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Oligomerization of Light Olefins with SILP Catalysts

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Oligomerization reaction of light olefins serves as a useful tool to convert light olefins to products with higher boiling point range that can be used as gasoline, jet fuel or diesel components after hydrogenation. In the past few years, supported ionic liquids have emerged as useful catalysts in many organic reactions. In the present study, the application of a silica-supported Brønsted acidic ionic liquid in the oligomerization of 1-butene and 1-pentene is investigated. The possibility of the conversion of a low boiling point range fraction of polypropylene cracking product to jet fuel or diesel components is also taken into account.

1. Introduction

Due to the growing demand for engine fuels and the tightening rules for their quality requirements, alternative sources should be found (e.g. application of biofuels (Mohsin et al., 2017)) and new routes should be developed to increase efficiency of the production of fuel components. Thermal (Lopez et al., 2017) and catalytic (Miandad et al., 2016) cracking processes of waste plastics result in the formation of mixtures of saturated and unsaturated hydrocarbons of different carbon number. After hydrogenation of the unsaturated compounds, the C_6-C_{10} fraction can be used for the blending of gasoline, while the C_{11}+ components can be utilized as jet or diesel fuel (Tóth et al., 2016). Hydrocarbons with carbon number lower then C_5 make a low value fraction that needs upgrading. Oligomerization of the olefin components of this fraction is a suitable method to produce higher molecular weight isoolefins that can be converted to isoparaffins via hydrogenation (Nicholas, 2017). These products can be used either as gasoline or jet fuel blending components, depending on their molecular weight (Kriván et al., 2016). Oligomerization can also be a suitable method for the conversion of gasoline fractions to jet or diesel fuel, if there is a change in market demands.

Oligomerization of light olefins can be carried out in the presence of different types of catalysts. Both Brønsted and Lewis acids can be used either in heterogeneous or homogeneous phase (Olah and Molnár, 2003). Both liquid (Raseev, 2003) and solid phosphoric acid was used industrially for the production of gasoline (Prinsloo, 2006), but due to environmental problems (Whitton, 1988), alternative solid acid catalysts, e.g. modified zeolites have been developed (Yoon et al., 2008). Ion-exchange resins were also tested in laboratory experiments, but these catalysts were sensitive to high temperature and their thermal stability was not satisfactory (Kriván et al., 2015).

Nowadays ionic liquids, often considered to be ‘green materials’, were used successfully as solvents and catalysts in many organic reactions including oligomerization of olefins (Fehér et al., 2014). Properties of ionic liquids, such as acidity, solubility, viscosity, etc., can easily be modified by the change in the structure of the anions and the cations (Ratti, 2014).

Oligomerization of C_2 - C_8 alkenes were investigated in the presence of chloroaluminate-type Lewis acidic ionic liquids. While unsaturated hydrocarbons were formed from propylene, significant amounts of C_4 saturated products were obtained from ethylene in the presence of a piridinium ionic liquid. In the first case, a long reaction time resulted in the accumulation of high molecular weight products consisting of saturated and unsaturated

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hydrocarbons, as well as chlorinated unsaturated hydrocarbons. (Goledzinowski and Birss, 1993). Oligoalkyl-substituted naphthene products were obtained with the same catalyst starting from 1-hexene (Azizov et al., 2010), 1-octene or 1-decene (Ibragimova et al., 2007). Ethene and propene were oligomerized to dimers, trimers and tetramers, while higher linear 1-olefins (up to C_8) gave dimers almost exclusively in the presence of [1-butyl-3-methylimidazolium][tetrachloroaluminate] (Stenzel et al., 2003). The total yield of oligomers decreased with increasing chain length of the monomer. 75 % selectivity for diisobutene plus triisobutene could be achieved in the oligomerization of isobutene with chloroferrate ionic liquids (Yang et al., 2009). However, in case of Lewis acidic ionic liquids, traces of water may lead to the release of hydrogen chloride. From this point of view, the more stable Brønsted acidic ionic liquids can be more attractive alternatives. A good selectivity towards C_8 and C_{12} products was obtained in the presence of SO_3H-functionalized ionic liquids starting from isobutene (Gu et al., 2003). On the contrary, isomerization was the main reaction of 1-butene and 1-hexene using the same catalyst. High viscosity of Brønsted acidic ionic liquids makes their handling often cumbersome. If they are immobilized on a solid material, e.g. silica, supported ionic liquid phases (SILP) are prepared (Riisager et al., 2006). SILPs often show higher catalytic activity due to the larger contact surface between the ionic liquid and the substrate and being solids, their manipulation becomes easier (Skoda-Földes, 2014).

During our previous work, supported Brønsted acidic ionic liquids were shown to be highly efficient catalysts in the oligomerization of isobutene (Fehér et al., 2012). Based on these findings, the application of a SILP catalyst in the oligomerization of 1-butene, 1-pentene and a gasoline fraction obtained from the cracking of polypropylene waste is reported in this study.

2. Experimental procedures

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 SPB-1 column. The assignment of the chromatographic peaks was carried out by GC-MS measurements (Shimadzu Q2010 Plus gas chromatograph, Shimadzu QP2010 SE mass spectrometer).

The specific surface area and pore size distribution of the fresh and catalysts in the micropore (0 – 2 nm), mesopore (2 – 50 nm), and the macropore (50 – 100 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 - 100 micrometers in diameter) volume values were calculated from the nitrogen desorption isotherms using the BJH (Barret–Joyner–Halenda) theory.

2.1 Preparation of the catalyst

Silica gel was pre-treated by heating for 5 h at 250 ºC in vacuo. Then it was allowed to cool to room temperature under argon. A mixture of silica gel (10 g), the ionic liquid (1-(4-sulfobutyl)-3-methylimidazolium trifluoromethanesulfonate) (10 mmol) and 25 mL MeOH was stirred at room temperature for 24 h (Fehér et al., 2012). MeOH was removed in vacuo and the catalyst was dried at 100 ºC in vacuo for 5 h to produce the supported ionic liquid. The IL content of the catalyst was 0.86 mmol/ g silica, based on the weight increase of the silica material.

2.2 Oligomerization experiments

The reactions were carried out in an autoclave under argon. The autoclave was cooled to -15 ºC and the olefins or a gasoline fraction of polypropylene cracking product (total volume of 6 mL) was charged into the reactor, which contained 1 g of the catalyst. The autoclave was pressurized with argon (50 bar, room temperature). The mixture was stirred at 150 ºC for 5 - 15 h. The autoclave was cooled to -15 ºC, the organic phase was separated and analyzed by gas chromatography. The SILP catalyst was washed with pentane (3 x 5 mL), dried in vacuo and reused.

3. Results and discussion

Oligomerization of isobutene in the presence of mesoporous (Fehér et al., 2012) and microporous (Fehér et al., 2013) supported ionic liquid catalysts, prepared by the adsorption of ionic liquids on silica, was reported previously. Based on the success of these experiments, oligomerization reactions of 1-butene and 1-pentene were carried out first under similar conditions (Table 1, entries 1 - 3), but due to the much lower reactivity of n-olefins, only poor conversions could be achieved. It should be mentioned that the trimers were the main products in the reaction of 1-butene even under these conditions.

At higher temperature (entries 4, 5) the conversions improved, but were still much lower than that observed for isobutene under the original conditions (entry 1). Moreover, dimers were the main products in both cases. The application of a longer reaction time led to high conversion and selectivity was pushed towards products with higher boiling point (entries 6, 7). The analysis of reaction mixtures obtained at 150 °C revealed the isomerization of the starting material in case of both of the substrates. The C_4 fraction of the reaction mixture of oligomerization of 1-butene (entry 4) contained only 2-butenes, while the C_5 components of the reaction mixture of 1-pentene corresponded to 1-pentene (5 %) and 2-pentenes (95 %).

Table 1: Oligomerization of olefins in the presence of the SILP catalyst

entry	substrate	r. temp. (°C)	r. time (h)	conv. (%)	selectivity (%)			
					dimer	trimer	tetramer	pentamer
1	isobutene	100	5	100	14	51	33	2
2	1-butene	100	5	29	47	53	0	0
3	1-pentene	100	5	10	93	7	0	0
4	1-butene	150	5	87	46	33	16	5
5	1-pentene	150	5	77	68	23	9	0
6	1-butene	150	10	98	18	31	31	13[a]
7	1-pentene	150	10	94	27	29	22	11[b]

[a] Higher molecular weight products were also produced in 7 %. [b] Higher molecular weight products were also produced in 11 %.

Recyclability of the catalyst was tested in reactions carried out at 150 °C. Although in five hour long reactions (Figures 1a, 1b) better results were obtained in the second runs that shows an activation of the catalyst in the first oligomerization experiment, a considerable loss of activity was observed in subsequent runs. This is reflected not only in the decrease in the conversion but also in the shift of the selectivity towards lighter products. A constant and even more pronounced deactivation could be detected when a longer reaction time was used (Figures 1c, 1d). Loss of activity was a bit slower in case of 1-butene in both 5 h long (Figures 1a, 1b) and 10 h long reactions (Figures 1c, 1d).

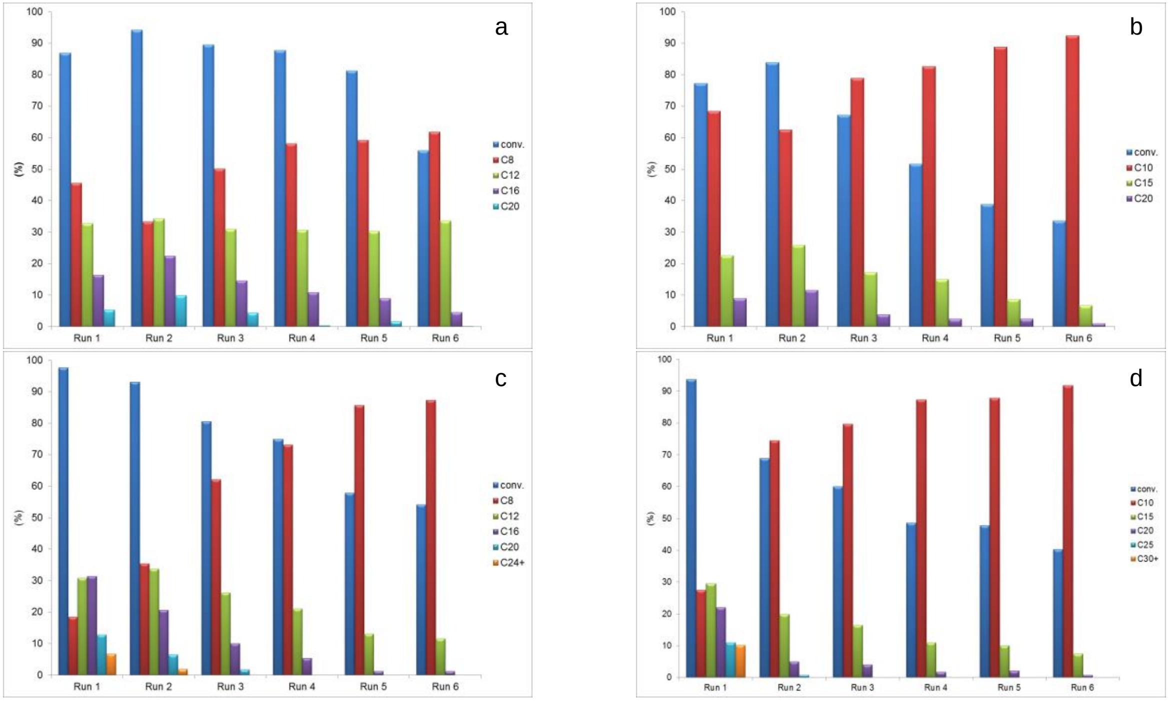

Figure 1: Catalyst recycling in the oligomerization of (a) 1-butene (150 °C 5 h) (b) 1-pentene (150 °C 5 h) (c) 1-butene (150 °C, 10 h) (d) 1-pentene (150 °C, 10 h)

The spent catalyst of the oligomerization experiments of 1-pentene (150 °C, 10 h) was tested in the reaction of isobutene, and it was found that the catalyst was still active, although the higher ratio of dimers showed some loss of the original activity.

Table 2: Oligomerization of isobutene with a fresh and a spent catalyst (100 °C, 5 h)

	conv (%)	selectivity (%)			
		dimer	trimer	tetramer	pentamer
fresh catalyst	100	7	72	18	3
spent catalyst[a]	99	36	43	20	1

[a] after 6 runs in the oligomerization of 1-pentene (150 °C, 10 h)

Based on this finding, oligomerization experiments were carried out by the alternate use of 1-pentene and isobutene as substrates. Even number runs were carried out with 1-pentene (Figure 2a) and odd number runs with isobutene (Figure 2b). Upon comparing the results depicted in Figures 1d and 2a, it can be concluded that the oligomerization of isobutene carried out with the spent catalyst resulted in a reactivation and slowed down the loss of activity in the oligomerization of 1-pentene. The analysis of reaction mixtures obtained with isobutene did not show a considerable change in the activity of the catalyst towards this substrate (Figure 2b).

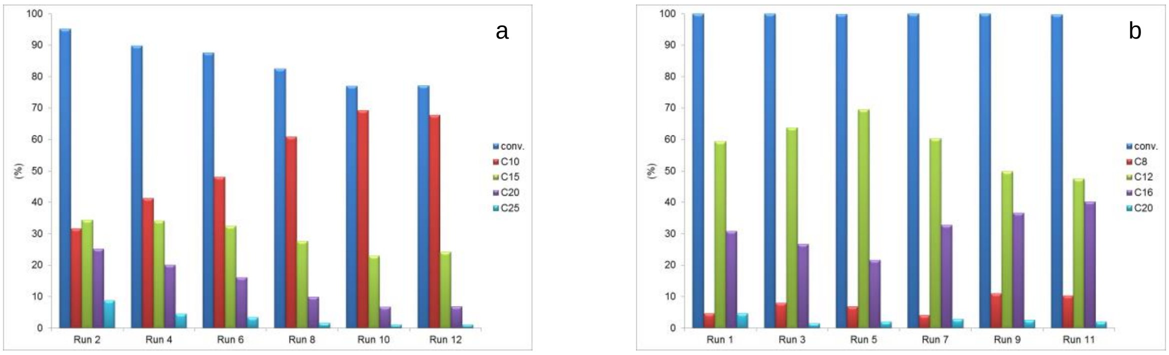

Figure 2: Results of oligomerization of (a) 1-pentene (150 °C, 10 h, odd number runs were carried out with isobutene) (b) isobutene (100 °C, 5 h, even number runs were carried out with 1-pentene)

The values of the specific surface area (S_{BET}) and pore volumes of the silica support and the fresh and spent SILP catalysts (Table 3) were determined from the experimental data of their nitrogen adsorption/desorption isotherms. Assuming that the pores have cylindrical shape, from the values of incremental pore volumes and the average pore diameter, the cumulative surface area (S_{BJH}) can be estimated on the basis of BJH phenomena. According to the results all of the material contained only mesopores. As it is expected, there was a loss of BET surface when the support was impregnated with the ionic liquid (entry 2). In case of the spent catalysts there was a further decrease in these values and the mean diameter of the pores became also smaller (Table 3 entries 3, 4). This shows that some of the products might get stuck in the pores and caused a decrease in the contact surface between the ionic liquid film and the fresh substrate. The application of isobutene as an alternate substrate between two oligomerization experiments with 1-pentene seemed to decrease this effect (entry 5) that may result in higher catalytic activity even towards the less reactive 1-pentene.

Table 3: Surface properties of the silica support and the fresh and spent SILP catalysts

entry		S_{BET} (m^2/g)	S_{BJH} 1.7nm-100nm	S_{micro} (m^2/g)	Pore volume $S_{1.7\text{-}100\ nm}$ (cm^3/g)	D_{mean} (nm)
1	silica support	480	582	0	0.74	6.1
2	SILP catalyst (fresh)	238	325	0	0.38	6.3
3	SILP catalyst (spent)[a]	172	262	0	0.33	5.1
4	SILP catalyst (spent)[b]	171	270	0	0.32	4.8
5	SILP catalyst (spent)[c]	182	278	0	0.34	4.9

[a] Obtained in the oligomerization of 1-butene after 6 runs. [b] Obtained in the oligomerization of 1-pentene after 6 runs. [c] Obtained in the oligomerization by alternate use of 1-pentene and isobutene.

Due to the growing demand on jet and diesel fuel, it might be necessary to increase their production at the expense of gasoline if the market requires so. As an example, olefin rich gasoline fractions obtained by the cracking of polypropylene waste can be converted into components with higher carbon number by oligomerization. Accordingly, an oligomerization experiment was carried out using such a mixture as the starting material. It contained unsaturated compounds in 82 %, with 2-methyl-1-alkenes (2,4-dimethyl-hept-1-ene and

2-methyl-oct-1-ene) as the main components (in a ratio of 30 %). In the first run (Figure 3), almost all of the unsaturated components underwent oligomerization and a high selectivity towards diesel boiling point range products (bp > 174 °C) was observed. Although the change in the composition of the product mixture showed some loss of activity upon catalyst recycling, a stable performance was observed after the 7th run with a ratio around 50 % for jet fuel range products (135 °C < bp < 270 °C) and around 40 % for diesel boiling point range products (bp > 174 °C).

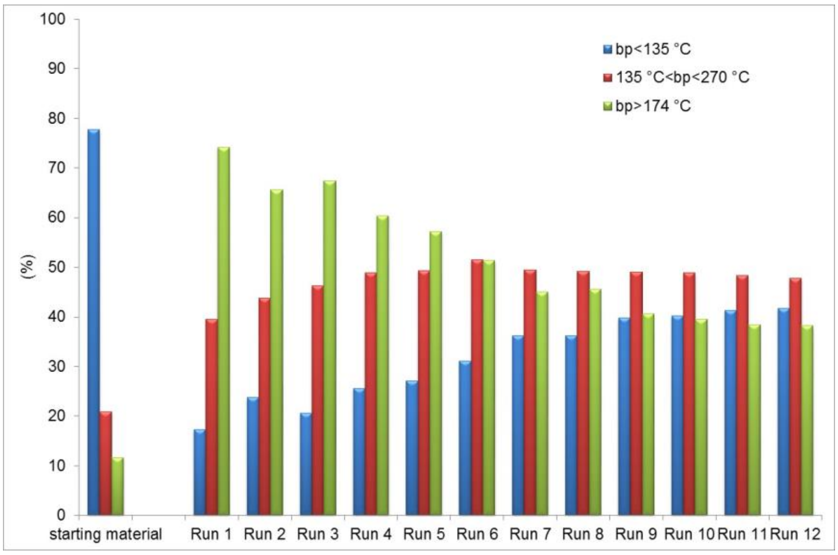

Figure 3: Oligomerization reaction using the cracking product of polypropylene waste as the starting material (150 °C, 15 h)

4. Conclusions

The continuously growing consumption of plastics results in a great increase in the formation of plastic wastes. Among possible methods for the recycling of waste polyolefines, their application as starting material for fuel production is an attractive alternative. The low boiling point fraction of the cracking process of polyolefines can be upgraded by subsequent oligomerization and hydrogenation to obtain fuel blending components. These fractions, especially obtained from polyethylene, usually contain 1-alkenes as the main components, so the possibility of the use of a SILP catalyst, obtained by the physisorption of 1-(4-sulfobutyl)-3-methylimidazolium trifluoromethanesulfonate on a silica support was investigated in the oligomerization of terminal olefins first. Its application resulted in a lower conversion in the oligomerization of 1-butene and 1-pentene than that of isobutene. The use of a higher temperature was required in these reactions in order to obtain oligomerization products in good yield. Unfortunately, the activity of the catalyst decreased during the reuse. The loss of activity could be reduced by an alternate application of isobutene and 1-pentene as substrate.

Moreover, it was shown that the catalyst could be used efficiently to enrich a low boiling point range fraction of polypropylene cracking product in components with higher molecular weight. In this reaction, that may make it possible to alter production according to the changes in market demands, the catalyst showed a stable performance after the 7th run.

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