JOURNAL OF CATALYSIS 153, 353–355 (1995)

NOTE

A Comparison of Aromatization Activities of the Medium Pore Zeolites, ZSM-5, ZSM-22, and EU-1

ZSM-5 is known to be an excellent catalyst for the aromatization of lower alkanes and alkenes (C_3–C_5) (1–7). Already a few commercial processes have been announced based on ZSM-5: M-2 forming, Mobil (6); Cyclar, BP/UOP (7); and Aroforming, IFP/SALUTEC (4). The cyclar process for the aromatization of LPG is already being used by BP on a semicommercial scale in Grangemouth. The activity of ZSM-5 in aromatizing alkanes has been attributed mainly to (i) high acidity and (ii) correct pore geometry. In this context it is interesting to compare the performance of other medium-pore high silica zeolites with different pore geometries. We now present a comparative study of the aromatization of n-hexane by three medium-pore zeolites viz., H–ZSM-5, H–ZSM-22, and H–EU-1. Though the aromatization of n-hexane over ZSM-5 has been already been reported (3, 8, 9) studies on other high silica, medium-pore zeolites such as ZSM-22 and EU-1 are not available in the literature. ZSM-22 and EU-1 were prepared as per published procedures (10, 11) and ZSM-5 was obtained from United Catalysts India, Ltd.

The Na-form of the zeolites was converted into the NH_4^+-form by three exchanges with ammonium nitrate solution (353 K, 6 h each). The NH_4-zeolites were then dried at 373 K (12 h) and calcined in air (773 K; 4 h) to yield the H-forms. The H-zeolites were compacted into discs (20 mm × 2 mm) using a hydraulic press and they were then broken into small pieces (16–20 mesh). The crushed pieces were washed with water and dried at 383 K for 6 h. Generally, 2-g samples of the catalysts diluted to 5 ml with quartz chips of suitable size were used in the studies.

The reactions were carried out under atmospheric pressure in a commercial down-flow reactor (Autoclave Engineers, Erie, PA). The reactor tube (SS/316) had an i.d. of 8 mm and a length/diameter ratio of about 10 was obtained when a 5-ml catalyst charge (including quartz chips) was used. The data reported were obtained 1 h after introduction of the feed. Both gas and liquid products were analyzed and mass balances (excluding H_2 and coke) were carried out. The gaseous and liquid products were analyzed in a GC (HP 5890) using a capillary column (HP1, 50 m × 0.5 mm).

All the samples had similar SiO_2/Al_2O_3 ratios of about 40. Their crystallite sizes were similar (3–4 μm) though their shapes were different; ZSM-5 and Eu-1 were nearly cuboid, while ZSM-22 was more elongated in one direction. The pore structure of ZSM-5 is bidimensional with two types of intersecting pores with cross sections of 0.54 × 0.56 nm and 0.51 × 0.55 nm, with the maximum diameter at the intersection being about 0.9 nm. EU-1 has a one-dimensional pore system (0.58 × 0.41 nm) but has fairly large side pockets (0.68 × 0.58 × 0.81 nm) where some bimolecular reactions can easily take place. ZSM-22 has the most "restricted" pore system of the three zeolites in that it has unidimensional pores of 0.55 × 0.45 nm.

The influence of the temperature of the reaction on conversion and product yields over the three zeolites is presented in Fig. 1. The conversion of n-hexane over ZSM-5 is nearly 100% at all temperatures in the range 723–813 K. In the same range of temperatures, there is between 60 to 90% conversion in the case of ZSM-22 and between 43 and 51% in the case of EU-1. The critical diameter of n-hexane is 0.47 nm and its length is 1.03 nm (12). The cracking of n-hexane over ZSM-5 has been reported by previous workers (13, 14) to be free of diffusion effects even in crystallites of sizes exceeding 5 μm. It is therefore very likely that n-hexane conversion is not diffusion-limited in our case either (where smaller crystallites have been used). As all the zeolites had similar SiO_2/Al_2O_3 ratios (and, consequently, a similar number of acidic sites), the lower conversions recorded over ZSM-22 and EU-1 suggest that the reaction is probably constrained by diffusion limitations in the case of the above two zeolites.

The apparent activation energies (E_a) for the cracking of n-hexane are 19 ± 2 and 22 ± 3 kJ/mole for EU-1 and ZSM-22 in the temperature range 573 to 673 K while the activation energy is 60 ± 4 kJ/mole for ZSM-5 in the temperature range 533 to 593 K. The rates of n-hexane cracking at 573 K (WHSV = 2 h^{-1}; H_2/n-C_6 (mole) = 1.5; pressure (total), 1 atm) for ZSM-5, ZSM-22, and EU-1 are respectively, 3.6×10^{-6}, 7.4×10^{-7}, and 5.8×10^{-7} moles/g/sec. The small E_a values for EU-1 and ZSM-22 also suggest the possibility of diffusion effects in these

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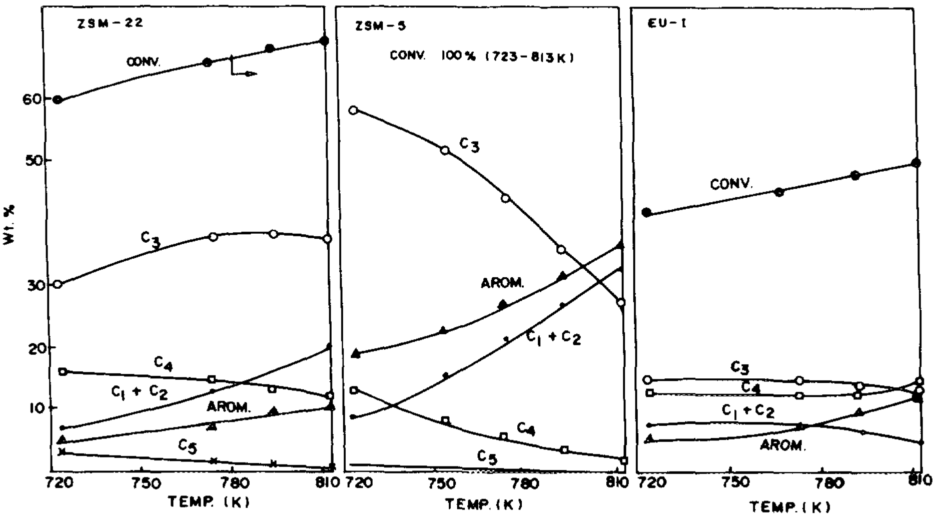

FIG. 1. Influence of temperature on conversion and product yield. WHSV = 2.0 h^{-1}; $H_2/n\text{-}C_6$ (mole) = 1.5; pressure 1 atm.

catalysts. In addition, other factors arising from differences in the location of the T_d–Al^{+3} sites and the inherent differences in activity per Al site could also explain the lower activities of ZSM-22 and EU-1 when compared to ZSM-5. The yield of aromatics is significantly greater over ZSM-5 than over ZSM-22 or EU-1. Apparently, again the pore size restrictions are responsible for the poorer aromatic yields over ZSM-22 and EU-1. The critical diameter of the benzene ring is 0.68 nm (12) which is much larger than the maximum pore diameters of these zeolites. In the case of ZSM-5, the aromatic compounds can easily be formed at channel intersections. EU-1 produces (Fig. 1) slightly more aromatics than ZSM-22 (12.3% vs 10.8%) at 813 K even though *n*-hexane conversion is lower (49.2% vs 89%). Again, the C_8^+ aromatics yield is also larger (2.52% vs 0.88%) at this temperature (Fig. 1). It appears likely that the large side pockets are responsible for the greater yields of aromatics.

The data obtained over ZSM-5 at low contact times at 793 K are presented in Fig. 2A, while the data for both ZSM-5 and ZSM-22 obtained at large contact times are presented in Fig. 2B. ZSM-5 is so active that nearly the same amount of aromatics (about 10.5%) is produced at a contact time nearly 10 times smaller than over ZSM-22 ((W/F) = 0.05 h for ZSM-5 and 0.48 h for ZSM-22); the *n*-hexane conversions at these contact times are 78% for ZSM-5 and 87% for ZSM-22. At a constant contact time of 0.48 h, the yield of aromatics is nearly three times greater over ZSM-5 than over ZSM-22 (32 and 10.3%).

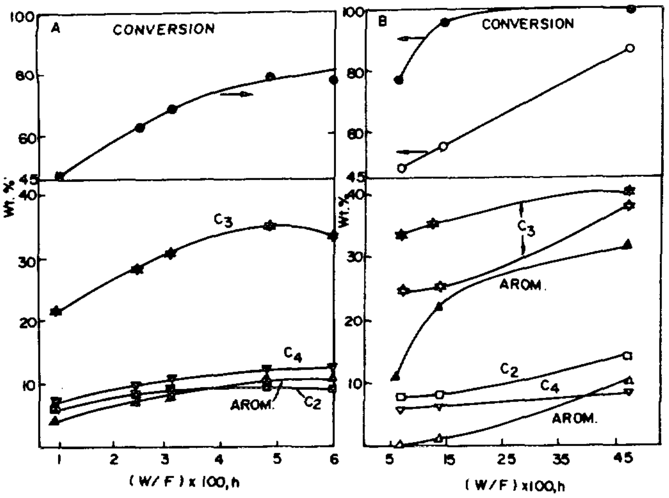

FIG. 2. Influence of *n*-hexane contact time on conversion and product yield. Temperature, 793 K; $H_2/n\text{-}C_6$ (mole) = 1.5 for H-ZSM-22 and 2.0 for H-ZSM-5; pressure, 1 atm; closed symbols, H-ZSM-5; open symbols, H-ZSM-22.

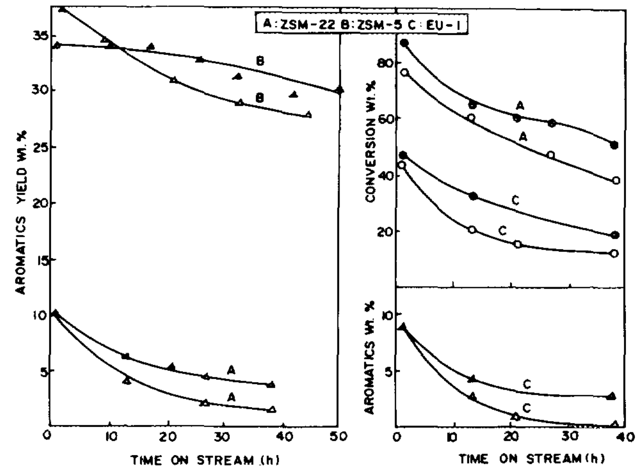

FIG. 3. Influence of duration of run on conversion and aromatic yield. Temperature, 793 K; WHSV = 2.2 h^{-1}; Gas/$n\text{-}C_6$ (mole) = 1.5; pressure, 1 atm; closed symbols, H_2; open symbols, N_2.

The deactivation characteristics of the three zeolites (at 793 K) are presented in Fig. 3. ZSM-5 deactivates the least even though it produces the greatest amount of aromatics. No significant decrease in conversion is noticed over ZSM-5 for about 50 h on stream (conversion ≃ 100%) in both H_2 and N_2 atmospheres. On the other hand, ZSM-22 and EU-1 deactivate quickly, with both conversion and aromatic yields decreasing rapidly with time (Fig. 3). The deactivation is faster in the presence of N_2. Apparently, the presence of H_2 helps in the removal of coke precursors from the catalyst surface leading to a longer life. The reason normally given for the low coking tendency of ZSM-5 is that bimolecular reactions involving large molecules leading to coke formation cannot take place inside the narrow pores of ZSM-5 (restricted transition state selectivity) (15). The rapid deactivation of ZSM-22 and EU-1 (also with similar narrow pores) is probably due to (i) the unidimensional nature of their pore systems; (ii) the greater propensity of ZSM-5 to crack down coke precursors; and (iii) the faster desorption of the coke precursors through the more open and relatively larger pore system in ZSM-5.

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Received April 22, 1994; revised December 1, 1994