Comparison of protonated zeolites with various dimensionalities for the liquid phase alkylation of *i*-butane with 2-butene

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Received 26 January 2001; accepted 21 March 2001

This study focused on the effects of structure on the catalytic performance of various three-, two-, and one-dimensional zeolites. The alkylation of isobutane with 2-butene was carried out under both mild and severe conditions with respect to the feed flow rate. It was observed that zeolite beta outperformed the other zeolites, exhibiting high olefin conversion and alkylate selectivity. For the olefin WHSV used in this work, LTL and USY deactivated rapidly. It is proposed that their fast deactivation was a result of the periodic expansions of their respective pore structures. In contrast to the behavior of other zeolites, the C_8 selectivities almost remained high and constant over LTL. The one-dimensional ZSM-12 was found to outperform in terms of activity many of the samples in this study because of its unique pore structure. A study of the carbonaceous material formed inside the zeolites pores discovered that their composition also depended on the zeolite pore structure. The results of this study indicate that the ability of certain zeolites to inhibit the formation of coke precursors because of their particular pore structures is an important parameter.

KEY WORDS: beta; mordenite; pore structure; acidity; dealumination

1. Introduction

As a result of increasing environmental concerns related to air quality, current and future legislation will require a decrease in the levels of olefins and aromatics in gasoline. In addition, the expected removal of MTBE from gasoline in the US because of its negative environmental impact in ground water [1] will further increase the need for high octane blending compounds in the gasoline pool. Hence, the alkylation of isobutane (i-C_4) with 2-butene has become an even more important process for production of high-octane gasoline. However, the widespread use of the alkylation process is limited [2] by the polluting and corrosive liquid acid catalysts (HF and H_2SO_4) currently used in industry.

The use of solid acid zeolites as catalysts for the alkylation process is currently being investigated with varying degrees of success. Several large-pore zeolites, including USY, beta, and mordenite, have been tested for this reaction. However, although these samples have been selective to the desired alkylate, they have invariably resulted in rapid deactivation either as a result of pore blocking or acid site poisoning. Studies comparing the activity of beta to faujasite zeolites [3,4] have shown that beta deactivates less rapidly, although the exact physicochemical properties governing this behavior remains unknown. Further development in this field will require investigations of new zeolite types and a deeper understanding of the functions of structure and acidity on the activity and deactivation of the catalysts.

This study focuses on the activity and selectivity of various three-, two-, and one-dimensional zeolites in the alkylation of isobutane with 2-butene under both mild (olefin WHSV $= 0.1\ h^{-1}$) and relatively severe (olefin WHSV $=$ $0.5\ h^{-1}$) deactivating conditions. Though all these zeolites have been studied before, they have not been brought together in one study and compared under the identical operating conditions. Therefore, this work is unique in that it investigates the performance of a number of different zeolites under conditions where a comparison is meaningful. This work also investigates the impact of structure. However, in order to understand the role of zeolite structure, the effects of acidity must be separated. Many factors influence the role of acidity; factors such as numbers of Brønsted or Lewis sites, acid strength, Al content which determines the location of and interaction between nearby acid sites, topology of the aluminum tetrahedra which is determined by the zeolite structure type, as well as a number of other factors. The role these parameters have in activity may be lessened, though not completely eliminated, by a proper choice of samples. When Si/Al ratios higher than about 25 are used, the influence of such factors plays a less significant role [5]. Samples with similar Si/Al ratios, and therefore comparable number of acid sites, were used in the present work.

2. Experimental

The USY sample was obtained from the PQ Corporation (CBV-760, protonated form) and was used as received. The mordenite sample was obtained from UOP. A cation exchange was performed on the mordenite sample by contacting the zeolite with a 2.0 M solution of NH_4Cl at 85 °C for 4 h. The sample was then dealuminated by heating at

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1011-372X/01/0600-0085$19.50/0

85 °C in a 1.0 N HCl solution for 4 h. The LTL sample was also obtained from UOP and underwent the same cation-exchange procedure. However, dealumination was performed by first heating the sample to 600 °C in the presence of steam followed by contacting the zeolite with an aqueous solution containing 1.4 g ammonium hexafluorosilicate (AHF) at 85 °C for 4 h. This steaming/AHF procedure was then repeated in order to obtain an LTL sample with Si/Al = 20. Though the desired Si/Al ratio for this study was 30, this LTL sample possessed the maximum Si/Al ratio for the LTL zeolites; further dealumination resulted in samples that were no longer crystalline. The beta and ZSM-12 samples were synthesized in the laboratory using a modified procedure of Rosinski and Ruben [6] and are described in detail by Gopal *et al.* [7]. The synthesized samples were calcined to remove the organic template and each underwent a cation-exchange procedure to obtain the ammonium form; no dealumination was performed on these samples.

The catalysts were characterized using inductively coupled plasma (ICP) spectroscopy, NH_3 stepwise temperature-programmed desorption (STPD), and XRD. The STPD experiments were performed in order to determine the acid site concentration and have been described elsewhere [8]. The characterization results are included in table 1.

The carbonaceous materials retained within the zeolite samples during reaction were analyzed using a GC (Shimadzu, GC-17A) equipped with a mass spectrometer (Shimadzu, GCMS-QP5050A). The zeolite was dissolved in a 49% hydrofluoric acid solution and the organic material was extracted using methylene chloride. The coke extracts were concentrated before GC analysis.

The alkylation reactions were performed in a high-pressure, fixed-bed reactor. For each run, one gram of catalyst (dry basis) was loaded into a half inch steel tube and was heated to 550 °C under a flow of 30 cm^3/min N_2 for 2 h followed by a flow of 30 cm^3/min O_2 at 450 °C for 2 h. The dead volume of the reactor was reduced with glass beads. The reactor was then cooled to 80 °C and then pressurized to 300 psig with N_2 using a Tescom back pressure regulator. The isobutane/olefin mixture (i/o molar ratio of 98) was then introduced with the use of an ISCO 500D syringe pump. Experiments were performed with an olefin WHSV of either 0.5 or 0.1 h^{-1}, thus representing a total WHSV of 10.25 and 50.25 h^{-1}, respectively. The breakthrough of the organic feed was taken to be the zero time on stream. Thereafter, samples were taken periodically and stored in a heated 16-port valve. After the reaction was complete, the samples were sent to a Hewlett–Packard 6890 GC/FID using a flow of helium. The HP injection valve was modified to allow the entire sample loop volume to be admitted onto the GC column (Supelco Petrocol DH 50.2), thus giving an excellent response for all products. Also, a high-resolution gas chromatograph (HP 5890 series II) equipped with a mass spectrometer (HP 5972 series II) was used for the qualitative identification of the products.

Table 1
Physicochemical properties of the samples.

Zeolite	Modifications	Si/Al ratio (bulk)	BET area (m^2/g)	Total acidity (mmol/g)
USY-30	As received	30[a]	720	0.40
Beta-31	Synthesized	31[b]	558	0.47
Mord-34	1.0 N HCl	34[b]	444	0.52
LTL-20	2 × (steam/AHF)	20[b]	288	0.70
ZSM12-31	Synthesized	31[b]	320	0.47

[a] Reported by company.

[b] Determined by chemical analysis.

3. Results and discussion

3.1. Activity of zeolites

The zeolites used in this study were chosen because their specific pore architecture allows an intensive study of both the effects of transport pathways and supercages. The zeolites with higher order of dimensionality possess more pathways through which reactants and products may diffuse, thus bypassing areas where coke is accumulated. Hence, it is expected to obtain higher time stability [9]. Supercages are large void spaces within the zeolite framework and in most cases they are significantly larger than the pore size; they effectively trap large molecules that are unable to diffuse through the pores. USY (pores of 7.4 Å with supercages of 13 Å) and beta (pores of 7.5 × 5.7 Å and 6.5 × 5.6 Å with supercages of about 9 Å) are both three-dimensional zeolites; mordenite is a two-dimensional zeolite (pores of 7.0 × 6.7 Å and 5.7 × 2.6 Å); and LTL (pores of 7.1 Å with expansions of 12.6 Å) and ZSM-12 (pores of 5.7 × 6.2 Å) are one-dimensional zeolites. The physicochemical properties of the zeolite samples are included in table 1.

The olefin conversion under relatively severe deactivating conditions (olefin WHSV of 0.5 h^{-1}) for the zeolite samples are shown in figure 1. The rapid deactivation of the catalysts that is inherent under these conditions occurred for all samples. In particular, the highest rate of deactivation was observed for the LTL and USY samples. The lowest rate of deactivation was observed for the beta sample. This result agrees well with previous studies [10–12] in demonstrating that beta zeolite possesses good activity and stability in this reaction. The effect of supercages may be determined by comparing beta and USY. Though beta and USY are both three-dimensional, the former zeolite exhibited better time stability as a consequence of its specific pore structure (absence of supercages). One should ignore the role of the hydride transfer capability as a possible reason for the difference in performance since the zeolites have approximately the same Si/Al ratio and number of acid sites. Furthermore, it is important to note that the one-dimensional zeolite ZSM-12 was more stable than mordenite, LTL, and the three-dimensional USY under both mild and severe deactivating conditions. In particular, this observation is much more apparent under less severe conditions; for reactions at an olefin WHSV of 0.1 h^{-1}, the ZSM12-31 sample remained at 98% conversion for 150 min while that obtained

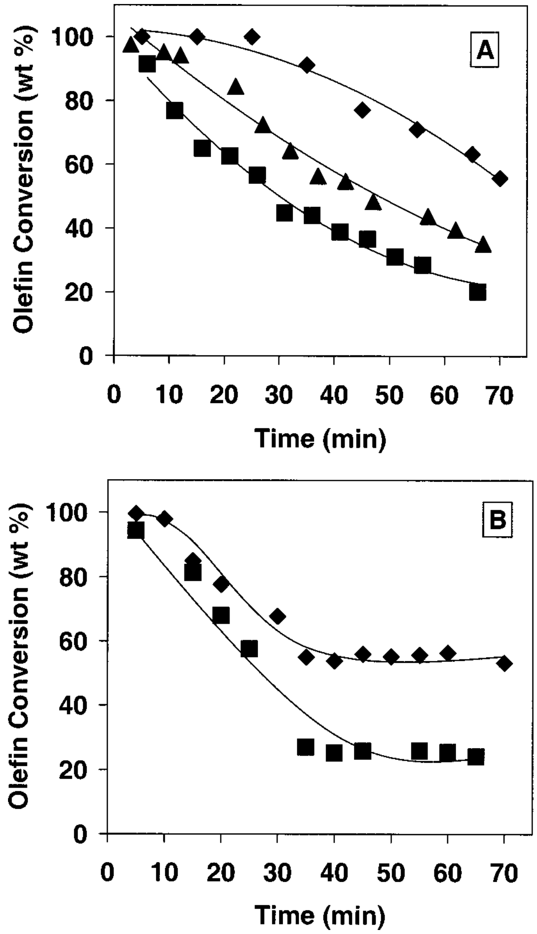


Figure 1. Olefin conversion *versus* time on stream under relatively severe conditions. (A) Three- and two-dimensional zeolites (■) USY-30, (♦) Beta-31, and (▲) Mor-34; (B) one-dimensional zeolites (■) LTL-20 and (♦) ZSM12-31. Reactions were performed at 300 psig, 80 °C, i/o = 98 (molar), and olefin WHSV of 0.5 h^{-1}.

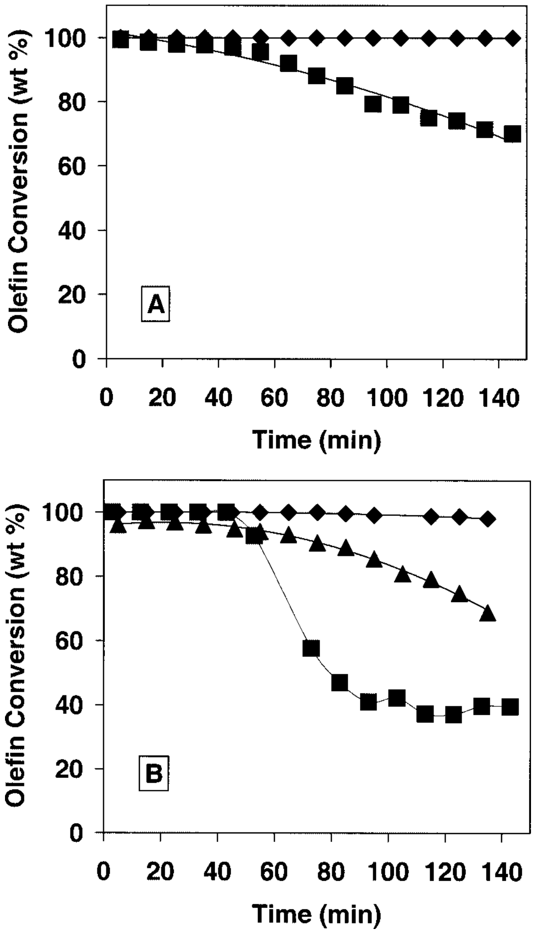
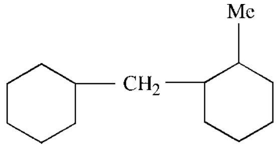
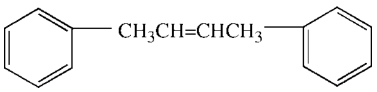
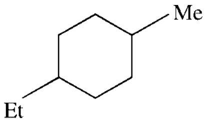
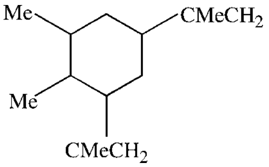


Figure 2. Olefin conversion *versus* time on stream under mild conditions. (A) Three-dimensional zeolites (■) USY-30 and (♦) Beta-31; (B) two- and one-dimensional zeolites (▲) Mor-34, (■) LTL-20, and (♦) ZSM12-31. Reactions were performed at 300 psig, 80 °C, i/o = 98 (molar), and olefin WHSV of 0.1 h^{-1}.

over the USY-30 sample steadily decreased with time (see figure 2). This observation directly contradicts the common belief that large-pore three-dimensional zeolites (those with “open structures”) are more time stable for alkylation than one-dimensional zeolites. This phenomenon was also observed in our earlier work for bifunctional zeolite catalysts in the hydroconversion of both normal and branched octanes [13–15]; ZSM-12 samples showed superior time stability in comparison to other, three-dimensional zeolites. This increased stability is believed to be a result of its pore architecture. The pore channels of ZSM-12 are uniform in size and lack of any expansions or contractions are capable of preventing the formation and buildup of bulky molecules to a greater extent than those of other zeolites. This concept may also be used to explain the good performance of beta; the channel intersections of beta (about 9 Å) are of relatively similar size as its pore openings when compared to USY. The supercages (about 13 Å) present in USY and the periodic expansions (12.6 Å) of LTL in combination with their smaller pore openings (about 7 Å) allow the formation of bulky carbonaceous compounds that potentially plug the zeolite pores, resulting in increased diffusion limitations and cover the acid sites [16].

The carbonaceous material remaining in the zeolite samples was identified in order to better understand the deactivation pathways. The major coke molecules found in the various zeolites are shown in table 2. In USY, the identified molecules were mainly bulky compounds, containing either two cyclohexane rings or two benzene rings. In the beta and ZSM-12 samples, however, large molecules were not detected to an appreciable extent. Therefore, we conclude that over these more stable samples, most compounds that are small enough to diffuse out of the zeolite are formed during the reaction. Large, multi-branched alkylates (see table 2) were identified within the LTL samples. These compounds were probably formed within the periodic expansions of the LTL pore structure and resulted in deactivation of the catalyst. These multi-branched compounds were formed via a polyalkylation mechanism as described by other researchers [11,17]. Carbonaceous material of intermediate size was found within the mordenite sample.

Table 2
The retained carbonaceous materials found inside spent zeolites.[a]

Sample	Retained materials	
USY-30	$C_{14}H_{26}$	
	$C_{18}H_{20}$	
Beta-31		ND[b]
Mord-34	C_9H_{16}	
	$C_{22}H_{34}$	
LTL-20	$C_{19}H_{40}$	2,6,10,14-tetramethylpentadecane
LTL-20	$C_{30}H_{62}$	2,6,10,15,19,23-hexamethyltetracosane
ZSM12-31		ND[b]

[a] Reactions were performed at 300 psig, 80°C, i/o = 98, and olefin WHSV of 0.5 h^{-1}.

[b] ND: not detected.

Table 3
Activity and product selectivities at initial time on stream.[a]

	Sample				
	USY-30	Beta-31	Mord-34	LTL-20	ZSM12-31
TOS (min)	5	5	3	5	5
Total product distribution (wt%)					
C_5	13.48	18.95	6.82	14.34	13.67
C_6	7.76	9.69	4.64	5.93	7.58
C_7	8.53	10.01	3.83	6.65	8.44
C_8	42.63	44.85	72.16	68.55	46.15
C_{9+}	27.60	16.50	12.55	4.53	24.16
Ole. conv. (wt%)	*90.71*	*100.00*	*97.44*	*93.16*	*99.50*
Detailed C_8 distribution (wt%)					
TMPs	*19.22*	*30.62*	*53.54*	*57.02*	*20.50*
2,2,3-TMP	0.70	0.26	0.27	3.52	0.00
2,2,4-TMP	7.42	17.00	24.02	22.81	12.10
2,3,3-TMP	4.29	4.26	4.12	9.23	2.38
2,3,4-TMP	6.81	9.10	25.13	21.46	6.02
DMHs	*18.59*	*13.27*	*17.66*	*10.53*	*21.50*
2,2-DMH	0.02	0.08	0.10	0.05	0.08
2,3-DMH	8.86	5.35	8.90	3.91	4.82
2,4-DMH	3.94	3.62	4.71	3.28	5.24
2,5-DMH	1.47	3.75	3.16	1.78	10.77
3,3-DMH	0.00	0.00	0.20	0.02	0.13
3,4-DMH	4.30	0.47	0.59	1.49	0.46
3-E,2-M-pentane	0.63	0.24	0.17	0.30	0.19
C_8 olefin	4.19	0.72	0.79	0.70	3.96

[a] The reaction was performed at 300 psig, 80°C, i/o = 98, and olefin WHSV of 0.5 h^{-1}.

3.2. Product selectivity

In describing the selectivity of the catalysts, the lower molecular weight hydrocarbons have been grouped together according to their carbon number (C_5–C_7 and C_8) and the high molecular weight products have been combined into one group (C_{9+}). The data for the TMPs, C_8 (including TMPs) and C_{9+} groups are presented in figure 3. The initial product distribution obtained over each catalyst using the high WHSV is presented in table 3. The selectivity obtained over USY was initially comparable with the other catalysts (see figure 3(A)). However, the production of the heavy end products quickly increased and surpassed that of the desired C_8s after 10 min on stream. Also, although the production of C_8s increased slightly with time (final C_8 selectivity was about 50 wt%), this was undesired, as this increase was primarily a result of the increased production of octenes; the production of the desired TMPs actually decreased with time to a level of about 5 wt%. This increased production of olefins was a result of the loss of the hydrogen transfer capability of the catalyst associated with the gradual decrease of the available acid sites.

The selectivity to C_8s (see figure 3(B)) obtained over beta zeolite remained relatively constant with time. However, it should be noted that within the C_8 fraction, the amount of TMPs gradually decreased with time in favor of olefins, while the amount of DMHs produced remained constant. The amount of C_{9+} produced increased to about 40 wt% within the first 60 min then remained constant while the amount of C_5–C_7 (not shown) products decreased continuously throughout the reaction. This decrease in cracking products and concurrent increase in oligomer products was seen for all samples and is usually attributed to the deactivation of the strong Brønsted acid sites responsible for the cracking activity. Of course, the loss of acidity of beta is significantly lower than that of USY. The acidity characterizations of mordenite indicated that it possessed a high concentration of strong acid sites; thus it was expected to exhibit high selectivity to the cracking products. However, this was not observed; the mordenite sample exhibited relatively low selectivity toward the C_5–C_7 products and quite high selectivity to the C_{9+} products. From the initial selectivity value of about 10 wt%, the amount of C_{9+} produced over mordenite continually rose to about 45 wt%. The amount of C_5–C_7 produced remained low at about 10 wt%, while the amount of C_8s gradually decreased from little over 70 to about 45 wt%. As in the case of the beta sample, the amount of TMPs decreased gradually in favor of octenes. The amount of DMHs decreased slightly with time [18].

Though the conversion obtained over LTL decreased quickly with time on stream (see figure 1) the selectivity toward the desired compounds remained high. Indeed, LTL acquired the highest values in comparison with the other samples. The amount of C_8s produced remained constant at about 70 wt% throughout the experiment, with the TMPs decreasing only slightly with time in favor of the C_8 olefins.

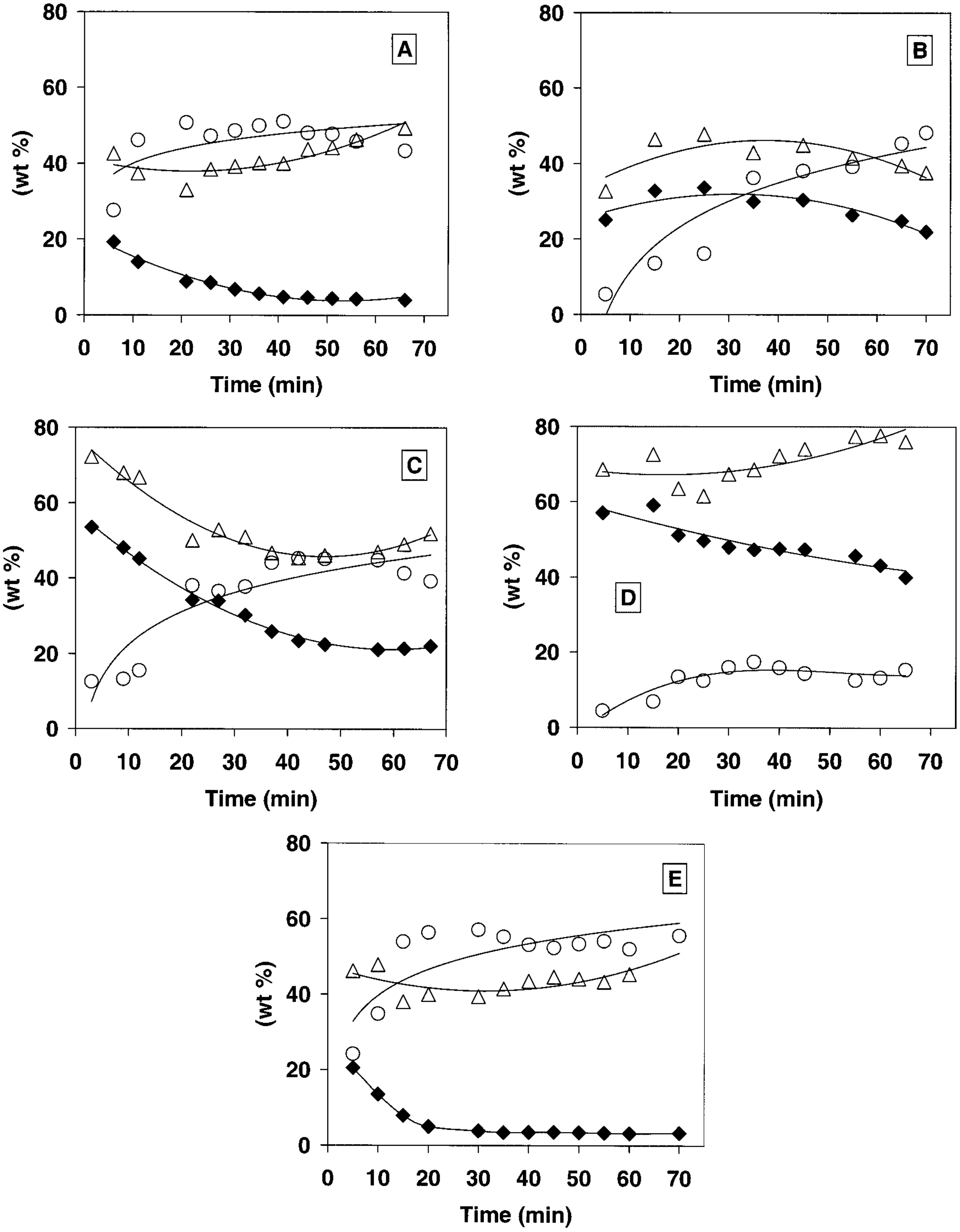


Figure 3. Selectivity *versus* time on stream under severe conditions for TMP (◆), C_8s (△) and C_{9+} (○) compounds. (A) USY-30, (B) Beta-31, (C) Mor-34, (D) LTL-20, and (E) ZSM12-31. Reactions were performed at 300 psig, 80 °C, i/o = 98 (molar), and olefin WHSV of 0.5 h^{-1}.

The amount of DMHs produced also remained constant. This unexpected behavior is in contrast to what one would expect since commonly, when significant deactivation occurs over a zeolite sample, the product distribution changes significantly. With time on stream, the amount of C_5–C_7 decreased slightly in favor of the C_{9+} fraction.

The C_5–C_7 selectivity obtained over ZSM-12 decreased quickly with time in favor of the C_{9+} fraction, which rose to about 55 wt% within the first 15 min of the reaction. The selectivity toward C_8s remained around 45 wt% throughout the experiment. The TMPs and DMHs, however, both decreased quickly for the first 20 min then remained constant at about 10 and 3 wt%, respectively. The low selectivities of TMPs observed is due to the relatively small pore openings of ZSM-12 which do not allow the formation of bulky transition state intermediates. The amount of C_8 olefins increased to about 33 wt%. This behavior is similar to that of the USY sample. The increased concentration of olefins and C_{9+} compounds over ZSM-12 is a direct result of the low rates of hydrogen transfer occurring.

4. Conclusions

The effect of zeolite pore structure for alkylation was studied over zeolites with similar Si/Al ratios. Beta and ZSM-12 were shown to outperform other zeolites under both mild and relatively severe deactivating conditions. This higher stability is believed to be a result of the specific pore architecture of beta and ZSM-12; the lack of expansions in these zeolites that are significantly larger than the pore openings prevent to some extent the formation of large carbonaceous compounds. USY and LTL deactivated rapidly because of their large supercages. Bulky carbonaceous materials, which are coking precursors, were found inside USY and LTL. However, hardly any large carbonaceous materials were detected over stable zeolites. Therefore, the zeolite pore structure plays a great role in the activity of olefin conversion and the formation of coking materials as well.

Acknowledgement

The authors wish to acknowledge the support of the National Science Foundation through the CAREER Award (CTS-9702081). Acknowledgement is made to the donors of The Petroleum Research Fund, administered by the ACS, for support of this research through the grant ACS-PRF 31606-G5.

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