Catalysis Letters 28 (1994) 203–209

Isobutane / 2-butene alkylation on faujasite-type zeolites (H EMT and H FAU)

Michael Stöcker [1], Helle Mostad and Tine Rørvik

Department of Hydrocarbon Process Chemistry, SINTEF Oslo,
PO Box 124 Blindern, N-0314 Oslo, Norway

Received 24 June 1994; accepted 28 June 1994

Dedicated to Professor Dr. Martin Klessinger on the occasion of his 60th birthday.

The alkylation of isobutane with 2-butene on hexagonal (protonated form = H EMT, investigated, for the first time on this reaction) and cubic faujasite (protonated form = H FAU) with Si/Al ratios of 3.5 was studied at 80°C and compared with the results obtained for a cerium exchanged Y zeolite (Ce Y). The alkylate composition consisted of 90% and about 80% C_8 paraffins for H EMT and H FAU/Ce Y, respectively. Within the C_8 fractions the three trimethylpentanes (TMP) 2,2,4-, 2,3,3- and 2,3,4-TMP were the dominating product compounds in all tests, whereas a higher content of dimethylhexanes (DMH) was observed for the H FAU and Ce Y. However, among the four trimethylpentanes 2,3,3,-TMP and 2,3,4-TMP were always the main compounds formed. Oligomerization was favoured only by the H FAU and Ce Y, with a strong increase of C_8 olefins after about one third of the observed reaction time. On the contrary, H EMT exhibited much less formation of C_8 olefins (and on a constant level) even after 300 min reaction time. The deactivated samples showed only formation of non-aromatic coke. The differences in the product pattern were attributed to the slightly larger size of the second type of supercage in EMT and to the stronger Brønsted acid sites in the hexagonal faujasite.

Keywords: hexagonal faujasite (EMT); cubic faujasite (FAU); isobutane/2-butene alkylation

1. Introduction

Alkylation of isobutane with butenes has been a well established technology connected to refinery processes, like FCC, in order to obtain high octane number gasoline. The present technology applies either hydrofluoric acid or concentrated sulfuric acid in a liquid phase reaction, leading to a number of problems such as separation procedures, environmental constraints, corrosion etc. The search for alternative, heterogeneous catalysts started already some decades ago, looking for solid acids like resins, sulfated metal oxides, zeolites etc. [1–16]. Some of the sys-

---

[1] To whom correspondence should be addressed.

tems described, showed an alkylate product distribution pattern (C_8 isomers) comparable to those obtained by HF or H_2SO_4 catalyzed reactions [3]. However, all the heterogeneous acid catalysts reported so far deactivate rapidly, mainly due to the loss of hydrogen transfer capacity leading to the formation of oligomers instead of alkylates.

In the case of zeolites, cubic faujasite (X and Y) [3,6,7,11–14,16], beta [10,17], ZSM-5 [15], ZSM-11 [15], ZSM-20 [10], ZSM-3 [10], ZSM-18 [10], mordenite [10], omega [10], zeolite L [10], ZSM-4 [10] and recently MCM-22 [10,17] have been investigated, with a strong focus on the modified cubic faujasite systems. Common for most of these large-pore zeolites is the fact, that they can adsorb TMPs, which are the most desired gasoline compounds in the alkylate formed.

In the present study we investigate the potential of the hexagonal faujasite (H EMT) as a catalyst in the alkylation of isobutane with 2-butene, with emphasis on the formation of the different TMPs (due to the high octane numbers needed for high quality gasoline) compared to the cubic faujasite (H FAU) of the same chemical composition and a Ce Y zeolite as reference catalyst (reported in the literature).

2. Experimental

Syntheses of H EMT and H FAU were performed according to the (slightly modified) procedures described by Delprato et al. [18], using 18-crown-6 and 15-crown-5 as templates, respectively.

A 250 ml Teflon bottle containing 90.6 g Ludox LS and 65.6 g of a sodium aluminate solution was stirred with an ultrastirrer for 1 min. 12.4 g 18-crown-6 ether crystals were added and the final gel was again stirred for 1 min. The molar ratio of the gel composition was calculated to 0.3 Al_2O_3 : 3.0 SiO_2 : 0.8 Na_2O : 0.3 18-crown-6 : 43.0 H_2O. The bottle content was then aged at room temperature for 18 h before placement at 110°C for four weeks. Pure crystals of EMT were then obtained after filtration, washing and drying.

FAU was synthesized in a 125 ml Teflon bottle containing 55.1 g Ludox LS and 38.1 g of a sodium aluminate solution by shaking vigorously for 1 min. 6.1 g 15-crown-5 ether were added and the final gel was again shaked for 1 min. The molar ratio of the gel composition was calculated to 0.3 Al_2O_3 : 2.9 SiO_2 : 0.7 Na_2O : 0.3 15-crown-5 : 40.0 H_2O. The bottle content was then aged at room temperature for 18 h before placement at 100°C for two weeks. Pure crystals of FAU were then obtained after filtration, washing and drying.

The H-forms of the faujasites were obtained by ion-exchange of the parent material with 2 M NH_4NO_3 solutions at 70°C (three times for 3 h each) and calcination at 540°C for 5 h in air (flow rate of 100 ml/min).

The reference catalyst Ce Y-98 (exchange degree 98%) was prepared according to the procedure by Weitkamp [6].

XRD diffractograms were recorded with CuK_α rays within the angle ratio $2\theta = 5$–90° on an X-ray diffractometer Philips PW 1730 equipped with a Siemens type F monochromator.

The MAS NMR spectra were recorded on a Varian VXR 300 S WB NMR spectrometer equipped with 7 mm zirconia rotors. Conditions for the ^{29}Si MAS NMR spectra: resonance frequency: 59.6 MHz, sweep width: 14000 Hz, pulse width: 7.5 μs, repetition time: 5 s, number of scans: 1000, MAS spinning speed: 5 kHz. Conditions for the ^{27}Al MAS NMR spectra: resonance frequency: 78.2 MHz, sweep width: 50000 Hz, pulse width: 4.0 μs, repetition time: 2 s, number of scans: 1000, MAS spinning speed: 5 kHz. Conditions for the ^{13}C CP/MAS NMR spectra: resonance frequency: 75.4 MHz, sweep width: 20000 Hz, pulse width: 7.5 μs, repetition time: 10 s, contact time: 3 ms, number of scans: 2200–7000, MAS spinning speed: 4 kHz.

Isobutane/2-butene reactor testing was performed in a liquid-phase 300 ml stirred semibatch autoclave, equipped with a cooled pulsation free displacement pump for charging the reactants. 5 g of the calcined catalyst (540°C/5 h in air, the moisture content was determined by TGA) was placed in the reactor and dried further (200°C/2 h) before adding the isobutane. The mixture was then heated to 80°C under nitrogen pressure. 2-butene was charged slowly until the molar ratio of isobutane/2-butene reached 10 : 1. The alkylation reaction was carried out with a WHSV of 1.2 h^{-1} (for 2-butene) and a stirring speed of 360 rpm. Differential one-phase liquid samples were taken regularly and analyzed by GC (capillary column from Hewlett Packard HP PNA 50 m × 0.22 mm, i.d. 0.5 μm, methylsilicone gum fused silica). Samples were thoroughly sucked to fill the transparent tubes, and injected directly into the GC for light component analysis. Excess liquid was collected in ice-cooled traps for off-line GC analysis (same column) of heavier products and separation of olefins. The amount of 2,3-dimethyl-butane was used to standardize the product distribution from both GC-runs.

3. Results and discussion

The pure crystals of EMT were checked by XRD (pure phase of EMT), microprobe (bulk Si/Al ratio = 3.6), ^{29}Si MAS NMR (framework Si/Al ratio = 3.9), ^{27}Al MAS NMR (only tetrahedrally coordinated aluminium), BET (surface area of 769 m^2/g), SEM (hexagonal crystals of a mean size of about 4 μm) and porosity measurements (pore volume of 0.28 ml/g). The pure crystals of FAU were checked by XRD (pure phase of FAU), microprobe (bulk Si/Al ratio = 3.6), ^{29}Si MAS NMR (framework Si/Al ratio = 3.7), ^{27}Al MAS NMR (only tetrahedrally coordinated aluminium), BET (surface area of 754 m^2/g), SEM (cubic crystals of a mean size of about 3 μm) and porosity measurements (pore volume of 0.25 ml/g).

The reference catalyst Ce Y-98 showed the following characteristics: BET surface area of 592 m^2/g and a pore volume of 0.20 ml/g.

Fig. 1 summarizes the distribution of the C_5–C_8 paraffins in the alkylate after running the isobutane/2-butene alkylation over a period of 180 min reaction time for both H EMT, H FAU and Ce Y-98. As shown in the figure, the C_8 paraffins are the dominating fractions, with a content of 90% for H EMT and about 80% for both H FAU and Ce Y-98. The alkylate yields (defined as g C_5–C_8 paraffins per g 2-butene charged) were calculated to 1.5, 0.6 and 0.1 for H EMT, H FAU and Ce Y-98, respectively. The selectivities, defined as g C_5–C_8 paraffins per g 2-butene converted were determined to 1.7, 0.9 and 0.3 for H EMT, H FAU and Ce Y-98, respectively.

The normalized distributions of the C_8 paraffins fractions after 180 min reaction time are shown in fig. 2. The H EMT exhibited less amounts of DMHs compared to H FAU and Ce Y-98. Among the three investigated catalysts, the distribution of the four TMPs is at about the same level and within the four TMPs, the isomers 2,3,3-TMP and 2,3,4-TMP were the dominating ones (see fig. 2), which is in contradiction to the equilibrium distribution of the TMP isomers at 80°C and to results obtained by application of macroporous systems, like resins or aluminosilicate [1,4,10]. At that temperature, the 2,2,4-TMP should be the superior isomer, whereas this compound is only formed to less extent (compared to both 2,3,3- and 2,3,4-TMP) applying our faujasites. Concerning the formation of 2,3,3- and 2,3,4-TMPs, the H EMT system produced a pronounced higher amount of these two C_8 paraffin isomers. On the other hand, 2,2,3-TMP has been reported as the less formed isomer [4], which is in line with our findings. However, according to the

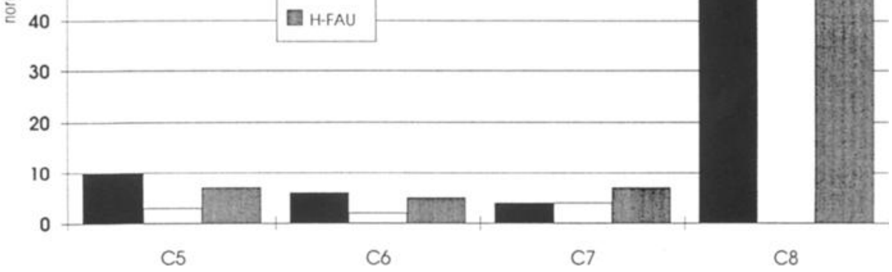

Fig. 1. Normalized distribution of the formed C_5–C_8 alkylates (in %) after isobutane/2-butene alkylation over H EMT, H FAU and Ce Y-98 (temperature: 80°C, WHSV (for 2-butene): 1.2 h^{-1}, stirring speed: 360 rpm).

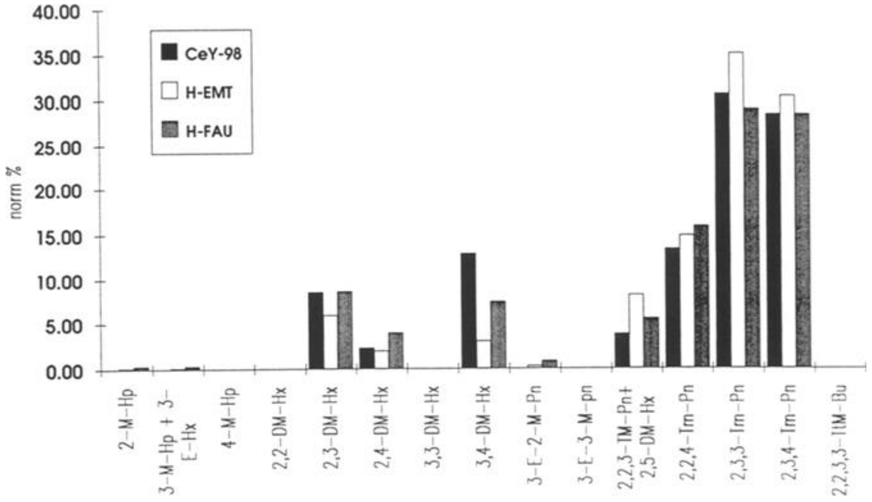

Fig. 2. Normalized distribution of the formed C_8 paraffins (in %) after isobutane/2-butene alkylation over H EMT, H FAU and Ce Y-98 (temperature: 80°C, WHSV (for 2-butene): 1.2 h^{-1}, stirring speed: 360 rpm).

thermodynamic equilibrium concentration at this temperature, this isomer should be produced to a larger extent [10]. The discrepancies related to the preferred formation of 2,3,3-and 2,3,4-TMP and to the less formed 2,2,3-TMP by use of hexagonal and cubic faujasites demonstrates obviously a kinetically favoured production of 2,3,3,- and 2,3,4-TMPs. In addition, a shape-selective effect of those molecular sieves might control the formation of these TMPs, compared to steric less restricted solid catalysts or homogeneous systems following a TMP product pattern corresponding to the thermodynamic equilibrium concentrations.

The composition of the four TMPs during the runs is almost constant for the H EMT (up to 300 min reaction time), whereas for H FAU a certain decrease was observed for 2,3,3- and 2,3,4-TMP and a slight decrease for 2,2,4-TMP (up to 210 min reaction time, thereafter following a constant level up to 300 min reaction time).

The higher degree of C_8 paraffin formation in the alkylate of H EMT can be traced back to the slightly lager size of the second type of supercage in the structure of the hexagonal faujasite, compared to the uniform size of supercages in the cubic FAU system (see fig. 3). Furthermore, with respect to the C_5–C_8 alkylate yield and selectivity, again the H EMT is the superior catalyst, which favours, in addition, less formation of undesired DMH.

The nature, number and strength of the acid sites in the investigated catalysts is probably important with respect to the result interpretation. Our acidity measurements (TPD of ammonia and IR spectroscopy) are not yet completed, however, the favourable role of EMT as an interesting new catalyst for the isobutane/2-butene alkylation can already now be emphasized. This conclusion is supported

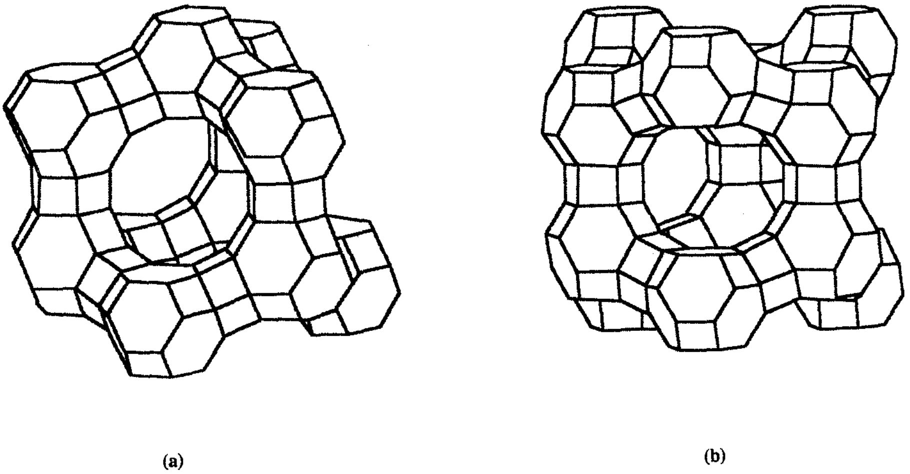

Fig. 3. Framework structures of cubic faujasite (FAU) (a) and hexagonal faujasite (EMT) (b).

by the fact that the wt% formation of isooctenes in the C_8 product composition after 180 min reaction time is much in favour of H EMT (1% compared to 20% for H FAU and 43% for Ce Y-98). This might indicate a larger number of weak acid sites in the cubic faujasite systems H FAU and Ce Y-98, responsible for the increase of the oligomerization rate. The claimed higher acid strength of H EMT [19,20] (compared to H FAU) will be investigated closer by our group and could be an explanation for the preferred alkylation behaviour of the hexagonal faujasite.

Finally, the conversion of 2-butene versus time of reaction was followed, concluding with an almost complete conversion of 2-butene applying the H EMT, whereas the conversions for the cubic faujasites H FAU and Ce Y-98 arrived at certain lower levels.

All three deactivated samples were checked by ^{13}C CP/MAS NMR spectroscopy, and only non-aromatic coke components (mainly of paraffinic character, like methyl groups connected to secondary carbon atoms (14 ppm), CH_2 groups linked to methyl groups (22 ppm) and methyl groups at quaternary carbon atoms (29 ppm)) were detected [12].

In conclusion, the EMT (to our knowledge studied for the first time on this reaction) seems to be a promising catalyst for the isobutane/2-butene alkylation and further emphasis will be made to improve the catalytic behaviour as well as the deactivation profile of this zeolite.

Acknowledgement

The authors are indebted to the Norwegian Research Council for financial support and to the European Commission for participation in the JOULE II programme. Furthermore, we thank Hanne Junggreen, Britt M. Hustad and Rune Wendelbo for their contributions to the successful experimental work.

References

[1] W.E. Garwood and P.B. Venuto, J. Catal. 11 (1968) 175.
[2] V.N. Ipatieff and L. Schmerling, Adv. Catal. 1 (1948) 27.
[3] J. Weitkamp, Acta Phys. Chem. 31 (1985) 271.
[4] T.J. Huang and S. Yurchak, Div. Petr. Chem. Am. Chem. Soc. 22 (1977) 358.
[5] F.W. Kirsch, J.D. Potts and D.S. Barmby, J. Catal. 27 (1972) 142.
[6] J. Weitkamp, in: *Proc. 5th Int. Zeolite Conf.*, ed. L.V.C. Rees (Heyden, London, 1980) p. 858.
[7] J. Weitkamp, in: *Catalysis by Zeolites*, Studies in Surface Sciences and Catalysis, Vol. 5, eds. B. Imelik, C. Naccache, Y. Ben Taarit, J.C. Vedrine, G. Coudurier and H. Praliaud (Elsevier, Amsterdam, 1980) p. 65.
[8] C. Guo, S. Liao, Z. Qian and K. Tanabe, Appl. Catal. A 107 (1994) 239.
[9] C. Guo, S. Yao, J. Cao and Z. Qian, Appl. Catal. A 107 (1994) 229.
[10] A. Corma and A. Martinez, Catal. Rev.-Sci. Eng. 35 (1993) 483.
[11] Kh.M. Minachev, E.S. Mortikov, S.M. Zenkovsky, N.V. Mostovoy and N.F. Kononov, Div. Petr. Chem. Am. Chem. Soc. 22 (1977) 1020.
[12] J. Weitkamp and S. Maixner, Zeolites 7 (1987) 6.
[13] Y.F. Chu and A.W. Chester, Zeolites 6 (1986) 195.
[14] R. Schöllner and H. Hölzel, Z. Chem. 15 (1975) 469.
[15] J. Weitkamp and P.A. Jacobs, in: *New Frontiers in Catalysis*, Proc. 10th Int. Congr. on Catalysis, eds. L. Guczi, F. Solymosi and P. Tétényi (Elsevier, Amsterdam, 1993) p. 1735.
[16] A. Corma, A. Martinez and C. Martinez, J. Catal. 146 (1994) 185.
[17] S. Unverricht, S. Ernst and J. Weitkamp, Lecture 6th German Workshop on Zeolites, Bochum, 7–8 March 1994.
[18] F. Delprato, L. Delmotte, J.L. Guth and L. Huve, Zeolites 10 (1990) 546.
[19] U. Lohse, I. Pitsch, B. Parlitz, K.-H. Schnabel and E. Schreier, Poster 6th German Workshop on Zeolites, Bochum, 7–8 March 1994.
[20] B.L. Su and D. Barthomeuf, Zeolites 13 (1993) 626.