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Research Note

Trimerization of isobutene over a zeolite beta catalyst

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Abstract

Oligomerization of isobutene has been investigated using several zeolite catalysts to produce triisobutenes that are useful as chemical feedstocks. Stable isobutene conversion and high selectivity for trimers are attained over a beta zeolite with high concentration of Lewis acid sites. Isobutene is quantitatively oligomerized over a beta zeolite with selectivity for trimers $>50\%$ up to 100 h at a high isobutene WHSV of 10 h^{-1}. Moreover, a deactivated catalyst can be easily regenerated by calcining in flowing air. Zeolite beta's high stability, quantitative conversion, high selectivity, and facile regeneration make it an attractive potential catalyst for isobutene trimerization.

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Keywords: Beta zeolite; Isobutene; Trimerization; Lewis acid site

1. Introduction

In the petrochemical industry, a C_4 stream including butenes is an important raw material that can be upgraded. Recently, trimerization of light olefins has attracted considerable attention as a method for the production of fuel additives [1] and separation of isoolefins from other olefins [2]. Triisobutenes, for example, are considered to be highly useful for the synthesis of specialty chemicals, including neo-acids [2]. After hydrogenation, triisobutenes can be used as premium solvents (odorless solvents without aromatics) and additives for kerosene and jet fuel [3].

The blending of MTBE (methyl-*tert*-butyl ether) in gasoline has been banned in California [4] since 2004 due to contamination caused by the dissolution of MTBE in underground water. Consequently, a surplus of isobutene is expected, because this is one of the main raw materials for the synthesis of MTBE. Thus, trimerization is a very promising reaction not only for the utilization and separation of isobutene, but also for the production of isobutene trimers. Nevertheless, the trimerization of isobutene has not received adequate attention compared with the dimerization of olefins [5–10]. Several solid acid catalysts, including a sulfated titania [1,11,12], a cation exchange resin [2,13], a heteropoly acid [14], and a zirconia [15], have been suggested for the trimerization reaction.

To the best of our knowledge, there has been no report on the use of zeolites in the isobutene trimerization reaction even though they are well-known acid catalysts. Consequently, we have undertaken the present work with the aim of studying the isobutene trimerization reaction over potential zeolite catalysts to produce isobutene trimers.

2. Experimental

Trimerization of isobutene (99.0%, 1-butene $<0.3\%$, *n*-butane $<0.3\%$, Rigas Korea) was carried out in the liquid phase using a fixed-bed continuous-flow reactor (316 stainless steel, 3/8 inch o.d., 0.035 inch thick) equipped with a backpressure regulator (Tescom). The reaction temperature and pressure used for the reaction were 40–100 °C and 15 bar, respectively. The reactor temperature was controlled by a water jacket in which water at constant temperature flowed continuously with the help of a circulator. The reactant (isobutene) and a diluent (*n*-butane, 99.5%, Rigas Korea), without further purification, were fed continuously using liquid mass flow controllers (Bronkhorst HI-TEC). The space velocity of isobutene, WHSV (weight-

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hourly space velocity, g of isobutene fed per g of catalyst per hour) was varied between 10 and 20 h^{-1} by controlling the flow rates of isobutene and *n*-butane. The feeding rates of the isobutene and the diluent were the same (50 wt%/50 wt%). Unless otherwise specified, the reaction temperature, pressure, and space velocity (isobutene WHSV) were 70 °C, 15 bar, and 10 h^{-1}, respectively.

The conversion of isobutene was determined by periodically analyzing the composition of the off-gas stream after condensing liquid products, using a gas chromatograph equipped with a thermal conductivity detector and an alumina column (J&W Scientific, 30 m × 0.53 mm). The conversion was cross-checked by measuring the total flow rates of isobutene and the diluent with a mass flowmeter (Brooks, 5850 E). Liquid products were analyzed by a gas chromatograph with a flame ionization detector containing a PONA column (HP, 50 m × 0.20 mm). The detailed analysis conditions were reported previously [13]. In this study, the selectivity of dimers, trimers, and tetramers is described in wt%.

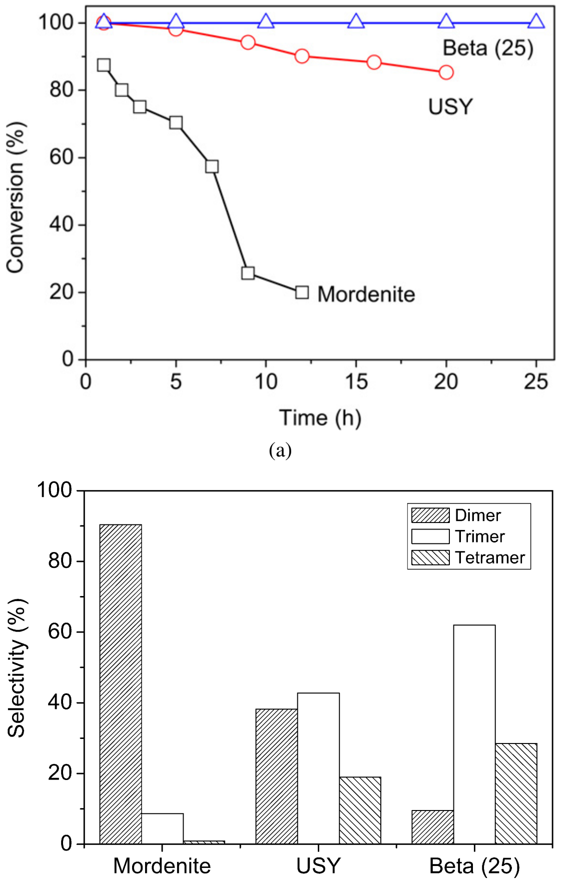
Several large-pore (12 membered-ring) commercial zeolites were used in this study without further purification. Three types of beta zeolites were obtained from Zeolyst; these were denoted as beta (*n*) for the sample, with *n* representing the SiO_2/Al_2O_3 ratio. Beta (18) (CP 814N, $SiO_2/Al_2O_3 = 18$, surface area = 680 m^2/g), beta (25) (CP 814E, $SiO_2/Al_2O_3 = 25$, surface area = 680 m^2/g), and beta (38) (CP 814C, $SiO_2/Al_2O_3 = 38$, surface area = 710 m^2/g) were calcined at 550 °C for 8 h in a muffle furnace to convert the ammonium form into a proton form. USY (Zeolyst-CBV 760, proton form, $SiO_2/Al_2O_3 = 60$, surface area = 720 m^2/g) and mordenite (Zeocat-FM-8H, proton form, $SiO_2/Al_2O_3 = 25$, surface area = 500 m^2/g) were purchased from Zeolyst and Zeocat, respectively. Before the start of the reaction, the zeolites in the reactor were dehydrated at 300 °C for 10 h under the flow of nitrogen.

FTIR spectra of adsorbed d_3-acetonitrile (Aldrich, 99.8 at% D) were obtained at room temperature using Nicolet FTIR spectrometer (MAGNA-IR 560). For this purpose, the zeolites were pelletized to a wafer and evacuated for 6 h at 300 °C under vacuum ($\sim 10^{-5}$ Torr). After the adsorption of d_3-acetonitrile at room temperature, the physisorbed d_3-acetonitrile was evacuated for 1 h.

3. Results and discussion

As depicted in Fig. 1a, the isobutene oligomerization over the three zeolites USY, mordenite, and beta (25) shows significant differences in the conversion of isobutene with time on stream. The conversion decreased sharply with reaction time over the mordenite and USY as has been observed in the dimerization of isobutene [16]. However, the beta (25) zeolite showed very stable catalytic performance up to 25 h. Moreover, the selectivity for trimers over the beta (25) was very high compared with that over the mordenite and USY up to 12 h (Fig. 1b).

The oligomerizations were conducted in wide reaction conditions, such as reaction temperature and space velocity (isobutene WHSV), over the beta (25) zeolite. The conversion and selectivity for trimers increase steadily with increasing temperature or decreasing isobutene WHSV (data not shown), as has been observed in the oligomerization over cation-exchange resins [13]. In contrast, dimer selectivity decreases with increasing reaction temperature or with decreasing isobutene WHSV. The conversion is nearly complete when the isobutene WHSV is up to 10 h^{-1} at 70 °C or higher temperature.



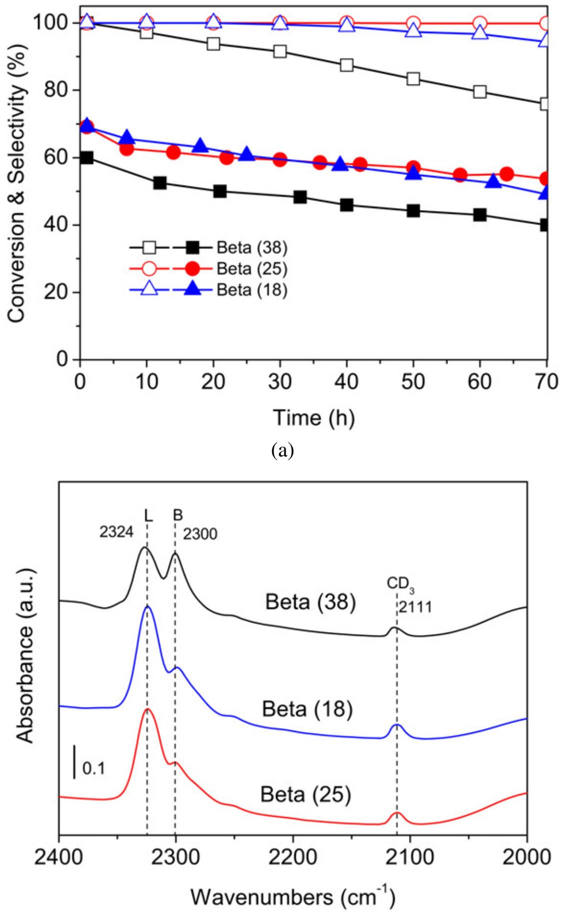
(a)

(b)

Fig. 1. Conversion and selectivity with type of zeolites and time on stream: (a) conversion with time on stream over various zeolites; (b) selectivities for oligomers with zeolites at 12 h of time on stream.

Three beta zeolites were compared in isobutene oligomerization under selected conditions (70 °C, 15 bar, isobutene WHSV 10 h^{-1}). As shown in Fig. 2a, only beta (25) shows stable performance of quantitative conversion and high selectivity for trimers up to 70 h. The beta (38) indicates very rapid deactivation from the beginning of the reaction, whereas the beta (18) deactivates gradually from about 20 h. The selectivity for trimers is also in the order beta (38) $<$ beta (18) $\leqslant$ beta (25) (Fig. 2a), because the selectivity for trimers is low when the isobutene conversion is low (see above and [13]).

It is hard to explain why the beta (25) shows the best performance among the three beta zeolites; the results cannot be explained by either the number of acid sites or the strength of acidity. The Lewis and Brønsted acid sites can be analyzed using the FTIR spectrum of adsorbed d_3-acetonitrile [9,17,18]. As shown in Fig. 2b, the relative concentration of Lewis acid sites (compared with Brønsted acid sites) increases in the order of beta (38) $<$ beta (18) $<$ beta (25), and this trend coincides



(a)

(b)

Fig. 2. Effect of type of beta zeolites on the isobutene trimerization and FTIR spectra (adsorbed d_3-acetonitrile): (a) conversion and selectivity for trimers with reaction time over three beta zeolites. Empty and filled symbols represent isobutene conversion and selectivity for trimers, respectively; (b) FTIR spectra of adsorbed d_3-acetonitrile on three beta zeolites.

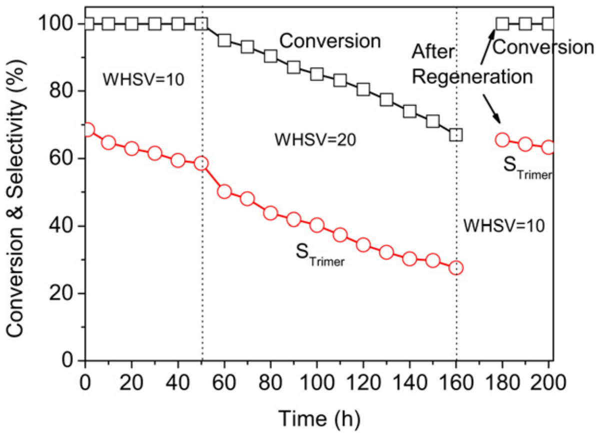


Fig. 3. Deactivation and regeneration of a beta (25) zeolite in the trimerization of isobutene. The space velocity is 10 or 20 h^{-1} (isobutene WHSV). The aged zeolite was regenerated by calcining at 550 °C for 6 h under the air flow.

with the catalytic performance, including conversion over the beta zeolites. Thus, we suggest that Lewis acid sites are beneficial for isobutene trimerization (especially for stable conversion), although more detailed study is needed to understand the trimerization over a beta zeolite. A study of the beneficial contribution of Lewis acid sites in the trimerization over Fe/USY or steamed Y zeolite is underway and will be reported elsewhere. Briefly, the stability and selectivity for trimers over a Y zeolite increase noticeably with increasing Lewis sites/Brønsted sites ratio. Recently, Mantilla et al. also demonstrated that the higher Lewis site-to-Brønsted site ratio corresponds to higher catalyst stability over a sulfated TiO_2 [1].

The long-term stability of isobutene oligomerization over the zeolite beta (25) was evaluated. Isobutene can be quantitatively converted to oligomers up to 100 h with the selectivity for trimers >50% (data not shown). This stable performance is remarkable considering the fact that the isobutene WHSV was very high compared with the relatively low isobutene WHSV of 0.5–1.0 over a sulfated titania [1,11] and about 1.0–3.0 h^{-1} over an Amberlyst-15 catalyst [2]. It has been generally accepted that the catalytic performance over a catalyst degrades rapidly at a high isobutene WHSV [11,13]. The production capacity of isobutene trimers is quite high. Our results suggest that this catalyst could generate roughly 500 tons of isobutene trimers per ton of catalyst, based on an isobutene WHSV of 10 h^{-1}, an operation time of 100 h, and a selectivity for trimers of 50%. If the catalyst could be regenerated 10 times (see below), then the production capacity could be 5000 tons per ton of catalyst, implying the potential application and subsequent commercial viability of the reaction/catalyst.

Compared with cation-exchange resins, zeolite catalysts have several advantages, including facile regeneration by air calcination and stability against the temperature fluctuation, because the stable operation temperature of a zeolite is much higher than that of resins (within 110–120 °C). The beta (25) zeolite aged (conversion ∼70%) by the operation for 50 h at an isobutene WHSV of 10 h^{-1} and for an additional 110 h at a high isobutene WHSV of 20 h^{-1} readily recovers the catalytic performance (Fig. 3) after a regeneration process (by calcination under air flow for 6 h at 550 °C), thus establishing the recyclability of the beta (25) zeolite in the production of isobutene trimers.

The present study reveals that a beta zeolite with high concentration of Lewis acid sites is one of the potential catalysts for the isobutene trimerization exhibiting high stability, quantitative conversion, high selectivity, and facile regeneration.

4. Conclusion

To find efficient catalysts for the production of triisobutenes, oligomerization of isobutene was investigated over several zeolite catalysts. Compared with USY and mordenite, beta (25) showed very stable isobutene conversion with high selectivity for trimers. The conversion of isobutene was nearly quantitative, and the selectivity for trimers was >50 wt% over the beta (25) zeolite even at a high isobutene WHSV of 10 h^{-1}, indicating that zeolite beta (25) has strong commercial potential for this reaction. The remarkable performance of zeolite beta (25) is presumably associated with the high Lewis site-to-Brønsted site ratio. Further work is underway to clarify the long-term stability of the catalyst.

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