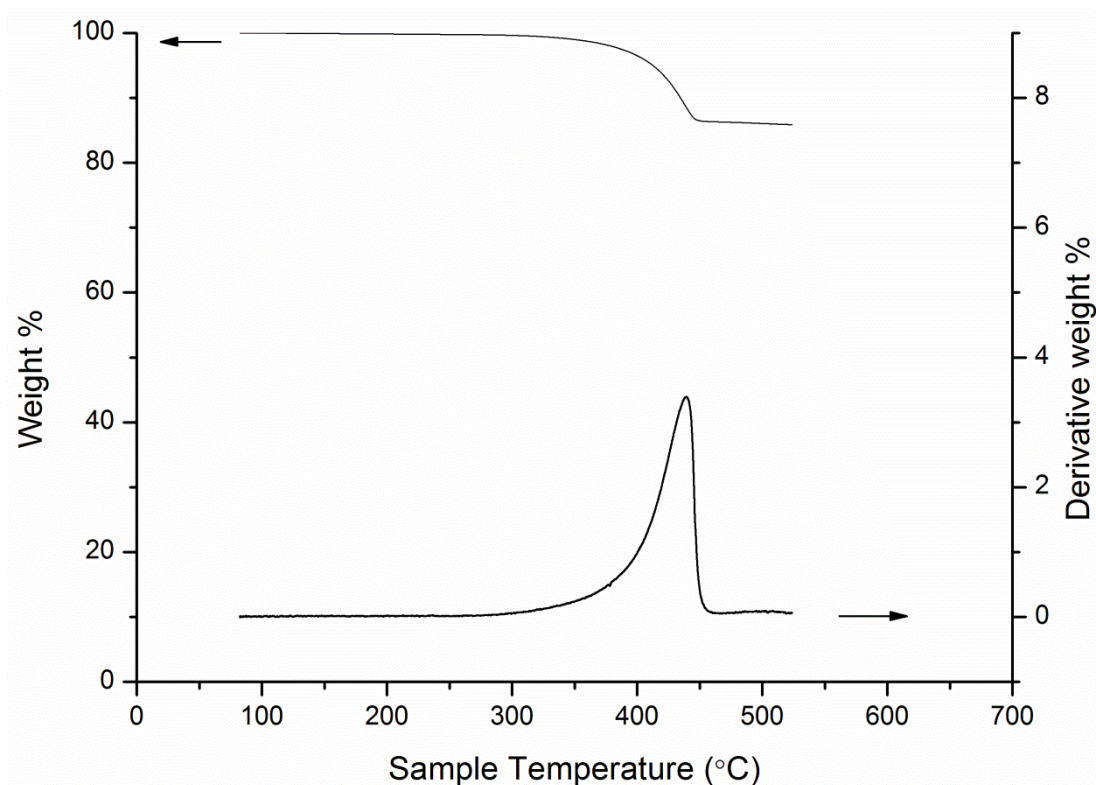


**Figure 4A-43** TG/DTG curve of [BMIM][NTf<sub>2</sub>] on CeO<sub>2</sub>.

### C2H Shift Determination by FT-IR Spectroscopy

Each IR spectra was collected in air at room temperature with a resolution of 4 cm<sup>-1</sup> and an average of 512 scans on Thermo Scientific Nicolet iS10 model instrument with an attenuated total reflection (ATR) cell.

Peak assignments of C2 proton of each IL was performed based on the assignments of Noack et.al.<sup>1</sup> A representative image of C2H vibrational frequency determination was given in Figure 4A-41.

In order to show the shift of vibrational frequency of C2 proton upon coating on different metal-oxides, normalized FT-IR graphs of each IL on four metal-oxides were plotted in between 2700-3600  $\text{cm}^{-1}$  with an exception of IL [BMIM][OAc] which was plotted in between 2637-3600  $\text{cm}^{-1}$ .

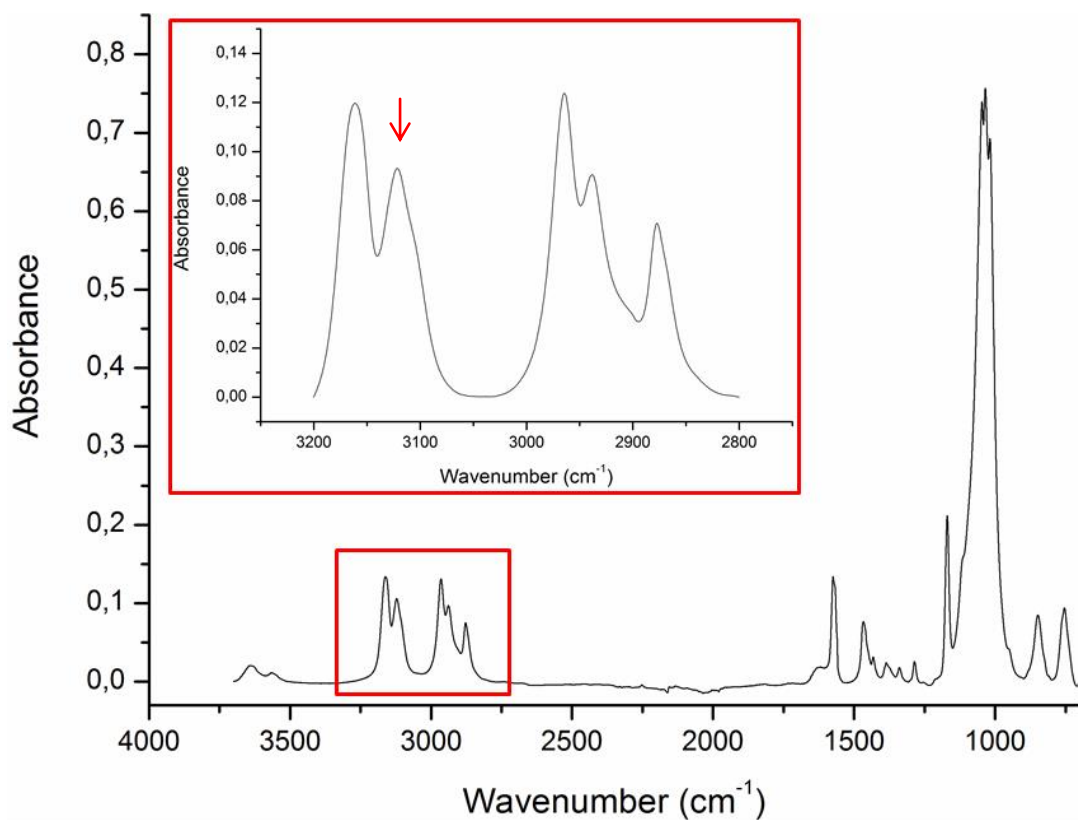


**Figure 4A-44** A representative image of C2H vibrational frequency determination of bulk [BMIM][BF<sub>4</sub>].

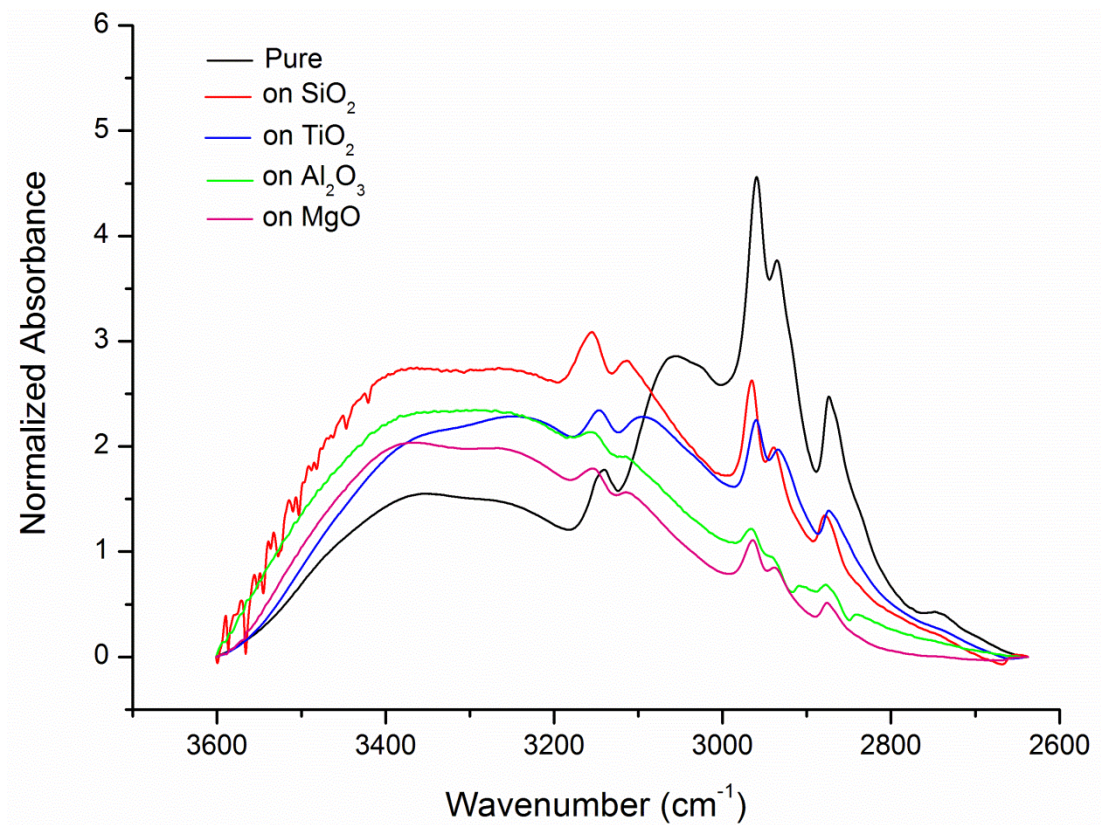


**Figure 4A-45** Shift of  $\nu(\text{C2H})$  of [BMIM][OAc] upon coating on metal-oxides.

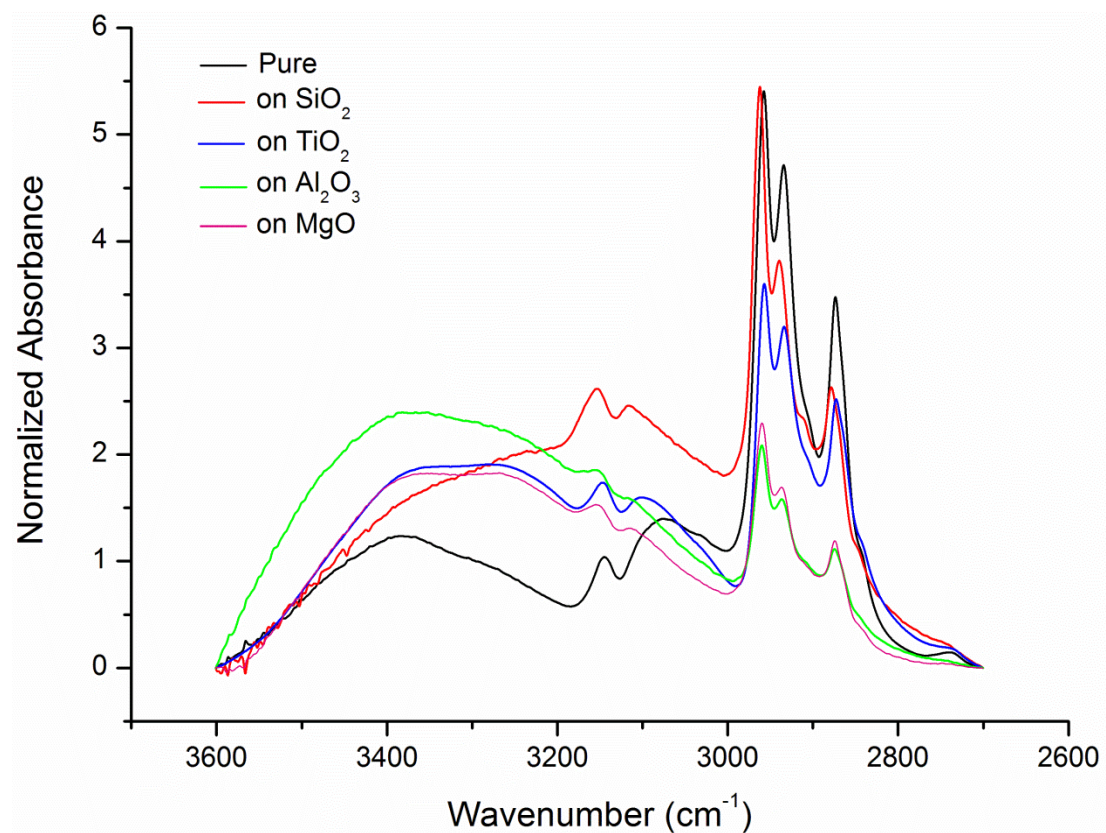


**Figure 4A-46** Shift of  $\nu(\text{C2H})$  of [BMIM][DBP] upon coating on metal-oxides.

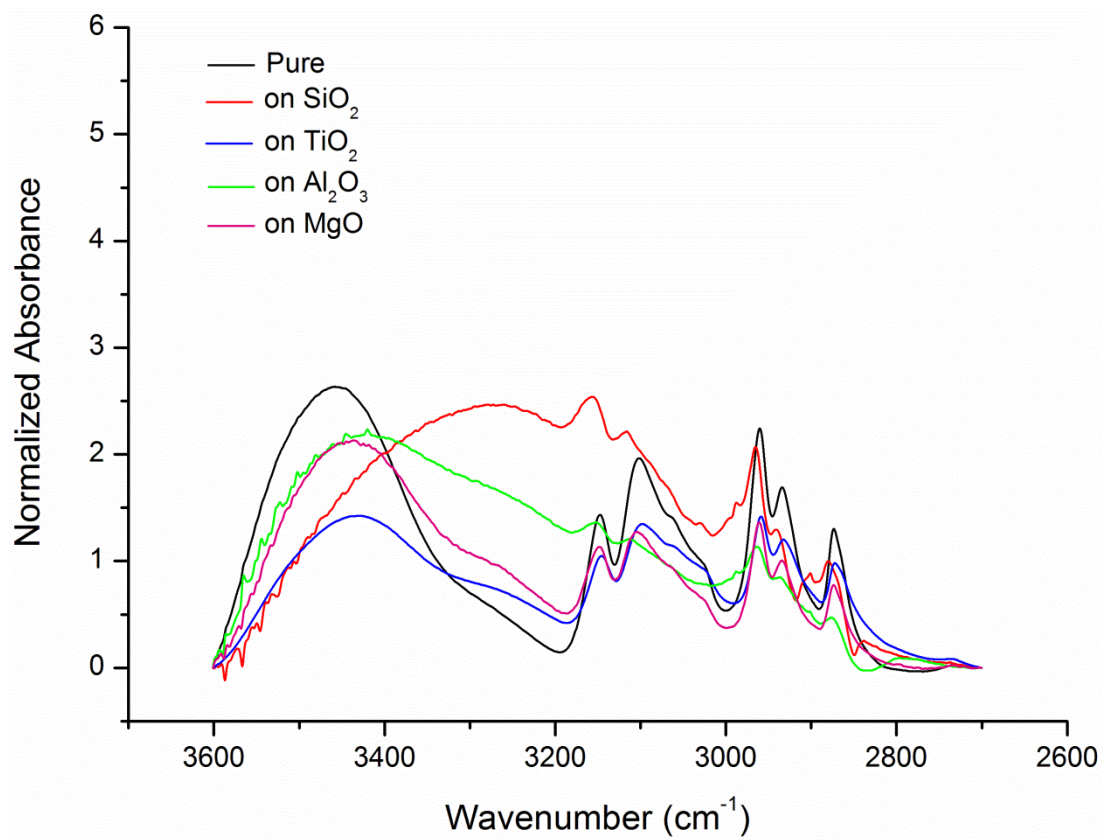


**Figure 4A-47** Shift of  $\nu(\text{C2H})$  of [BMIM][TOS] upon coating on metal-oxides.

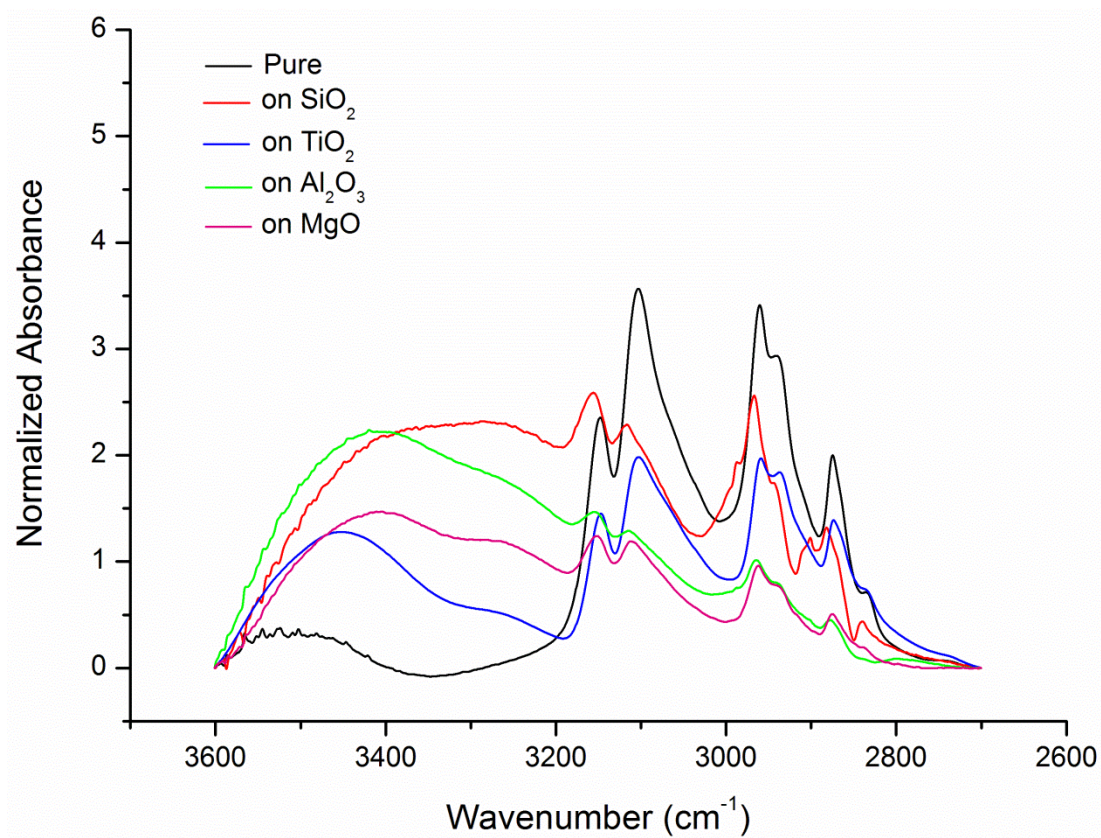


**Figure 4A-48** Shift of  $\nu(\text{C2H})$  of [BMIM][HSO<sub>4</sub>] upon coating on metal-oxides.

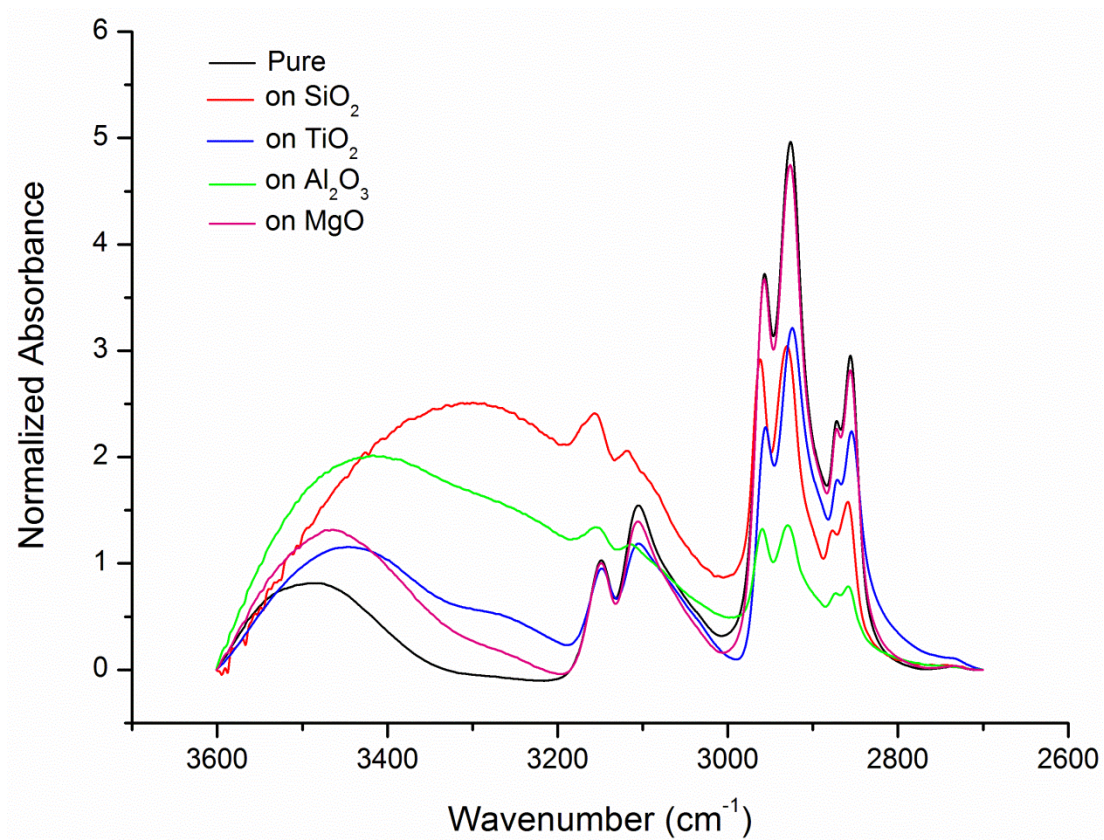


**Figure 4A-49** Shift of  $\nu(\text{C2H})$  of [BMIM][OS] upon coating on metal-oxides.

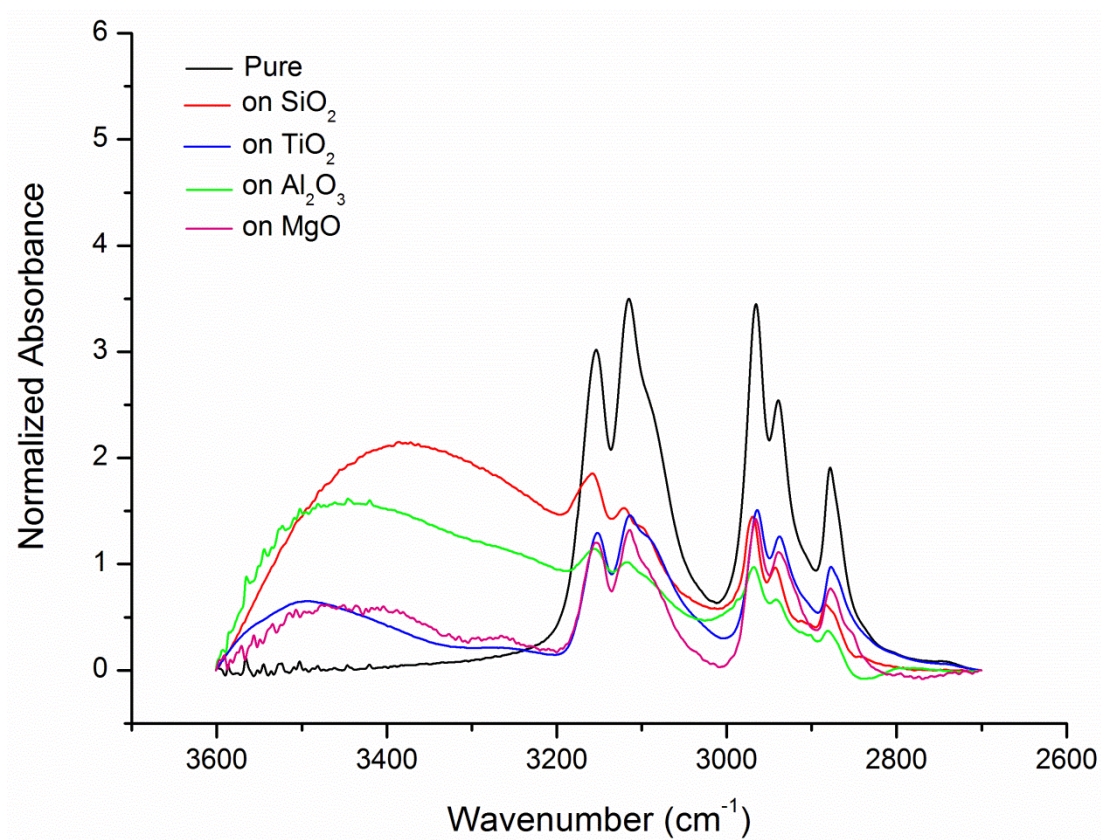


**Figure 4A-50** Shift of  $\nu(\text{C2H})$  of [BMIM][TfO] upon coating on metal-oxides.

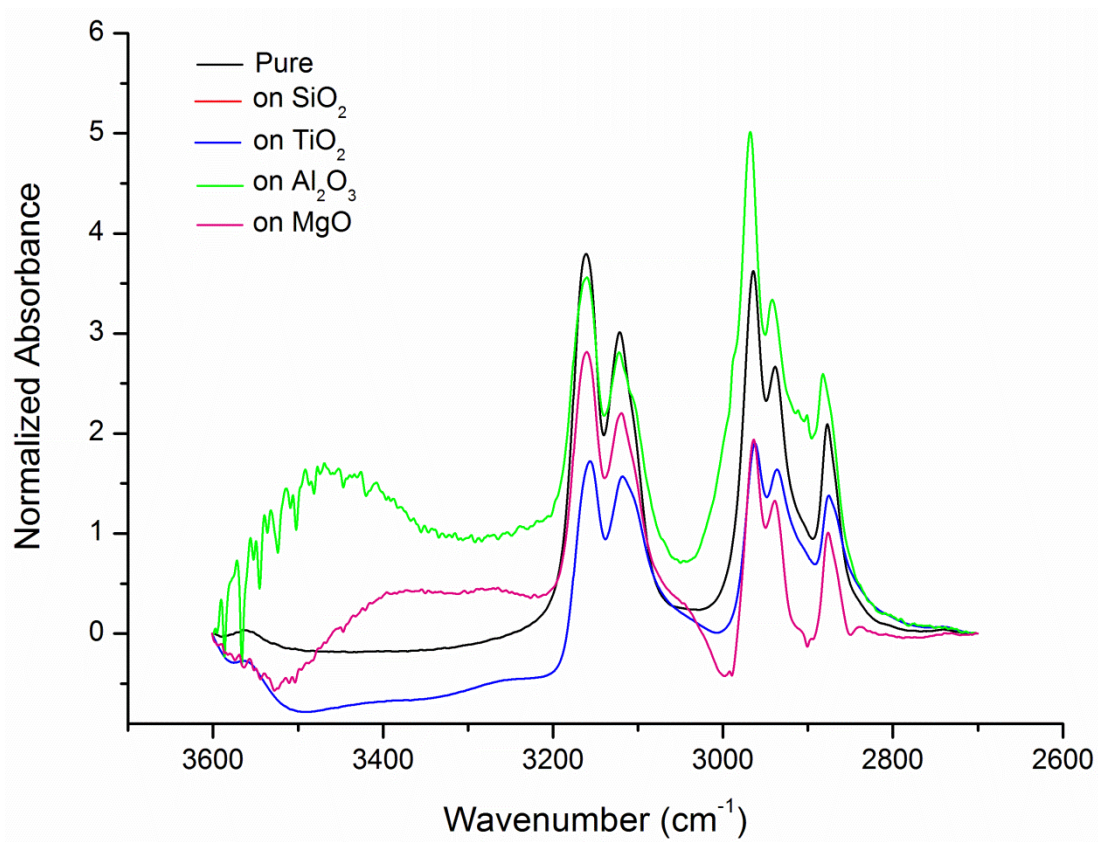


**Figure 4A-51** Shift of  $\nu(\text{C2H})$  of [BMIM][BF<sub>4</sub>] upon coating on metal-oxides.

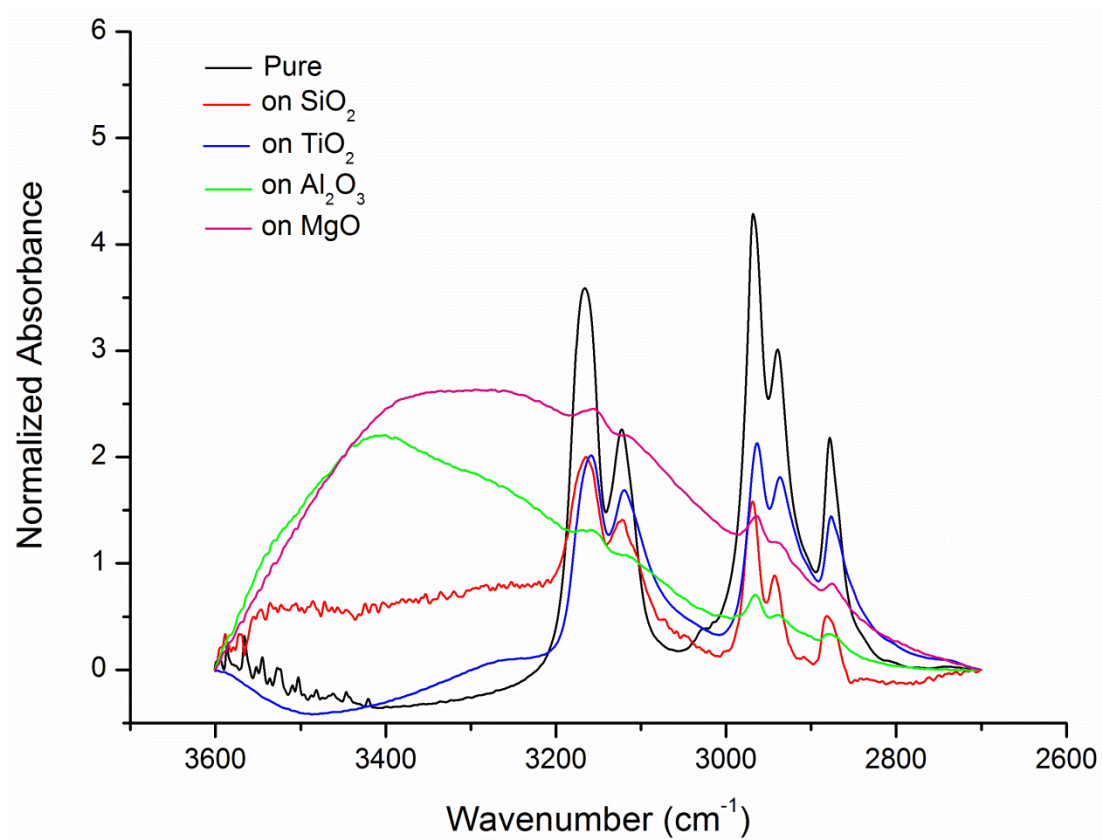


**Figure 4A-52** Shift of  $\nu(\text{C2H})$  of [BMIM][SbF<sub>6</sub>] upon coating on metal-oxides.

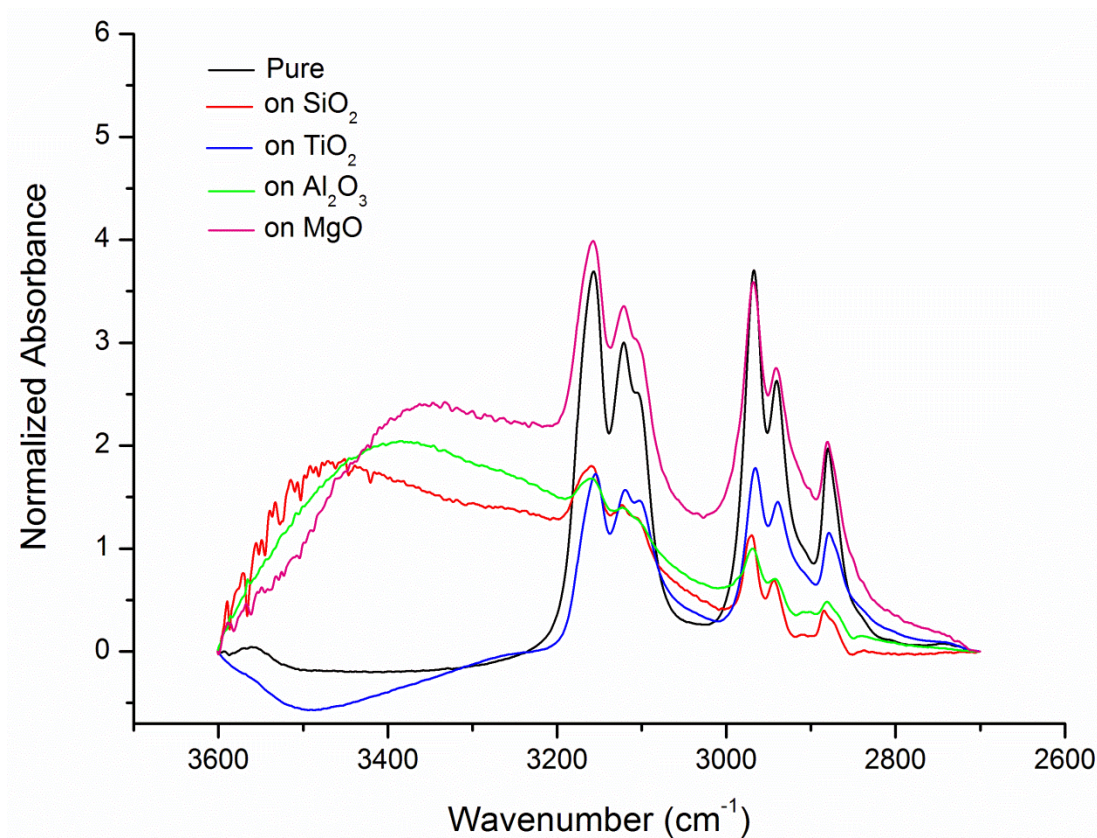


**Figure 4A-53** Shift of  $\nu(\text{C2H})$  of  $[\text{BMIM}][\text{NTf}_2]$  upon coating on metal-oxides.

**Table 4A-1** Individual percent error values of each supported-ILs with indicated maximum, minimum and average values.

| Metal-oxides   | ILs                           | Model $T'_{\text{onset}}$ | $T'_{\text{onset}}$ | Error (%) |
|----------------|-------------------------------|---------------------------|---------------------|-----------|
| $\text{SiO}_2$ | $[\text{BMIM}][\text{OAc}]$   | 193.8                     | 191                 | 1.5       |
|                | $[\text{BMIM}][\text{DBP}]$   | 245.7                     | 222                 | 10.7      |
|                | $[\text{BMIM}][\text{TOS}]$   | 307.5                     | 303                 | 1.5       |
|                | $[\text{BMIM}][\text{HSO}_4]$ | 310.0                     | 318                 | 2.5       |
|                | $[\text{BMIM}][\text{TfO}]$   | 339.6                     | 352                 | 3.5       |
|                | $[\text{BMIM}][\text{BF}_4]$  | 357.0                     | 331                 | 7.8       |
|                | $[\text{BMIM}][\text{SbF}_6]$ | 359.4                     | 337                 | 6.7       |
|                | $[\text{BMIM}][\text{NTf}_2]$ | 361.9                     | 360                 | 0.5       |
| $\text{TiO}_2$ | $[\text{BMIM}][\text{OAc}]$   | 186.8                     | 187                 | 0.1       |
|                | $[\text{BMIM}][\text{DBP}]$   | 238.5                     | 246                 | 3.1       |

|                                          |                           |       |     |      |
|------------------------------------------|---------------------------|-------|-----|------|
| $\gamma$ -Al <sub>2</sub> O <sub>3</sub> | [BMIM][TOS]               | 299.9 | 322 | 6.9  |
|                                          | [BMIM][HSO <sub>4</sub> ] | 302.4 | 312 | 3.1  |
|                                          | [BMIM][TfO]               | 331.9 | 350 | 5.2  |
|                                          | [BMIM][BF <sub>4</sub> ]  | 349.1 | 341 | 2.4  |
|                                          | [BMIM][SbF <sub>6</sub> ] | 351.6 | 363 | 3.2  |
|                                          | [BMIM][NTf <sub>2</sub> ] | 354.0 | 352 | 0.6  |
|                                          | [BMIM][OAc]               | 123.3 | 135 | 8.7  |
|                                          | [BMIM][DBP]               | 170.8 | 162 | 5.4  |
|                                          | [BMIM][TOS]               | 227.3 | 218 | 4.3  |
|                                          | [BMIM][HSO <sub>4</sub> ] | 229.6 | 220 | 4.3  |
|                                          | [BMIM][TfO]               | 256.7 | 273 | 6.0  |
|                                          | [BMIM][BF <sub>4</sub> ]  | 272.5 | 263 | 3.6  |
|                                          | [BMIM][SbF <sub>6</sub> ] | 274.8 | 269 | 2.2  |
|                                          | [BMIM][NTf <sub>2</sub> ] | 277.1 | 296 | 6.4  |
|                                          | [BMIM][OAc]               | 119.2 | 127 | 6.1  |
|                                          | [BMIM][DBP]               | 146.1 | 143 | 2.2  |
| MgO                                      | [BMIM][TOS]               | 178.1 | 176 | 1.2  |
|                                          | [BMIM][HSO <sub>4</sub> ] | 179.3 | 164 | 9.4  |
|                                          | [BMIM][TfO]               | 194.7 | 204 | 4.6  |
|                                          | [BMIM][BF <sub>4</sub> ]  | 203.7 | 209 | 2.6  |
|                                          | [BMIM][SbF <sub>6</sub> ] | 204.9 | 209 | 1.9  |
|                                          | [BMIM][NTf <sub>2</sub> ] | 206.2 | 206 | 0.1  |
| Fe <sub>2</sub> O <sub>3</sub>           | [BMIM][DBP]               | 188.1 | 171 | 10.0 |
|                                          | [BMIM][BF <sub>4</sub> ]  | 296.3 | 308 | 3.8  |
|                                          | [BMIM][NTf <sub>2</sub> ] | 301.1 | 313 | 3.8  |
|                                          | [BMIM][DBP]               | 152.7 | 158 | 3.4  |
| CeO <sub>2</sub>                         | [BMIM][BF <sub>4</sub> ]  | 238.1 | 252 | 5.5  |
|                                          | [BMIM][NTf <sub>2</sub> ] | 241.9 | 266 | 9.1  |
| Average Error (%)                        |                           |       |     | 4.3  |
| Maximum Error (%)                        |                           |       |     | 10.7 |
| Minimum Error (%)                        |                           |       |     | 0.1  |

**References**

1. Noack, K.; Schulz, P. S.; Paape, N.; Kiefer, J.; Wasserscheid, P.; Leipertz, A., The role of the C2 position in interionic interactions of imidazolium based ionic liquids: a vibrational and NMR spectroscopic study. *Phys. Chem. Chem. Phys.* **2010**, *12* (42), 14153-14161.