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# Oligomerisation of isobutene with silica supported ionic liquid catalysts†

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Brønsted acidic ionic liquids, supported on silica gel, have been used effectively in oligomerisation of isobutene. The supported catalysts could be used several times without loss of activity or change in selectivity. The ratio of the products could be influenced by the proper choice of the ionic liquid component of the catalyst and the reaction temperature.

# 1. Introduction

The oligomerisation 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 oligomerisation catalysts in either a homogeneous ( $H_2SO_4$ , organometallic complexes, *etc.*) or heterogeneous (mixed oxides, zeolites, clays, ion exchange resins *etc.*) phase.<sup>1</sup> Solid phosphoric acid catalysis has been applied industrially since the early 1930s for the production of gasoline through the oligomerisation reaction.<sup>2</sup>

The main challenges in the design of catalysts for this reaction are focused on reaching high conversion and high selectivity. Consequently, several solid acid catalysts of different types have been developed for the oligomerisation of lower alkenes, such as isobutene.<sup>3</sup> These include cation exchange resins,<sup>4-7</sup> sulfated zirconia<sup>8</sup> and titania,<sup>9</sup> SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>,<sup>10</sup> zeolites,<sup>11-18</sup> zeolites modified with Lewis acids,<sup>19</sup> zeolites doped with nickel,<sup>20-24</sup> silica supported heteropolyacids<sup>25-27</sup> and mixed metal oxides.<sup>28,29</sup>

Several Ni-based homogeneous catalysts containing phosphine ligands<sup>30,31</sup> have also been introduced. 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 oligomerisation<sup>32</sup> by cationic nickel complexes in chloroaluminate<sup>33–36</sup> or hexafluorophosphate<sup>37</sup> ionic liquids as solvents. In 1998, an industrial process based on chloroaluminate ionic liquids and nickel catalysts, known as the Difasol process, was commercialised.<sup>38</sup> Oligocyclisation of 1-hexene was performed in similar ionic liquids using Ti-complexes as catalysts.<sup>39</sup>

Seddon observed that chloromaluminate ionic liquids with Lewis acidic character catalyzed oligomerisation themselves, without the addition of transition metal complexes or salts.<sup>40</sup> These catalysts were proved to be very efficient for the oligomerisation of linear 1-olefins.<sup>41–43</sup> Similar ionic liquids prepared with anhydrous iron(III) chloride, instead of AlCl<sub>3</sub>, were shown to catalyze isobutene oligomerisation with high selectivity toward diisobutene and triisobutene.<sup>44</sup>

Selective dimerisation of  $\alpha$ -methystyrene, producing 4methyl-2,4-diphenyl-1-pentene in high yields, was carried out in 3-alkyl-1-methylimidazolium ionic liquids with acid additives.<sup>45</sup> Imidazolium ionic liquids with SO<sub>3</sub>H functionalized side chains were also found to be excellent and reusable catalysts in oligomerisation of various alkenes.<sup>46</sup> The selectivity of the reaction was greatly dependent on the length of the side chains. The use of an ionic liquid with imidazolium cations with smaller side chains led to higher selectivity for dimeric products.

Generally, ionic liquids (ILs) have gained increasing attention because they can be considered as environmentally friendly solvents with multiple applications in synthesis and catalysis.<sup>47</sup> 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.<sup>48</sup>

Based on these findings, we decided to explore the possibility of the use of silica-supported  $SO_3H$ -functionalised ILs as catalysts in the oligomerisation of isobutene. In this paper, we report on our results concerning the effects of the changes in the catalytic system and reaction conditions (the nature of the cation and the anion of the IL, the reaction time and temperature) on the outcome of the oligomerisation reaction.

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Scheme 1 Synthesis of ionic liquids IL-1 and IL-2 and supported ionic liquids SILP-1-SILP-7.

## 2. Experimental

### 2.1. Synthesis of the ionic liquids

The ionic liquids were synthesized by methods analogous to literature procedures (Scheme 1).<sup>49,50</sup>

**1-(4-Sulfobutyl)-3-alkylimidazolium betaine** (**4**: alkyl = methyl, **5**: alkyl = butyl).<sup>49</sup> 1,4-Butanesultone (**3**) (2.72 g, 20 mmol) was added slowly to 1-alkylimidazole **1** or **2** (20 mmol). The mixture was stirred at room temperature for 48 h. The product was washed with toluene ( $3 \times 10$  ml) and diethylether ( $2 \times 10$  ml) to remove any unreacted starting material. Evaporation of any volatiles *in vacuo* at 60 °C gave 3.62 g (83%) of 1-(4-sulfobutyl)-3-methylimidazolium betaine (**5**).

Spectroscopic data for 4: <sup>1</sup>H-NMR  $\delta$  (D<sub>2</sub>O) 8.64 (s, 1H); 7.40 (m, 1H); 7.34 (m, 1H); 4.15 (t, 7.3 Hz, 2H); 3.79 (s, 3H); 2.85 (t, 7.3 Hz, 2H); 1.93 (quint., 7.3 Hz, 2H); 1.65 (quint., 7.3 Hz, 2H).). IR (KBr): 1575 (C=C), 1177 (SO), 1042 (SO) cm<sup>-1</sup>. Analysis calculated for C<sub>8</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub>S (218.28): C, 44.02; H, 6.46; N, 12.83; found: C, 43.87; H, 6.61; N, 12.99. Water content: 0.68%.

Spectroscopic data for **5**: <sup>1</sup>H-NMR  $\delta$  (D<sub>2</sub>O) 8.72 (s, 1H); 7.40– 7.43 (m, 2H); 4.15 (t, 7.3 Hz, 2H); 4.10 (t, 7.3 Hz, 2H); 2.84 (t, 7.3 Hz, 2H); 1.93 (quint., 7.3 Hz, 2H); 1.76 (quint., 7.3 Hz, 2H); 1.64 (quint, 7.3 Hz, 2H); 1.21 (sext, 7.3 Hz, 2H); 0.82 (t, 7.3 Hz, 3H). IR (KBr): 1556 (C=C), 1183 (SO), 1041 (SO) cm<sup>-1</sup>. Analysis calculated for C<sub>11</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub>S (260.36): C, 50.75; H, 7.74; N, 10.76; found: C, 50.59; H, 7.81; N, 10.56. Water content: 0.53%.

**1-(4-Sulfobutyl)-3-alkylimidazolium** trifluoromethanesulfonates (IL-1: alkyl = methyl, IL-2: alkyl = butyl).<sup>49</sup> A mixture of the 1-(4-sulfobutyl)-3-alkylimidazolium betaine **4** or **5** (30 mmol) and trifluoromethanesulfonic acid (4.50 g, 30 mmol) was stirred at 150 °C for 5 h under argon. After being allowed to cool to room temperature, the ionic liquid was washed repeatedly with toluene ( $3 \times 20$  ml) and diethylether ( $3 \times 20$  ml) to remove non-ionic residues, and dried *in vacuo* at 110 °C to give 1-(4sulfobutyl)-3-methylimidazolium trifluoromethanesulfonate (IL-1) (10.82 g, 98%) or 1-(4-sulfobutyl)-3-butylimidazolium trifluoromethanesulfonate (**IL-2**) (11.93 g, 97%). Water content: 1.25% (**IL-1**), 1.92% (**IL-2**).

**1-(4-Sulfobutyl)-3-alkylimidazolium hydrogensulfates (IL-3:** alkyl = methyl, **IL-4**: alkyl = butyl).<sup>50</sup> A mixture of the 1-(4-sulfobutyl)-3-alkylimidazolium betaine **4** or **5** (15 mmol) and sulfuric acid (1.47 g, 15 mmol) was stirred at 150 °C for 5 h under argon. After being allowed to cool to room temperature, the ionic liquid was washed repeatedly with toluene ( $3 \times 10$  ml) and diethylether ( $3 \times 10$  ml) to remove non-ionic residues, and dried *in vacuo* at 110 °C to give 1-(4-sulfobutyl)-3-methylimidazolium hydrogensulfate (**IL-3**) (4.55 g, 96%) or 1-(4-sulfobutyl)-3-butylimidazolium hydrogensulfate (**IL-4**) (5.21 g, 97%). Water content: 2.05% (**IL-3**), 2.91% (**IL-4**).

#### 2.2. Preparations of supported ionic liquids (SILP-1-SILP-7)

Supported ionic liquids were prepared by a method analogous to a literature procedure.<sup>51</sup>

Silica gel (Kieselgel 60 (0.040–0.063 mm), Merck) was pretreated by heating for 5 h at 150, 250 or 450 °C (see Table 1). After that it was allowed to cool to room temperature in a desiccator and was stored under argon. A mixture of silica gel (10 g), the ionic liquid (**IL-1**, **IL-2**, **IL-3** or **IL-4**) (10 mmol) and 25 ml

 Table 1
 Supported ionic liquid catalysts used in oligomerisation of isobutene

Catalyst	Ionic liquid <sup>a</sup>	Temp. of silica pre-treatment [°C]
SILP-1	IL-1	150
SILP-2	IL-1	250
SILP-3	IL-1	450
SILP-4	IL-2	150
SILP-5	IL-2	250
SILP-6	IL-3	250
SILP-7	IL-4	250

<sup>*a*</sup> **IL-1**: 1-(4-sulfobutyl)-3-methylimidazolium trifluoromethanesulfonate, **IL-2**: 1-(4-sulfobutyl)-3-butylimidazolium trifluoromethanesulfonate, **IL-3**: 1-(4-sulfobutyl)-3-methylimidazolium hydrogensulfate, **IL-4**: 1-(4-sulfobutyl)-3-butylimidazolium hydrogensulfate. MeOH was stirred at room temperature for 24 h. MeOH was removed in vacuo and the catalyst was dried at 60 °C in vacuo for 1 h to produce the supported ionic liquids.

#### 2.3. Oligomerisation of isobutene

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-7). 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  $(3 \times 5 \text{ ml})$ , dried *in vacuo* and reused.

#### 2.4. Physical measurements

<sup>1</sup>H- spectra were recorded on a BRUKER AVANCE 400 spectrometer in  $D_2O$ . Elemental analyses were measured on a 1108 Carlo Erba apparatus. Water content was determined by a Mettler DL35 Karl Fischer Titrator. The specific surface area and pore size distribution in the micropore (0-2 nm), mesopore (2-50 nm), and the macropore (50-300 nm) diameter ranges were determined by nitrogen adsorption/desorption isotherms measured with a Micromeritics ASAP 2000-type instrument on samples previously out gassed overnight in a vacuum at the temperature of 150 °C. The surface areas of the samples ( $S_{\text{BET}}$ ) were determined by the BET method from the corresponding nitrogen adsorption isotherm.52 The meso- and macropore volume values were calculated from the nitrogen desorption isotherms using the BJH (Barret-Joyner-Halenda) theory.53 The pore volume of pores have 1.7-300 nm in diameter range were determined by mercury penetrance method using Carlo Erba Porozimetro'70 device.

#### 3. **Results and discussion**

Four Brønsted acidic ionic liquids (IL-1-IL-4) were prepared and were immobilised on silica gel by adsorption to give catalysts SILP-1—SILP-7 (Scheme 1, Table 1).

IL-1 and another ionic liquid with a longer side chain (1-(4sulfobutyl)-3-hexylimidazolium trifluoromethanesulfonate) had been proved to be efficient oligomerisation catalysts by Deng et al. before.<sup>46</sup> They found, that isobutene oligomerisation could be carried out with excellent selectivity toward  $C_8 + C_{12}$  products. Besides, the use of the ionic liquid with the longer side chain led to an increase in the ratio of  $C_{12}$  products, probably due to the higher solubility of C<sub>8</sub> in this ionic liquid.

Our main goal was to test the efficiency of the immobilised catalysts. Nevertheless, in order to compare the selectivity of immobilised and non-immobilised ionic liquids, oligomerisation was carried out first in IL-1 and IL-2 under our conditions (100 °C, 5 h). Almost total conversion was obtained in both cases and the ratio of  $C_{12}$  products was higher in IL-2 than in IL-1, as it had been expected (Table 2, entries 1,2).

All of the supported ionic liquid catalysts (SILP-1-SILP-7) were found to be active (Table 2, entries 3-9). Interestingly, immobilisation of the ionic liquids resulted in a change in the

Table 2	Oligomerisation	of isobutene	in the presence	of ionic liquid
based cat	alysts <sup>a</sup>			

Ratio of products [%] <sup>b</sup>								
C <sub>20</sub>	C <sub>16</sub>	C <sub>12</sub>	$C_8$	TOF [h <sup>-1</sup> ]	TON	Conv. [%] <sup>b</sup>	Catalyst	Entry
	1	24	75	1.13	5.6	98	IL-1	1
	7	60	33	1.14	5.7	99	IL-2	2
1	34	46	19	11.5	57.5	100	SILP-1	3
1	29	54	16	11.5	57.5	100	SILP-2	4
2	24	60	14	11.5	57.5	100	SILP-3	5
1	19	48	32	11.5	57.5	100	SILP-4	6
1	10	35	54	11.5	57.5	100	SILP-5	7
		17	83	9.8	48.9	85	SILP-6	8
		18	82	10.6	52.9	92	SILP-7	9
	10 	55 17 18 GC	54 83 82 wed by	9.8 10.6	57.5 48.9 52.9	100 85 92	SILP-5 SILP-6 SILP-7	/ 8 9 " Reac

selectivity of oligomerisation in some cases (compare entries 1, 3, 4, 5 and 2, 6, 7). (It should be mentioned that silica gel itself had no catalytic activity in this reaction.) The use of SILP-1, SILP-2 or SILP-3 (entries 3-5) led to the C<sub>12</sub> compounds as the main products, instead of  $C_8$ , obtained with good selectivity in IL-1 (entry 1). On the contrary, in the presence of SILP-5 (entry 7), an increase in C<sub>8</sub> selectivity was observed, compared to the results obtained with IL-2 (entry 2). The temperature of pre-treatment of the silica gel also seems to affect selectivity. A shift toward lighter oligomers was observed with catalysts pretreated at higher temperature ( $C_{16} \rightarrow C_{12}$  with supported IL-1, entries 3–5 and  $C_{12} \rightarrow C_8$  with supported IL-2, entries 6, 7).

The catalysts containing ionic liquids with hydrogensulfate anion showed somewhat lower activity, but excellent selectivity toward the dimers (entries 8, 9).

These results show that the selectivity of oligomerisation is affected by several factors, such as the substituent on the imidazolium cation, the nature of the anion and the pretreatment of the solid support.

BET surface area, pore volume and pore diameter of pretreated silica gels and SILP catalysts were measured (Table 3). BET surface area of SILP catalysts obtained from IL-1 are higher than those prepared from IL-2. A decrease in the BET surface was observed with an increase in the temperature of pre-treatment in both cases. The pore volume values showed a similar tendency.

The above mentioned changes of selectivity using the same ionic liquid (supported IL-1 or supported IL-2) but with different pre-treatment temperature may be partly due to the change in the BET surface area. At the same time, no detectable difference in the selectivity of oligomerisation was observed

Table 3 BET surface area, pore volume and pore diameter of the SILP catalysts

Catalyst	BET surface area [m <sup>2</sup> g <sup>-1</sup> ]	Pore volume [cm <sup>3</sup> g <sup>-1</sup> ]	Pore diameter [nm]
SILP-1	261	0.41	6.1
SILP-2	238	0.38	6.3
SILP-3	233	0.38	6.4
SILP-4	224	0.33	5.9
SILP-5	195	0.31	6.3
SILP-6	269	0.43	6.2
SILP-7	188	0.29	6.0

using **SILP-6** and **SILP-7** in spite of the difference in the BET surface area values between the two catalysts.

The possibility of reusing the SILP catalysts was also investigated. SILP-1 (Fig. 1), SILP-2 (Fig. 2), SILP-3 (Fig. 3), SILP-4 (Fig. 4) and SILP-5 (Fig. 5) were reused several times without loss of activity or a remarkable change in selectivity. At the same time, a considerable drop of activity was observed even in the second run when either of the catalysts with ILs with the hydrogensulfate anion (SILP-6 and SILP-7) were used (Fig. 6).



**Fig. 1** Oligomerisation of isobutene in the presence of **SILP-1** (100 °C, 5 h).



**Fig. 2** Oligomerisation of isobutene in the presence of **SILP-2** (100 °C, 5 h).



**Fig. 3** Oligomerisation of isobutene in the presence of **SILP-3** (100 °C, 5 h).



**Fig. 4** Oligometrisation of isobutene in the presence of **SILP-4** ( $100 \degree C$ , 5 h).



**Fig. 5** Oligometisation of isobutene in the presence of **SILP-5** (100  $^{\circ}$ C, 5 h).



Fig. 6 Oligometisation of isobutene in the presence of (a) SILP-6 and (b) SILP-7 (100  $^{\circ}$ C, 5 h).

Combined product mixtures of subsequent runs with catalysts **SILP-2** (eight runs) and **SILP-7** (six runs) were evaporated and the residues were examined by <sup>1</sup>H NMR and were identified as ionic liquids **IL-1** and **IL-4**, respectively. Total catalyst leaching of the eight runs was 2.0% of the original load in the case of **SILP-2** and 4.8% in the case of **SILP-7**. A higher rate of catalyst leaching might be one of the factors that led to inactivation of the catalysts with ILs with hydrogensulfate anion (**SILP-6** and **SILP-7**) upon reuse.

In the presence of ionic liquids immobilised on silica gel pretreated at 150 °C (**SILP-1** and **SILP-4**), the main products were the  $C_{12}$  oligomers, irrespective of the length of the alkyl chain

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of the imidazolium cation (Fig. 1 and 4). At the same time, considering the minor components, the use of **SILP-1** led to  $C_{16}$  oligomers in yields comparable to those of  $C_{12}$  products, while with **SILP-4**  $C_8$  compounds prevailed over  $C_{16}$  oligomers.

This difference was even more apparent when the ionic liquids were immobilised on silica gel pre-treated at 250 °C (SILP-2 and SILP-5). SILP-2 showed good selectivity toward  $C_{12} + C_{16}$  products, resulting in oligomeric mixtures with  $C_{12}$  as the main components (Fig. 2). On the contrary, in the presence of SILP-5, dimers were obtained in yields higher than 50% and the ratio of  $C_{16}$  products was only around 10% (Fig. 5).

Only a small difference in the composition of reaction mixtures, produced with **SILP-2** and **SILP-3** catalysts (obtained with silica gel pre-treatment at 250 °C and 450 °C, respectively), was observed.

Although immobilisation of ionic liquids slightly affects the selectivity of oligomerisation, these catalysts can efficiently be used and recycled in this reaction. By the proper choice of the catalyst, either  $C_8 + C_{12}$  or  $C_{12} + C_{16}$  products can be obtained with good selectivity.

The turnover numbers and frequencies of the SILP catalysts are ten times higher than those of the ILs (see Table 2). When using the SILP catalysts, a smaller amount of the relatively expensive ionic liquid was sufficient for the reaction. Due to the high viscosity of the ionic liquids, the mass transport into the ionic liquid phase can be rate limiting. By dispersing the ILs on support materials this drawback can be circumvented. Furthermore, the solid catalysts are easier to handle than the ionic liquids themselves, so separation and recovery of even small amounts of catalyst are simple.

The effect of the reaction conditions on the outcome of the oligomerisation was explored with supported catalysts prepared from **IL-1** and **IL-2**. The use of **SILP-2** (Fig. 7) resulted in total conversion of isobutene even after 1 h (TOF: 57.5 h<sup>-1</sup>). With **SILP-5** (Fig. 8), conversion was above 98% after 1 h (TOF: 28.1 h<sup>-1</sup>) and reached 100% after 5 h. With the increase in the reaction time, a slight change in selectivity toward heavier oligomers was observed in both cases.



Fig. 7 Oligomerisation of isobutene in the presence of SILP-2 (100 °C).

The effect of the change of the reaction temperature was also investigated using three of the supported ionic liquid catalysts (SILP-2 (Fig. 9), SILP-4 (Fig. 10) and SILP-5 (Fig. 11). The data depicted in the figures are average values of three subsequent runs at the given temperature). Total conversion was



Fig. 8 Oligomerisation of isobutene in the presence of SILP-5 (100  $^{\circ}$ C).



**Fig. 9** Oligomerisation of isobutene in the presence of **SILP-2** at different temperatures (average values of three subsequent runs at the given temperature, reaction time: 5 h).



**Fig. 10** Oligomerisation of isobutene in the presence of **SILP-4** at different temperatures (average values of three subsequent runs at the given temperature, reaction time: 5 h).

obtained with each catalyst at 100 °C, but with the exception of the use of **SILP-2**, conversions were above 90% even at 60 °C. At 60 °C, very good selectivity toward C<sub>8</sub> products was obtained in each case. With an increase in the temperature, an increase of the ratios of higher oligomers was observed. The best selectivity for C<sub>8</sub> and C<sub>12</sub> products can be reached by using **SILP-5** at 60 °C and **SILP-2** at 100 °C, respectively.



**Fig. 11** Oligomerisation of isobutene in the presence of **SILP-5** at different temperatures (average values of three subsequent runs at the given temperature, reaction time: 5 h).

# Conclusions

Supported Brønsted acidic ionic liquids were proved to be efficient catalysts in isobutene ologomerisaton. The use of the solid phase catalysts ensures easy separation and recycling. The catalysts comprising the trifluoromethanesulfonate anion could be reused several times without loss of activity.

The selectivity of oligomerisation is influenced by various factors, such as the length of the *N*-alkyl chain of the imidazolium cation, the nature of the anion, the pre-treatment of the support and the reaction temperature. Best  $C_8$  selectivity was achieved with imidazolium hydrogensulfate type catalysts (SILP-5 and SILP-6), but a great drop of activity was observed upon reuse.

Excellent C<sub>8</sub> selectivity (87%) was obtained with **SILP-5** at 60 °C, while the use of **SILP-2** resulted in good C<sub>12+</sub> selectivity (above 84%) at 100 °C.

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

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