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Support effect on the catalytic activity and selectivity of SILP catalysts in isobutene trimerization

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ABSTRACT

Oligomerization of isobutene has been carried out using silica supported Brønsted acidic ionic liquid catalysts. Silica supports with different particle size and textural properties have been used to prepare the catalysts. A close relationship between these properties and catalytic activity of the SILP material was observed. Silica supports with mesoporous structure could be converted to very active catalysts. On the other hand, the use of microporous supports resulted in the formation of catalysts with excellent C_{12} selectivity.

1. Introduction

The C_4 stream, including isobutene, is an important raw material in the petroleum and petrochemical industry. By the hydrogenation of dimerization products of low molecular weight olefins, an excellent gasoline blend stock with high octane number and low volatility can be produced. A further advantage of these blending components is the complete absence of sulphur and aromatic compounds [1]. At the same time, trimerization and following hydrogenation of light olefins has also attracted considerable attention recently, as a method for the production of blending components for jet fuel [2]. Trimerization of isobutene can be carried out using acid resins [3,4], WO_x/ZrO_2 [5], sulfated titania [6] or special zeolites [7–10].

Beside the solid acid catalysts, ionic liquids with Lewis acidic [11,12] or Brønsted acidic [13] character were shown to catalyze isobutene oligomerization efficiently. In most cases, selective dimerization was observed, but selectivity could be influenced slightly by the *N*-alkyl chain length of the imidazolium-type ionic liquid catalyst. The use of an ionic liquid with imidazolium cations with longer side chains led to higher selectivity for trimeric products [13].

Recently, we have shown that silica supported 1-(4-sulfobutyl)-3-alkylimidazolium ionic liquids are easy-to-handle and reusable catalysts for isobutene oligomerization [14]. It was shown that various factors, such as pretreatment of the solid support, the choice of cation and anion, as well as the reaction time and temperature, affected considerably the outcome of the reaction.

Although the SILP technique (supported ionic liquid phase) has been used for the heterogenization of a great variety of homogeneous catalysts lately, there is little information about the effect of the structure of the supports. In this paper, we report on the synthesis and investigation of morphological properties and oligomerization activity of catalysts obtained by the adsorption of 1-(4-sulfobutyl)-3-methylimidazolium trifluoromethanesulfonate on different silica supports.

2. Experimental

1-(4-Sulfobutyl)-3-methylimidazolium trifluoromethanesulfonate was synthesized as described before [14]. Silica supports were purchased from Merck (particle size 0.040–0.063 mm (**S-1**) and FLUKA (particle size: 0.2–0.5 mm (**S-2**), 1–3 mm (**S-3**) and 3–6 mm (**S-4**).

2.1. Preparation of supported ionic liquids (*SILP-1–SILP-7*)

The methods for preparation of supported ionic liquids are summarized in Table 1. The amount of adsorbed ionic liquid was determined by measuring the weight increase after heating the material to constant weight at 150 °C in vacuo.

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Table 1
Supported ionic liquid catalysts used in oligomerization of isobutene.

Catalyst	Silica support	Particle size of support [mm]	Preparation method	Amount of attached IL[a,b] [mmol IL/g silica]
SILP-1	**S-1**	0.040–0.063	A	0.86
SILP-2	**S-2**	0.2–0.5	A	0.99
SILP-3	**S-4**	3–6 (amorphous)	B	0.30
SILP-4	**S-4**	3–6 (amorphous)	C	0.32
SILP-5	**S-4**	3–6 (amorphous)	D	0.49
SILP-6	**S-4**	3–6 (amorphous)	E	0.42
SILP-7	**S-3**	1–3 (spherical)	E	0.35

[a] IL: ionic liquid.
[b] Based on the weight increase of the silica material.

Method A. Silica gel was pre-treated by heating for 5 h at 250 °C. Then 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 (10 mmol) and 25 ml 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 liquid.

Method B. Silica gel was pre-treated by heating for 5 h at 250 °C. Then it was allowed to cool to room temperature in a desiccator and was stored under argon. A mixture of silica gel (20 g) and the ionic liquid (10 mmol) was refluxed in 50 ml MeOH for 5 h. MeOH was removed in vacuo and the catalyst was dried at 60 °C in vacuo for 1 h to produce the supported ionic liquid.

Method C. Silica gel was pre-treated by heating for 5 h at 250 °C. Then it was allowed to cool to room temperature in a desiccator and was stored under argon. A mixture of silica gel (20 g) and the ionic liquid (10 mmol) was refluxed in 50 ml MeOH for 5 h. MeOH was removed in vacuo and the catalyst was dried at 150 °C in vacuo for 5 h to produce the supported ionic liquid.

Method D. Silica gel was pre-treated by heating for 5 h at 250 °C. Then it was allowed to cool to room temperature in a desiccator and was stored under argon. A mixture of silica gel (20 g) and the ionic liquid (10 mmol) was refluxed in 50 ml MeOH for 5 h. MeOH was removed in vacuo. Then 50 ml oligomer product mixture was added and the mixture was heated at 150 °C for 5 h. The catalyst was filtered, washed with pentane (3× 20 ml) and dried at 150 °C in vacuo for 5 h to produce the supported ionic liquid.

Method E. Silica gel was pre-treated by heating for 5 h at 250 °C. Then it was allowed to cool to room temperature in a desiccator and was stored under argon. A mixture of silica gel (20 g) and the ionic liquid (10 mmol) was refluxed in 50 ml MeOH for 5 h. MeOH was removed in vacuo. Then 50 ml toluene was added and the mixture was refluxed for 5 h. The catalyst was filtered, washed with pentane (3× 20 ml) and dried at 150 °C in vacuo for 5 h to produce the supported ionic liquid.

2.2. *Oligomerization 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 (1 g (**SILP-1**, **SILP-2**) or 2 g (**SILP-3**–**SILP-7**)). The autoclave was pressurized 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 analyzed by gas chromatography. The SILP catalysts were washed with pentane (3× 5 ml), dried in vacuo and reused.

2.3. *Analysis of product mixtures*

The conversion and selectivity of the reactions were determined by analyzing the composition of the reaction mixtures with a GC equipped with a FID detector and a 30 m HP-1 column. The assignment of the chromatographic peaks was carried out by GC–MS measurements (HP-5890A GC, HP 5971A MSD). The mass spectra were compared to literature data [4].

2.4. *Analysis of the supported catalysts*

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 vacuum at the temperature of 150 °C. The surface areas of the samples (S_{BET}) were determined by the BET method from the corresponding nitrogen adsorption isotherm. The meso and macropore (2–300 nm in diameter) volume values were calculated from the nitrogen desorption isotherms using the BJH (Barret–Joyner–Halenda) theory.

Acidity of the catalysts fresh and reused were determined by means of NH_3 pulse chemisorption at a steady temperature (30 °C) with the aid of a PulseChemisorb type 2705 instrument produced by Micromeritics Instrument Corp. The samples (200 mg) were heated for 4 h at 250 °C under an ultrapure He (Messer GmbH >99.9995%) gas flow, then cooled to 30 °C overnight and the controlled amount of ammonia gas (Messer GmbH >99.98%) was injected. The gas interacts with each active site until all sites have chemisorbed. Once the active sites have completely filled, the discretely injected ammonia gas volume elutes from the sample tube unchanged. The amount of chemisorbed NH_3 is the difference between the total amount of the injected gas and the amount of the gas eluted from the sample. The quantity (μmol/g catalyst sample) of each pulse of chemisorbed gas was determined by the volume of syringe injections.

3. Results and discussion

3.1. *Catalytic experiments*

Previously, we reported on the oligomerization of isobutene in the presence of supported ionic liquid catalysts prepared by the adsorption of ionic liquids on **S-1**. In quest of a suitable catalyst to scale up the process, silica supports of larger particle size (**S-2**–**S-4**) were impregnated with 1-(4-sulfobutyl)-3-methylimidazolium trifluoromethanesulfonate. The efficiency of the new catalysts was tested in the oligomerization of isobutene.

SILP-1 [14] and **SILP-2** catalysts, obtained by impregnation of silica supports with 0.040–0.063 mm and 0.2–0.5 mm particle size, respectively, showed similar performance. They were used several times without loss of activity (Fig. 1). Total conversion was obtained in each case. The main products were the C_{12} isomers obtained with 49–59% and 51–58% selectivity with **SILP-1** and **SILP-2**, respectively. Slightly higher activity of **SILP-2** can be demonstrated by