Transformations of Xylenes in Trimethylammonium Hydrochloride – Aluminum Chloride Ionic Liquid

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Abstract: Isomerization of m-, o- and p-xylenes in the presence of trimethylammonium hydrochloride – AlCl₃ ionic liquid with different composition was studied. Ionic liquids with the following ammonium salt : AlCl₃ molar ratios were used: 1 : 2, 1 : 1.5 and 1 : 1.25. It was shown that isomerization of xylenes proceeds under mild conditions at temperatures from 60 °C to 110 °C. It was found that the activity and selectivity of the ionic liquids depends on their composition. The most effective catalyst was the ionic liquid with the ammonium salt : AlCl₃ molar ratio equal to 1 : 2.

Keywords: xylenes, isomerization, ionic liquid, biphasic catalysis

1 Introduction

Ionic liquids (or room-temperature molten salts) are presently considered as an alternative to conventional heterogeneous and homogeneous catalysts, especially to AlCl₃ and other aggressive Friedel-Crafts catalysts [1, 2]. Quaternized derivatives of N-heterocycles, such as chlorometallates, fluoroborates and fluorophosphates of N-alkylpyridinium, dialkylimidazolium and polyalkylammonium salts are known to exist in a liquid state over a wide temperature range (from ≈ 0 °C to ≈ 200 °C). They are promising as media for a wide range of catalytic reactions including downstream oil processing, basic organic synthesis, and fine chemicals production. Among these processes, of potential commercial interest are dimerization, alkylation, hydrogenation, metathesis, hydroformylation, and oligomerization of olefins. Chloroaluminate systems have been known since the 70s [3]. However,

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Nowadays ionic liquids are mostly used as solvents in the catalytic processes. In the recent review on use of ionic liquids in catalysis [4], a large number of catalytic processes where they are used as solvents are listed; only a few examples of the application of ionic liquids as catalysts are mentioned.

It is widely known [5] that isomerization of xylenes proceeds over acid-type catalysts, such as aluminum chloride, BF$_3$ – HF, aluminosilicates, and zeolites. However, these catalysts have some disadvantages. They require either high reaction temperatures (300–400 °C), or aggressive medium (in the case of AlCl$_3$ or BF$_3$), or the necessity of using hydrogen, etc. Since xylene isomerization plays an important role in the petrochemical industry, mainly for phthalic and terephthalic acid production, research in this area is of great interest. Recent achievements in this field are presented in a number of articles [6-9]. The best results for xylene isomerization in these publications provide product mixtures close to the xylene thermodynamic equilibrium [8], but the temperature required was rather high: from ≈ 300 °C to ≈ 400 °C. In [6] the conversion of xylene did not exceed 30–35% at ≈ 400 °C. In the other studies, the authors used flow reactors, which prevents a direct comparison of the efficiency of the catalysts used with that of ionic liquids.

Data on the use of ionic liquids as media for isomerization of aromatic hydrocarbons are lacking in open literature or patents. Some ionic liquids possess high Hammett acidity ($H_0$ ~ 19) [10], and are known to be superacids. They can therefore serve as effective catalysts for isomerization of xylenes.

The goal of the present research was to study the catalytic activity of trimethylammonium hydrochloride (TMAH) – AlCl$_3$ ionic liquid in the isomerization of o-, m- and p-xylenes. The influence of the ammonium salt : AlCl$_3$ molar ratio in the composition of the ionic liquid on activity and selectivity was also investigated.

### 2 Experimental

#### 2.1 Catalyst preparation.

Ionic liquid TMAH – aluminum chloride with a molar ratio 1 : 2 was prepared from TMAH and freshly sublimed aluminium chloride in an inert atmosphere, following the procedure described in [11]. The loading of 26.7 g (0.2 mol) of AlCl$_3$ was added to 9.6 g (0.1 mol) of TMAH under intensive stirring. For the preparation of ionic liquids with molar ratios 1 : 1.5 and 1 : 1.25, the AlCl$_3$ loadings were changed to 20.0 g (0.15 mol) and 16.7 g (0.125 mol), respectively. Since the reaction is exothermic, the reaction mixture was cooled to maintain the temperature below 50 °C. The molten salts obtained were stirred in an inert atmosphere for 30 min at room temperature. Light-brown ionic liquids were obtained with a density of ~ 1.3–1.4 g/cm$^3$. 
2.2 Catalytic experiments.

Isomerization of xylenes was carried out in a three-neck (25 ml) flask with a reflux condenser and a magnetic-type stirrer. A mixture of 4.0 g of a hydrocarbon (o-, m-, or p-xylene) and 1.0 g of the ionic liquid was loaded into the reaction vessel, which had first been purged with He, and stirring was started. The reaction was carried out with stirrer rotation speed ≈ 400–450 rpm, and at temperatures 60 °C, 90 °C, or 110 °C. The reaction mixture represented a two-phase system: the lower layer was the ionic liquid with partly dissolved aromatic hydrocarbons (about 25 % wt.), and the upper was the hydrocarbon phase. The volume ratio of the two phases substrate : catalyst was about 5.5 : 1.

Samples for GC analysis were taken every 30 min. After 3 h of the experiment, in order to calculate the mass balance of hydrocarbons in upper layer and hydrocarbons dissolved in ionic liquid, the lower layer of ionic liquid and dissolved aromatic hydrocarbons was decomposed with water. After decomposition two layers were obtained, i.e. water layer and organic layer, the latter was separated and analyzed by GC. It was found that its composition was the same as the composition of the upper layer, i.e. hydrocarbon layer (that is why only the results after 3 h of experiments are presented). A capillary column (50 m) with PEG 20M was used. The duration of each catalytic experiment was about 3 h.

3 Results and discussion

The results of the experiments on isomerization of xylenes (reaction duration is 3 hours) are presented in Tables 1–3.

As it is seen from Table 1, in the case of o-xylene as a substrate, we can observe the formation of m- and p-xylenes. With an increase in the TMAH : AlCl₃ molar ratio from 1 : 2 to 1 : 1.25, the isomerization activity of the ionic liquid significantly decreased. This effect was observed in the whole range of temperatures used (60–110 °C). As we can see from the data presented, the selectivity to isomerization is close to 80–90%, and at low conversions it approaches 100%. Disproportionation to toluene and trimethylbenzenes (TMB) proceeds along with o-xylene isomerization. At the temperatures 60 °C and 90 °C, the yield of side products was insignificant, about 2–5%. As a whole, the yield of byproducts did not exceed 10% (at 110 °C).

Table 2 presents the results obtained for m-xylene isomerization under the same conditions as o-xylene isomerization. In these experiments, regularities similar to those in the o-xylene isomerization were observed: (1) the increase in the m-xylene conversion with an increase in the process temperature and (2) the growth of the ionic liquid activity with a change of the ammonium salt : AlCl₃ molar ratio from 1 : 1.25 to 1 : 2. The conversion of m-xylene increases from 13.0% to 52.5% with an increase in the reaction temperature from 60 °C to 110 °C for the ionic liquid with the component molar ratio 1 : 2 and from 10.5 to 32.3% for the ionic liquid with the ratio 1 : 1.5. It should be pointed out that
the observed yields of o- and p-xylenes are closely similar in these experiments. This is in good agreement with the scheme of xylene transformations discussed in the literature [5, 12, 13]. Moreover, in the presence of the ionic liquid with the composition TMAH : AlCl₃ = 1 : 2, the ratio of the xylenes reached the thermodynamic equilibrium at 110 °C (o-xylene 18.9%, m- xylene 56.8%, p-xylene 24.2%) [5]. As with o-xylene isomerization, the selectivity was high enough, i.e. 80–90%, decreasing to 60–70% with an increase in the reaction temperature. Toluene and trimethylbenzenes were the side products of the reaction. Side reactions proceed more intensively in the case of m-xylene isomerization than with o-xylene, and the yield of toluene and trimethylbenzenes reached 30%.

The results for p-xylene isomerization are presented in Table 3. Once more we can see the same regularities in changes of the ionic liquid catalytic activity with changing composition and process temperature as with o- and m-xylene isomerization. Thus, the conversion of p-xylene reached 76% in the ionic liquid TMAH – AlCl₃ (molar ratio 1 : 2) at 110 °C. However, the selectivity to p-xylene isomerization was significantly lower (40–60%), and more dependent on the reaction temperature and the ionic liquid composition. Side products of the process are the same, i.e. toluene and trimethylbenzenes.

Although a clear relationship between activity and selectivity of the ionic liquids was not observed, there was a general trend toward increasing conversion and decreasing selectivity with increasing process temperature.

It should be pointed out that the decrease of the ionic liquid catalytic activity with an increase of TMAH : AlCl₃ molar ratio from 1 : 2 to 1 : 1.25 can be explained in terms of the acidity of ionic liquids. It is known that the acidity of ionic liquids depends on the molar ratio of the organic part to the inorganic, for instance, in the case of chloroaluminate ionic liquids, on the mole fraction of AlCl₃. The higher the mole fraction of AlCl₃, the higher the acidity of the ionic liquid [10]. The ionic liquid with the molar ratio TMAH : AlCl₃ =1 : 2 is the most acidic, and, consequently, more active in xylene isomerization, than the ionic liquid with the molar ratio equal to 1 : 1.5, which, in its turn, is more active than the TMAH – AlCl₃ (1 : 1.25 mol.) ionic liquid. The latter two ionic liquids contain a mixture of AlCl₄⁻ and Al₂Cl₇⁻ anions, whereas the former contains only Al₂Cl₇⁻ anions, possessing strong Lewis acidity [10].

Figure 1 illustrates the best data on isomerization of xylenes in the ionic liquid TMAH – AlCl₃ (molar ratio 1 : 2) at 110 °C. The best results were obtained for o-xylene isomerization. On the other hand, the m-xylene isomerization system was inferior both in terms of conversion and selectivity.

4 Conclusion

Ionic liquids are capable of catalyzing isomerization of xylenes at relatively low temperatures (60–110 °C) and the thermodynamic equilibrium is attained. The conversion of xylenes strongly depends on the component molar ratio in the ionic liquid composition and on the process temperature. The highest conversion (70–75%) and selectivity (80–90%) were achieved with the ionic liquid ammonium salt – AlCl₃ with the molar ratio
1 : 2 at 110 °C. Toluene and trimethylbenzenes were the side products of the reaction.

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Table 1 Isomerization of o-xylene in the TMAH – AlCl₃ ionic liquid with different component ratio (reaction duration is 3 h).

*) Isomerization selectivity was calculated by dividing the overall yield of m- and p-xylenes by the conversion.
Table 2 Isomerization of m-xylene in the TMAH – AlCl₃ ionic liquid with different component ratio (reaction duration is 3 h).

*) Isomerization selectivity was calculated by dividing the overall yield of o- and p-xylene by the conversion.
### Table 3

Isomerization of p-xylene in the TMAH – AlCl₃ ionic liquid with different component ratio (reaction duration is 3 h).

*) Isomerization selectivity was calculated by dividing the overall yield of o- and m-xylenes by the conversion.
Fig. 1 Isomerization of xylenes in the ionic liquid TMAH-AlCl$_3$ (1 : 2 mol) at 110 °C.