

## OLIGOMERIZATION OF IZOBUTENE IN THE PRESENCE OF IONIC LIQUID – BASED CATALYSTS

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In the petrochemical industry, the C<sub>4</sub> stream including isobutene is an important raw material that can be upgraded. Oligomerization of isobutene is a very promising reaction, as the hydrogenation products of dimers and trimers, obtained from isobutene, can be used as gasoline and diesel additives, respectively. In the present paper, our results concerning the use of Brønsted acidic ionic liquids as oligomerization catalysts are presented. The ionic liquids were supported on silica. Most of the solid catalysts were reused several times without loss of activity. By the proper choice of the ionic liquid and reaction conditions, good selectivity towards either C<sub>8</sub> or C<sub>12+</sub> products could be achieved.

**Keywords:** oligomerization, isobutene, ionic liquid

### Introduction

The oligomerization of light olefins is an important alternative for the production of higher molecular weight hydrocarbon mixtures useful as fuels (e.g. gasoline or diesel). Both Brønsted and Lewis acids have been used as oligomerization catalysts in either homogeneous (H<sub>2</sub>SO<sub>4</sub>, organometallic complexes, etc.) or heterogeneous (mixed oxides, zeolites, clays, ion exchange resins etc.) phase. [1]

The main challenges in the design of catalysts for this reaction are focused to reach high conversion and high selectivity. Consequently, several solid acid catalysts of different types have been developed for the oligomerization of lower alkenes, such as isobutene. [2]

At the same time, Ni-based catalysts containing phosphine ligands can be used efficiently in the homogeneous phase in the presence of various additives. [3, 4] However, a great drawback of homogeneous catalytic reactions is the problem of catalyst recovery and recycling. The use of a two-phase solvent system, together with a transition metal complex, is an attractive alternative, as it enables catalyst separation and reuse. This methodology was found to be very efficient in alkene oligomerization by cationic nickel complexes in chloroaluminate [5-8] or hexafluorophosphate [9] ionic liquids as solvents.

Chloroaluminate ionic liquids with Lewis acidic character were shown to catalyze oligomerization themselves, without the addition of transition metal complexes or salts. [10] These catalysts were applied in the oligomerization of linear 1-olefins. [11] Imidazolium ionic liquids with SO<sub>3</sub>H functionalized side chains were

also found to be excellent and reusable catalysts in oligomerization of various alkenes. [12]

Generally, ionic liquids (ILs) have gained increasing attention with multiple applications in synthesis and catalysis. [13] Despite their advantages, there are also some drawbacks, including the difficulties in product purification or IL recycling and the problems for application in fixed bed reactors. Also, biphasic ionic liquid-organic systems require large amounts of the expensive ILs, which hinders industrial applications. These difficulties can be overcome by the use of supported ionic liquid phases (SILPs) prepared by the immobilization of ionic liquids on solid supports. [14]

Based on these findings, we decided to explore the possibility of the use of silica-supported SO<sub>3</sub>H-functionalised ILs as catalysts in the oligomerization of isobutene. In this paper, we report on our results concerning the effects of the changes in the reaction conditions on the outcome of the oligomerization reaction.

### Experimental

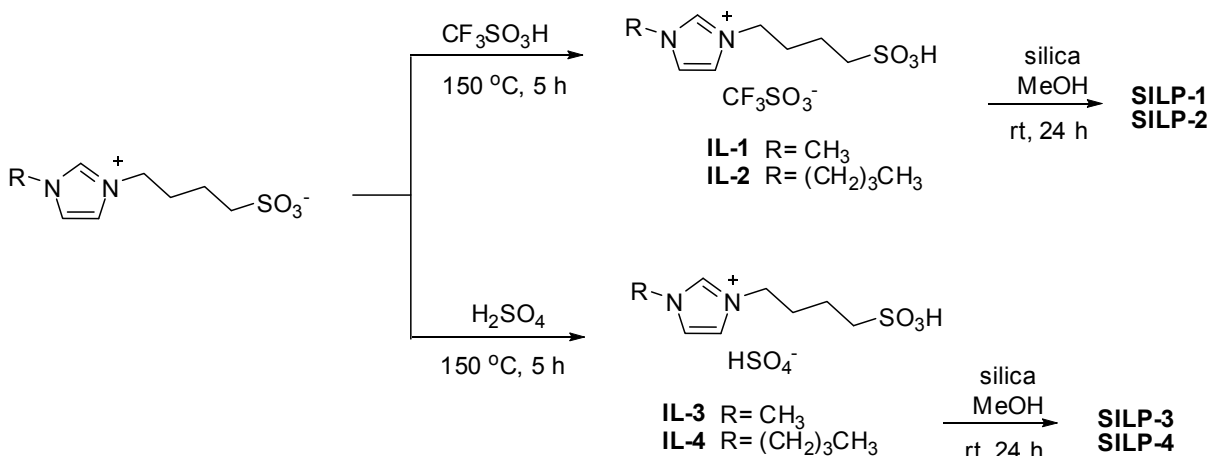
#### Materials

The ionic liquids (**IL-1** — **IL-4**) were synthesized by methods analogous to literature procedures. [15, 16] The supported catalysts (**SILP-1** — **SILP-4**) were obtained by reacting the ionic liquid (**IL-1**, **IL-2**, **IL-3** or **IL-4**) (10 mmol) and silica gel (Kieselgel 60 (0.040–0.063 mm), pre-heated at 250 °C for 5 h) (10 g) in 25 ml MeOH at

room temperature for 24 h. MeOH was removed in vacuo and the catalyst was dried at 60 °C in vacuo for 1 h.

### Oligomerization experiments

The reactions were carried out in an autoclave under argon. The autoclave was cooled to -15 °C and isobutene (5 ml, 57.5 mmol) was charged into the reactor, which contained the catalyst (10 mmol of **IL-1** or **IL-2** or 1 g of the supported ionic liquids **SILP-1** — **SILP-4**). The autoclave was pressurised with argon (22 bar, room temperature). In a typical reaction the mixture was stirred at 100 °C for 5 h. The autoclave was cooled to -15 °C, the organic phase was separated and analysed by gas chromatography. The SILP catalysts were washed with pentane (3x5 ml), dried in vacuo and reused.



Scheme 1: Synthesis of ionic liquids **IL-1** and **IL-2** and supported ionic liquids **SILP-1** — **SILP-4**

To compare the activity and selectivity of immobilized and non-immobilized ionic liquids, oligomerization was carried out first in **IL-1** and **IL-2** under the standard conditions (100 °C, 5 h). In these reactions, the isobutene/catalyst ratio was 57.5/10. Almost total conversion was obtained in both cases and the ratio of C<sub>12</sub> products was higher in **IL-2** than in **IL-1** (Table 1, entries 1, 2). This phenomenon can be explained by the higher solubility of C<sub>8</sub> in the ionic liquid with the longer side chain. Similar change in the selectivity of oligomerization with increasing alkyl chain length of the ionic liquid catalysts had been observed by Deng et al. before [12].

The supported ionic liquid catalysts (**SILP-1** — **SILP-4**) were also found to be active in the oligomerization (Table 1, entries 3-6). Immobilization of the ionic liquids resulted in a change in the selectivity of the reaction (compare entries 1, 3 and 2, 4). In the presence of **IL-1**, the dimers were obtained as the main products (entry 1). At the same time, good C<sub>12+</sub> selectivity was observed using the immobilized version of the same catalyst (**SILP-1**, entry 3). On the contrary, immobilization of **IL-2** led to an increase in C<sub>8</sub> selectivity (entry 4), compared to the results obtained with **IL-2** (entry 2). It should be mentioned, that in the case of the reactions carried out with the immobilized catalysts, the

### Analytical methods

Reaction mixtures were analyzed by gas chromatography using a Hewlett Packard 4890D instrument equipped with a FID detector and a 30 m HP-1 column. GC-MS measurements were carried out with a Hewlett Packard 5971A GC-MSD.

### Results and discussion

Four Brønsted acidic ionic liquids (**IL-1** — **IL-4**) were prepared and were immobilized on silica gel by adsorption to give catalysts **SILP-1** — **SILP-4** (Scheme 1).

substrate/ionic liquid ratio was much lower (57.5/1 instead of 57.5/10). Despite this, the conversion of isobutene was similar, or even a little higher under the same reaction conditions.

Table 1: Oligomerization of isobutene in the presence of ionic liquid based catalysts<sup>a</sup>

Entry	Catalyst	Conv. [%] <sup>b</sup>	Ratio of products [%] <sup>b</sup>			
			C <sub>8</sub>	C <sub>12</sub>	C <sub>16</sub>	C <sub>20</sub>
1	<b>IL-1</b>	98	75	24	1	-
2	<b>IL-2</b>	99	33	60	7	-
3	<b>SILP-1</b>	100	16	54	29	1
4	<b>SILP-2</b>	100	54	35	10	1
5	<b>SILP-3</b>	85	83	17	-	-
6	<b>SILP-4</b>	92	82	18	-	-

<sup>a</sup> Reaction conditions: 100 °C, 5 h <sup>b</sup> Determined by GC

The catalysts containing ionic liquids with hydrogensulfate anion showed the best selectivity toward the dimers but their activity was found to be somewhat lower (entries 5, 6) compared to the other two supported catalysts.

The possibility of the reuse of the supported catalysts was also investigated. **SILP-1** (Fig. 1) and **SILP-2** (Fig. 2)

were reused several times without loss of activity or considerable change in selectivity.

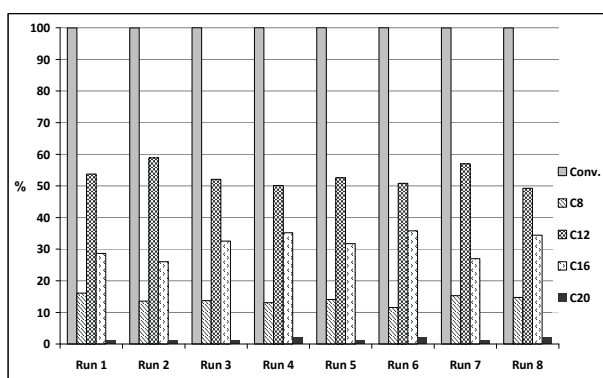


Figure 1: Oligomerization of isobutene in the presence of **SILP-1** (100 °C, 5 h)

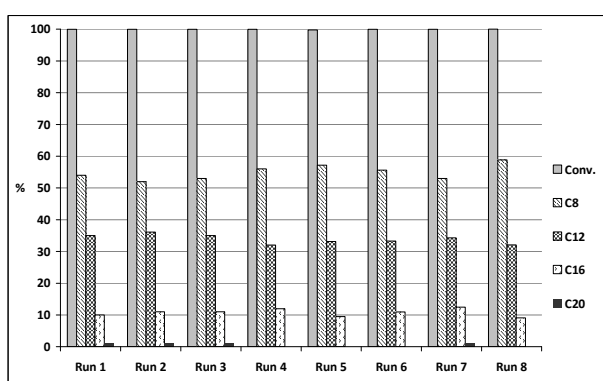


Figure 2: Oligomerization of isobutene in the presence of **SILP-2** (100 °C, 5 h)

**SILP-1** showed good selectivity toward  $C_{12}+C_{16}$  products, resulting in oligomeric mixtures with  $C_{12}$  as the main components (Fig. 1). On the contrary, in the presence of **SILP-2**, dimers were obtained in yields higher than 50 % and the ratio of  $C_{16}$  products was only around 10 % (Fig. 2).

The supported catalysts obtained with ILs with hydrogensulfate anion (**SILP-3** and **SILP-4**) showed lower activity than **SILP-1** or **SILP-2**, similarly to the non-immobilized versions of these catalysts (see Table 1). Besides, a great drop of activity was observed even in the second run when **SILP-3** or **SILP-4** was recycled (Fig. 3). That means that in spite of the excellent selectivity that can be achieved with these catalysts, their use is unfavourable from an economic point of view.

The effect of the change in the temperature on the outcome of oligomerization was explored with supported catalysts **SILP-1** (Fig. 4) and **SILP-2** (Fig. 5).

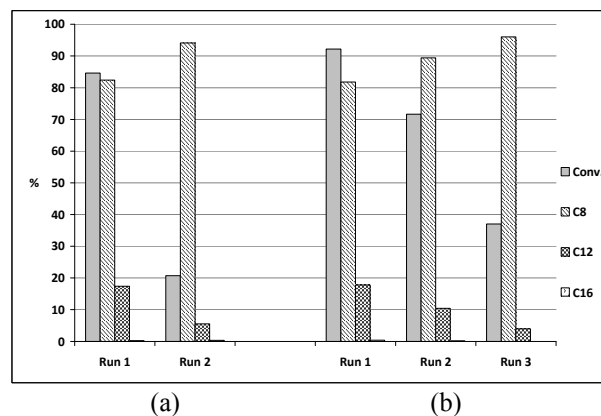


Figure 3: Oligomerization of isobutene in the presence of (a) **SILP-3** and (b) **SILP-4** (100 °C, 5 h)

As it was expected, an increase in the temperature led to an increase in the conversion. With **SILP-1**, total conversion of isobutene (in 5 h) was observed only at 100 °C or above, but in the presence of **SILP-2**, the conversion was higher than 90 % even at 60 °C. An increase in the temperature led to a decrease in the  $C_8$  selectivity of the reaction with both of the catalysts.

The best selectivity for  $C_8$  and  $C_{12}$  products can be reached by using **SILP-2** at 60 °C and **SILP-1** at 100 °C, respectively.

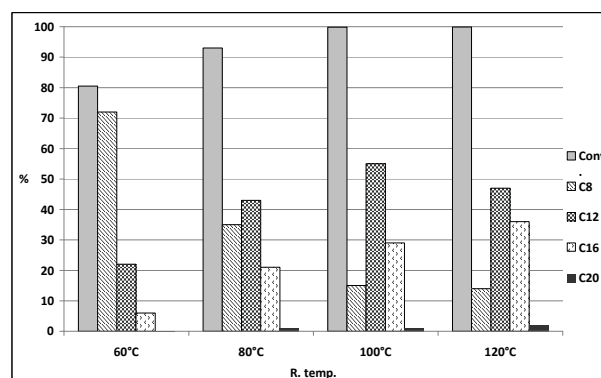


Figure 4: Oligomerization of isobutene in the presence of **SILP-1** at different temperatures

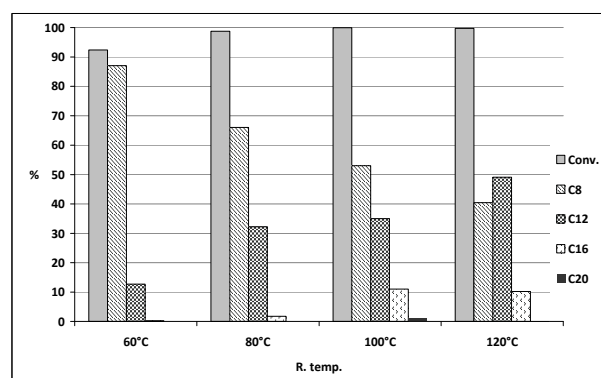


Figure 5: Oligomerization of isobutene in the presence of **SILP-2** at different temperatures

## Conclusions

Supported Brønsted acidic ionic liquids were proved to be efficient catalysts in isobutene oligomerization. The solid catalysts are easier to handle than the ionic liquids themselves, so separation and recovery of even small amounts of catalysts are simple.

Although immobilization of ionic liquids affects slightly the selectivity of oligomerization, the catalysts with the trifluoromethanesulfonate anion can efficiently be used and recycled. By the proper choice of the ionic liquid and reaction temperature, either C<sub>8</sub> or C<sub>12+</sub> products can be obtained with good selectivity.

These results clearly show that this type of supported catalysts can be applied flexibly to follow the changing demands of fuel production.

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