Isobutene Trimerization over $FeCl_3$-modified HY Zeolites: Effect of Lewis Acid Sites

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Oligomerization of isobutene has been investigated using $FeCl_3$-modified HY zeolite catalysts in order to produce triisobutenes or remove/separate isobutene from C_4 streams. Stable isobutene conversion and high selectivity for trimers are attained over the modified zeolite with high concentration of Lewis acid sites, suggesting that a potential trimerization catalyst can be obtained easily by loading a Lewis acid into an acidic zeolite catalyst.

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.[2] Triisobutenes, after hydrogenation, can be used as premium solvents and additives for kerosene and jet fuel.[3]

A surplus of isobutene is expected because 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. Hence, the 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 in comparison with the dimerization of olefins.[5–10] Several solid acid catalysts such as sulfated titania,[1,11,12] a cation-exchange resin,[2,13] a heteropoly acid,[14] and zirconia[15] have been suggested for the trimerization reaction.

To the best of our knowledge, there are only a few reports on the utilization of zeolites[16,17] in the isobutene trimerization reaction even though they are well-known acid catalysts. Very recently, it has been suggested that high concentration of Lewis acid sites is beneficial to the isobutene trimerization.[1,16] However, the effect of Lewis acid is not understood well, and the method to control the Lewis sites for the trimerization, especially in zeolites, needs further investigation. Therefore, we have undertaken the present work with an objective to develop a zeolitic catalyst, useful for isobutene trimerization, containing high concentration of Lewis acid sites by a simple procedure of loading Lewis acids into a zeolite catalyst.

NH_4Y zeolite ($SiO_2/Al_2O_3 = 2.75$) was purchased from Strem and converted into HY by calcination at 550 °C. $FeCl_3$-loaded HY was prepared by following the reported procedures.[18–20] In a glove box, $FeCl_3$ (Aldrich, 97%, 3 wt % to the dried zeolite) was loaded into HY (dried at 400 °C for 4 h) and ground well for 10 min. The mixture was heated to 550 °C in a furnace (heating rate: 1 °C/min) and maintained at that temperature for 6 h. The length of the catalyst bed for both calcinations was maintained very short to eliminate any dealumination. The catalyst was designated as Fe/HY (Cl/Fe = 0.94 atom/atom, determined by EDS) and was used for the reaction after cooling to room temperature. Prior to the commencement of the reaction, the zeolites in the reactor were dehydrated at 300 °C for 10 h under the flow of nitrogen.

Trimerization of isobutene (99.0%, Rigas Korea) was carried out in the liquid phase using a fixed-bed continuous flow reactor (SS 316, OD 3/8 inch). The reaction temperature (70 °C) and pressure (15 bar) were controlled by a water jacket and a back-pressure regulator (Tescom), respectively. The isobutene and a diluent (*n*-butane, 99.5%, Rigas Korea) were continuously fed (1/1 wt/wt) by using liquid mass flow controllers (Bronkhorst HI-TEC). The space velocity of isobutene, WHSV (weight-hourly space velocity, g of isobutene fed per g of catalyst per hour) was $10\,h^{-1}$.

The conversion of isobutene was determined by analyzing the composition of the off-gas stream, after condensing liquid products, by using a GC equipped with a TCD and an alumina column (J&W Scientific, 30 m × 0.53 mm). Liquid products were analyzed by a FID GC containing a PONA column (HP, 50 m × 0.20 mm). The selectivity is described in wt %. The contribution of pentamers or higher oligomers was neglected in this work because the concentration was less than 0.5 wt %. The experimental conditions were described in detail elsewhere.[13]

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

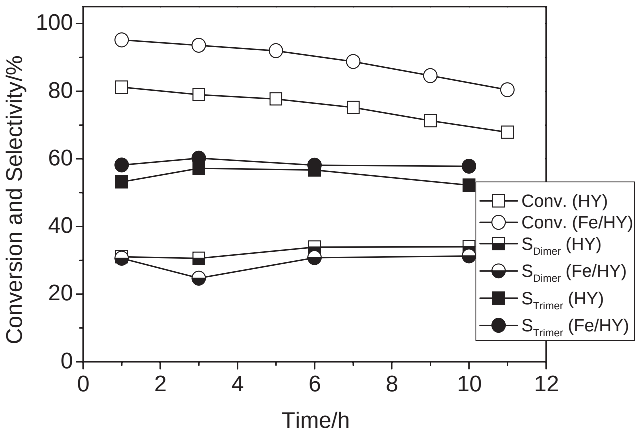

Figure 1. Variation of conversion and selectivities with time on stream over HY and Fe/HY catalysts.

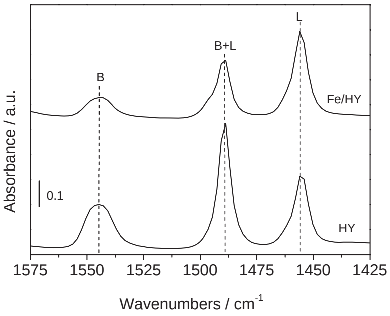

Figure 2. FT-IR spectra of adsorbed pyridine on HY and Fe/HY.

As illustrated in Figure 1, the isobutene oligomerization over the two zeolites shows significant differences in the isobutene conversion. The conversion of isobutene over Fe/HY is noticeably higher than that over HY through out the reaction time even though the surface area of Fe/HY is considerably low (probably owing to pore blocking or pore modification by the loaded iron species) compared with the original HY (Supporting Table 1). Moreover, the trimer selectivity is slightly higher over Fe/HY, which may be due to the lower dimer selectivity. Additionally, the tetramer selectivity is higher (Supporting Table 1)[22] over Fe/HY because of the higher reactivity. Compared with other zeolite catalyst,[17] the tetramer selectivity is relatively high probably owing to the large super cage or pore size of the HY and Fe/HY zeolites. Therefore, the trimer selectivity is not so high (even with the high conversion) because of the increased tetramer selectivity.

As shown in Figure 2 and Supporting Table 1, the relative concentration of Lewis acid sites (compared with Brønsted acid sites) increases with the loading of $FeCl_3$ on HY. The concentration of Brønsted acid sites decreases with the loading because the Lewis sites are generated by the consumption of Brønsted sites with the removal of HCl.[20] Therefore, it is confirmed that Lewis acid sites are effective for the isobutene trimerization (especially for high conversion) even though more detailed study is necessary to understand the role of Lewis acidity in trimerization. We have also investigated the beneficial role of Lewis acid sites on the isobutene trimerization for stable conversion and high trimer selectivity in the trimerization by a dealuminated HY zeolite and by a zeolite loaded with other Lewis acids. The outcome of this study will be published elsewhere.[21] Similarly, very recently, our group and Mantilla et al. have also suggested that the high Lewis site-to-Brønsted site ratio in a catalyst[1,16] corresponds to high catalyst stability or trimer selectivity.

Facile regeneration of a catalyst is very important for commercial applications, especially for large-scale production of chemicals. Zeolite catalysts are superior to cation-exchange resins because of high thermal stability and regenerability by simple calcination.[16,17] The aged Fe/Y catalyst was calcined at 550 °C for 6 h under the flowing air to confirm the regeneration of the catalyst. As shown in Figure 3, the catalytic performance including activity and selectivities are completely restored after simple calcination, suggesting the commercial applicability of the Fe/Y catalyst.

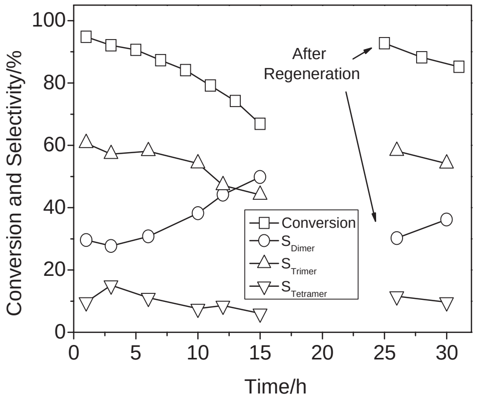

Figure 3. Catalytic performance of regenerated Fe/HY by simple calcination.

In summary, the present study reveals that a zeolite with high concentration of Lewis acid sites, generated by the simple loading of a Lewis acid on an acidic zeolite, is one of the potential catalysts for the isobutene trimerization exhibiting high activity, high trimer selectivity, and facile regeneration. Moreover, this modified catalyst is very easy to prepare by simple mixing and calcination, suggesting a facile method to develop an effective catalyst for isobutene trimerization.

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