Influence of Pore Confinement on the Catalytic Dehydration of Isobutyl Alcohol on H-ZSM-5

M. A. Makarova, C. Williams, V. N. Romannikov and K. I. Zamaraev*

Institute of Catalysis, Academy of Sciences Siberian Branch, Novosibirsk, 630090, USSR

J. M. Thomas*

Davy Faraday Research Laboratory, The Royal Institution, 21 Albemarle Street, London W1X 4BS

The dehydration of isobutyl alcohol has been used as a test to probe the differences in catalytic behaviour between an (acidic) amorphous aluminosilicate and samples of H-ZSM-5 of various crystallite size but of similar acidity ($[H^+] \approx 3 \times 10^{20} \text{ g}^{-1}$) as the amorphous aluminosilicate. Dehydration rates are shown to be independent of crystallite size (in the range 0.5–20 µm), but rates of oligomerization of the product butene are higher for the large crystallites.

The dehydration of isobutyl alcohol is an industrially important reaction, not least because it yields iso-butene (2-methylpropene) which, upon treatment with methanol, produces methyl-t-butyl ether, a key additive for the improvement of gasoline. However, the dehydration of all the various butanols is of fundamental interest since this family of alcohols provides a convenient testing group to explore the role of molecular shape in dictating both the diffusion and the precise set of reactions (*e.g.* oligomerization and isomerization) that occur inside the channels of zeolitic catalysts such as the pentasils.¹⁻⁵ The various C₄ alcohols are ideally suited for a systematic study of pore confinement since their dimensions are comparable to those of the diameters (*ca.* 5.5 Å⁶) of the pentasils.

Zeolitic molecular sieves differ from most other acidic heterogeneous catalysts in that the active sites (which are sites of detachable protons) are uniformly localized⁵ predominantly inside the body of the crystal. Diffusion of reactant and/or products is, therefore, often of crucial importance; and the particular form of the porosity of the zeolite is the basis of its so-called shape-selectivity.^{1,7} Confinement inside the pores of a zeolitic catalyst may influence the rates of diffusion of products out of the crystallites, thereby resulting in either a shift of the 'equilibrium' of possible product molecules in favour of the most mobile, or in the deactivation of the catalyst owing to the blocking of pores and/or competitive adsorption of product on the active sites.

It is to be expected that a non-crystalline macroporous aluminosilicate will behave differently from microporous zeolitic analogues even though their intrinsic (acidic) catalytic activities are comparable. In this work we demonstrate the truth of this statement and, in particular, establish the conditions required for a definitive assessment (to be discussed in later papers) of the role of pore confinement in the catalytic performance of H-ZSM-5. In common with other studies of ZSM-5 (for example the dehydration of methanol,⁸ disproportionation of nitrotoluene,^{9,10} the methylation of toluene^{10,11} and the cracking of cumene,¹²) we have examined rates as a function of crystal size, to test whether or not diffusion control is important.

Experimental

Four ZSM-5 samples, with different crystallite sizes, were used (table 1 and fig. 1). Sample 2 has a rather broader particle size distribution than the others. Samples 1, 3 and 4 were synthesized¹³ using different organic templates (n-butyl

alcohol, tetraethylammonium bromide and ethylenediamine, respectively). Sample 2 was kindly supplied by Dr S. A. I. Barri. All the samples were converted into the acid (H⁺) form via NH_4^+ ion exchange and calcination at 550 °C. The acidity of these samples was characterised as described elsewhere, by FTIR spectroscopic studies,^{14,15} ¹H NMR studies and pyridine poisoning experiments.¹⁶ In all cases, the concentration of Lewis-acid sites is low (< 10% of the Al content). We have, therefore, taken the concentration of H⁺ ions to be that determined from chemical analysis for Al and unexchanged Na [for more details see ref. (16)]. An amorphous aluminosilicate sample, containing 15% Al₂O₃, was used for comparative studies. Pretreatment of samples with acetonitrile immediately prior to catalytic testing (so as to poison the Lewis-acid sites) did not result in a decrease of catalytic activity, showing that the active sites for alcohol dehydration are indeed the Brønsted-acid sites. Isobutyl alcohol (AR) was distilled and stored over dehydrated 4A molecular sieve to remove any remaining traces of water. All gases were dried over molecular sieves prior to use. The residual water content was < 10 ppm.

The dehydration reaction was studied in a flow microcatalytic reactor shaped in the form of a U-tube. Isobutyl alcohol was fed into the reactor as a gaseous mixture with helium (alcohol concentration 0.8 mol% at an overall pressure of 1 atm[†]). The gas flow rate was typically 40 cm³ min⁻¹, while the catalyst loading varied from 0.005 g to 0.05 g. The dehydration of isobutyl alcohol was studied in the temperature range 100–150 °C. During the course of a catalytic run (typically 1 h) the temperature varies by $< \pm 0.7$ °C. Water, butene isomers and unreacted alcohol were analysed by on-line gas chromatography.

The reaction rate \hat{W} (expressed in terms of butene evolution) is defined as:

$$W(C_4H_8) = F[C_4H_8]/m$$

where F is the helium-alcohol flow rate in $\text{cm}^3 \text{ s}^{-1}$, $[C_4H_8]$ is the butene concentration, molecule cm^{-3} and m is sample mass (g).

The samples were pelletised (0.3-0.5 mm diameter) for catalytic studies. Experiments with finer pellet fractions gave identical reaction rates, showing that intercrystalline diffusion is not rate limiting. Prior to reaction, the sample was pretreated in a flow of oxygen (500 °C, 1 h) and then in helium (450 °C, 2 h). Conversion was kept to less than 10%

^{† 1} atm = 101 325 Pa.

 Table 1. Characterisation of ZSM-5 samples

sample	crystallite size (SEM)/µm	Si/Al	H^+ ions g^{-1a}
1	<1	42	2.3×10^{20}
2	0.5–4	20	$3.3 \times 10^{20 b}$
3	4-6	35	2.8×10^{20}
4	15–20	35	2.8×10^{20}

^{*a*} per gram of dehydrated sample. ^{*b*} Na/Al = 0.35.

by varying the sample mass from 0.005 g in the high-temperature region to 0.05 g at lower temperatures.

Results and Discussion

The results for the dehydration of isobutyl alcohol on the different samples of ZSM-5 are shown in fig. 2. Here the rate of evolution of butene per active centre (H^+) is plotted as a function of time. In the initial region, alcohol is adsorbed onto the dehydrated sample and the rate of butene evolution increases smoothly in parallel with the increasing extent of alcohol adsorption [fig. 2(b)]. Eventually the sample becomes saturated with adsorbed alcohol, and, at that stage, the rate of butene evolution levels off, to a value we call W_{sat} . This behaviour in the initial region is exhibited by all four ZSM-5 samples and the results at 124 °C are shown in fig. 2(a). W_{sat} is, within experimental error, essentially, identical for samples 1-3; and even for sample 4, with the largest crystallite sizes (15-20 μ m), W_{sat} is quite similar in magnitude to that of W_{sat} for the other samples. After 1 h on stream the reaction rate remains unchanged for sample 1 (particles $<1 \mu m$). Thus in this case W_{sat} is synonymous with the steady-state rate. For samples 2 and 3 (intermediate crystallite sizes) the reaction rate decreases slightly during the hour on stream to a value that is slightly outside the bounds of experimental error. For

J. CHEM. SOC. FARADAY TRANS., 1990, VOL. 86

sample 4 (largest crystallites), the decrease in reaction rate after 1 h is a significant 30%. From independent spectroscopic and other measurements we know that this decrease with time arises from oligomerisation of butene within the pores. Under our experimental conditions these oligomers remain adsorbed on the active sites, resulting in gradual deactivation.^{16,17}

Clearly, when oligomerisation is minimal (as with sample 1), a steady rate of reaction (W_{sal}) is observed for the dehydration. For samples 2, 3 and especially 4, we see that oligomerization processes in the pores are significant. Under these circumstances, the initial steady-state value W_{sat} [after 10 min or so at 124 °C; see fig. 2(a)] is the true measure of the rate of dehydration. Demonstrably this rate is independent of crystallite size, and so we conclude that dehydration is not diffusion limited.

It is also apparent from fig. 2(a), and especially from fig. 2(c), that the subsequent processes of oligomerization do depend on crystallite size, the fall in reaction rate being steeper the larger the crystallite size. Owing to there being a longer diffusion length, and hence a greater degree of pore confinement in the larger crystallites, the probability of oligomerization rises. At the lower temperatures [124 °C, fig. 2(a)] the diminution in rate as a consequence of oligomerization is relatively small for samples 1–3 under the particular conditions of flow rate and degree of conversion that prevail.

We also have evidence that suggests that isobutyl alcohol, apart from being a reactant, also plays an important part in suppressing the rate of subsequent oligomerization of the butene generated by catalytic dehydration. This evidence comes from experiments (fig. 3) in which rates of butene evolution are measured after interrupting the isobutyl alcohol–He feed gas and replacing it with other gas combinations. Thus, if, after a period of time on stream, the isobutyl alcohol–He flow is replaced by a flow of pure He, then the rate of evolution of butene decreases rapidly (at 124 °C). On returning to



Fig. 1. Typical scanning electron micrographs for ZSM5 samples: (a) sample 1, $< 1 \mu m$; (b) sample 2, 0.5–4 μm ; (c) sample 3, 4–6 μm ; (d) sample 4, 15–20 μm .

J. CHEM. SOC. FARADAY TRANS., 1990, VOL. 86



Fig. 2. The kinetics of butene formation in the dehydration reaction of isobutyl alcohol on H-ZSM-5, with crystallites of different sizes. Sample: ($\mathbf{0}$, 1; Δ , 2; \bigcirc , 3; ($\mathbf{0}$, 4 (butene evolution). (a) At $T_{\text{reaction}} = 124 \,^{\circ}\text{C}$. (b) More detailed view of the initial region of (a), including alcohol adsorption curve (\times). (c) At $T_{\text{reaction}} = 147 \,^{\circ}\text{C}$.

the alcohol-He flow, however, the new rate of dehydration (measured by butene evolution) has dropped to ca. 50% of the original value. In pure He there is obviously a greater degree of oligomerization, leading to a deactivation of a significant proportion of the active sites. Desorption in flows of



Fig. 3. Dehydration of isobutyl alcohol on H-ZSM-5 (sample 2) at 124 °C, and subsequent desorption of butene when alcohol flow is stopped. \bullet , Desorption in pure helium; \bigcirc , desorption in He-H₂O; \triangle , desorption in He-benzene. The horizontal line on the extreme right denotes the reaction rate after returning to the isobutyl alcohol-He mixture.

water-He or benzene-He results in a less rapid diminution in the rate of butene evolution (fig. 3) than that observed in pure He. Note that the resulting deactivation is still greater than that observed in the isobutyl alcohol-He stream.

Finally, we report (fig. 4) the rate of dehydration of isobutyl alcohol using a more open (accessible) amorphous acid aluminosilicate catalyst. Such a comparison is justified since it is known^{18–20} that Brønsted sites in zeolites and amorphous silica-alumina are similar. The similarity in the acid



Fig. 4. Dehydration of isobutyl alcohol on amorphous aluminosilicate at $124 \,^{\circ}$ C, and subsequent desorption of butene when the Healcohol mixture is replaced by pure helium. The horizontal line on the extreme right denotes the reaction rate after returning to the isobutyl alcohol-He mixture.

strength of these catalysts is verified by the measured shift in OH stretching frequency on adsorption of bases, as described in ref. (14) and (15). Even though experiments were conducted under exactly the same conditions (at 124 °C) for the amorphous and for the crystalline microporous catalysts, there is now no deactivation during the 1 h time period on stream. Moreover, on switching to the He flow we observe a much more gradual decay in butene evolution rate; and on returning to the isobutyl alcohol-He stream the original rate of reaction (dehydration) is fully restored. With this amorphous aluminosilicate catalyst, owing to the absence of pore confinement, no deactivation of active sites takes place.

Conclusion

In the temperature range 100-150 °C the rate of catalytic dehydration of isobutyl alcohol is independent of both crystallite size and pellet size. Hence, neither intra- nor intercrystalline diffusion processes are rate limiting. However, subsequent oligomerization of the butene generated inside the pores is dependent upon crystallite size, there being a steeper drop in rate of butene evolution for larger than for smaller crystallites.

Experiments involving interrupted gas flow, and using an amorphous macroporous aluminosilicate show that deactivation of the catalyst by the subsequent oligomerization of the butene is appreciable in the case of the pore confinement that occurs in ZSM-5 catalysts. The conditions under which reliable data, free from the complicating effects of diffusion and product oligomerization, on isobutyl alcohol dehydration on ZSM-5 have now been established. These are required for a mechanistic study of the dehydration, the subject of another article.16

The authors thank Dr Dudarev (Institute of Catalysis) for zeolite sample 1, and Dr E. A. Paukshtis for IR studies of acidity. C. W. would like to thank the Royal Society and the USSR Academy of Sciences for a one year fellowship to the Soviet Union, and J. M. T. the S.E.R.C. for general support.

J. CHEM. SOC. FARADAY TRANS., 1990, VOL. 86

References

- 1 P. B. Weisz, Pure Appl. Chem., 1980, 52, 2091.
- 2 W. O. Haag, R. M. Lago and P. B. Weisz, Nature (London), 1984, 309, 589.
- P. T. Reischman, K. D. Schmitt and D. H. Olson, J. Phys. Chem., 1988, 92, 5165.
- A. K. Cheetham, J. Gale, A. K. Nowak, S. D. Pickett and J. M. Thomas, Faraday Discuss. Chem. Soc., 1989, 87, 79
- J. M. Thomas, Angew. Chem. Int. Ed. Engl., 1988, 27, 1673.
- G. T. Kokotailo, S. L. Lawton, D. H. Olson and W. M. Meier, 6 Nature (London), 1978, 272, 437.
- (a) S. M. Csicsery, Zeolites, 1984, 4, 202; (b) E. G. Derouane, J. M. Andre and A. A. Lucas, J. Catal., 1988, 110, 58.
- H. J. Doelle, J. Heering, L. Riekert and L. Marosi, J. Catal., 8 1981, 71, 27.
- P. Beltrame, P. L. Beltrame, P. Carniti, L. Forni and G. Zuretti, Proc. Int. Symp. Zeol. Catal. Siofok, 1985, 349.
- 10 P. Ratnasamy, P. N. Joshi, V. P. Shiralkar and B. S. Rao, Rec. *Add. Catal., Catal. React. Eng. (Hyderabad), 1986, 664.* V. Ducarme and J. C. Vedrine, *Appl. Catal., 1985, 17, 175*
- 11
- A. Maleck, A. Bielanski, J. Berak and J. Datka, Bull. Polon. 12 Acad. Sci. Chem., 1987, 35, 133.
- V. N. Romannikov, V. M. Mastikhin, S. Hocevar and B. Drzaj, 13 Zeolites, 1983, 3, 311.
- R. I. Soltanov, E. A. Paukshtis and E. N. Yurchenko, Kinet. Katal., 1982, 23, 164.
- E. A. Paukshtis and E. N. Yurchenko, Uspech. Khim., 1983, 52, 15 426.
- C. Williams, M. A. Makarova, L. Malisheva, E. A. Paukshtis, 16 E. P. Talsi, J. M. Thomas and K. I. Zamaraev, to be submitted.
- J. Haner, J. Komorek-Hlodik and J. Romotowski, Zeolites, 1982, 2, 179. 17
- A. A. Alekseev, V. Yu. Borovkoy and V. B. Kazansky, Dokl. Akad. Nauk. SSSR, 1982, 264, 625. 18
- 19 R. G. Rouxhet and R. E. Sempels, J. Chem. Soc., Faraday Trans 1, 1974, 70, 2021.
- 20 L. V. Kustov, A. A. Alekseev, V. Yu. Borovkoy and V. B. Kazansky, Dokl. Akad. Nauk. SSSR, 1981, 261, 1377.

Paper 9/02945A; Received 11th July, 1989

584