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DEHYDRATION OF n-BUTANOL ON HNa-ZSM-5 **

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It is generally agreed that the conversion of methanol to hydrocarbons on pentasil type zeolites proceeds via the formation of dimethyl ether [1,2]. Some studies have been carried out on C-2 and C-3 alcohol dehydration on wide pore zeolites and amorphous aluminosilicates [3–6], and in cases where ethers were detected among the reaction products, it was concluded that olefin and ether formation are parallel reactions. On the other hand, in [7,8], the authors conclude that the dehydration of n-butanol on H-ZSM-5 takes place via n-dibutyl ether, since alcohol molecules are adsorbed in the ratio of 2 per zeolite OH group. However this obtained experimental result (2 : 1 ratio) is more likely a reflection of the peculiarities of alcohol adsorption than of the mechanism of its transformation. In the present study, we aim, by means of kinetic studies, to clarify the mechanism of the dehydration of n-butanol on HNa-ZSM-5 (65% H^+, 35% Na^+) and the role played by n-dibutyl ether in this reaction.

The sample characterization and full experimental details of catalytic testing are described in [9,10]. Briefly, the reaction is carried out in a micro-catalytic flow reactor with on-line g.c. product analysis. We use a helium-alcohol or a helium-ether mixture at 1 atm. pressure; the alcohol or ether concentration in the mixture can be varied and is typically 0.7 mol% for the alcohol and 0.8 mol% for the ether. The degree of conversion is kept to less than 10%. The reaction is studied in the temperature interval 115–185 ° C, with a typical flow rate of 40 cm^3/min, catalyst loading in the range 0.005–0.05 g (to keep conversion to less than 10%). We work in conditions of zero order with respect to alcohol and ether.

Conditions were established whereby diffusion to and from the active centres (zeolite acid OH groups) is not rate limiting, all the acid OH groups are accessible to reagent molecules, and the secondary reaction of butene product oligomerization is minimal. These experiments are described in more detail in [9]. At low

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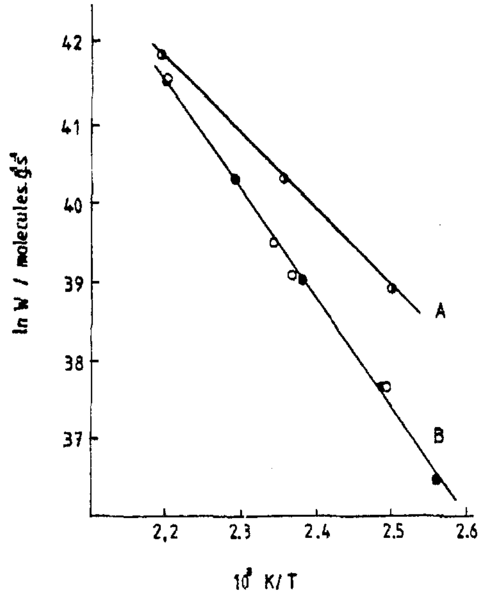

Fig. 1. Arrhenius plots for the dehydration of: (A) n-butanol to butene and di-butyl ether (B) n-di-butyl ether to butene, ○ W_{Bu} (n-Bu$_2$O), ● W_{Bu} (n-BuOH), ○ $W_{Bu} + W_{Bu_2O}$ (n-BuOH), where $W_x(y)$ refers to the rate of formation of product x on dehydration of reagent y.

temperature, 115 °C, the main product of butanol dehydration (80%) is n-dibutyl ether, the remaining 20% being butene. As the reaction temperature increases, the selectivity changes in favour of butene. The overall rate of alcohol dehydration can be determined from the sum of the rates of formation of butene and ether: $W_{C_4H_8} + W_{(C_4H_9)_2O}$. The energy of activation for n-butanol dehydration determined from the Arrhenius plot in fig. 1 (curve A) is 18 kcal/mol. If we only follow the rate of formation of butene in the dehydration reaction, $W_{C_4H_8}$ then the observed energy of activation for butene formation will be significantly higher, as a result of the change in selectivity of the dehydration reaction with temperature. In this case the observed activation energy is 28 kcal/mol (fig. 1, curve B).

We have then taken n-di-butyl ether as the initial reactant, and under identical reaction conditions, we observe that the rate of formation of butene from n-butanol and from n-di-butyl ether are identical in the studied temperature interval. As can be seen from fig. 1, the results for alcohol dehydration to olefin and ether dehydration to olefin lie on the same line B, giving the same activation energy of 28 kcal/mol. This suggests that the alcohol dehydration reaction proceeds via fast ether formation and subsequent slower decomposition of ether:

$$\begin{tikzcd}
\text{n-BuOH}_{\text{ads}} \arrow[r, "\text{fast}"] & \text{n-Bu}_2\text{O}_{\text{ads}} \arrow[r, "\text{slower}"] \arrow[d, "\text{fast}"] & \text{Bu}_{\text{ads}} \arrow[d, "\text{fast}"] \\
\text{n-BuOH}_{\text{gas}} \arrow[u, "\text{fast}"] & \text{n-Bu}_2\text{O}_{\text{gas}} & \text{Bu}_{\text{gas}}
\end{tikzcd}$$

The high value for the observed energy of activation for butene formation in this case arises from the preferred, intermediate formation of butyl ether and the energetic barrier to its subsequent decomposition to butene and alcohol.

Acknowledgments

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References

[1] C.D. Chang, Cat. Rev. Sci. Eng. 25 (1983) 1.
[2] C.D. Chang and A.J. Silvestri, J. Catal. 47 (1977) 249.
[3] M.G. Palekar and R.A. Rajadhyaksha, Cat. Rev. Sci. Eng. 28 (1986) 371.
[4] S.J. Gentry and K.J. Rudham, J. Chem. Soc. Faraday I, 70 (1974) 1685.
[5] P.A. Jacobs, M. Tielen and J.B. Uytterhoeven, J. Catal. 50 (1977) 98.
[6] F. Figueras, L. de Mourgues and Y. Trambouze, J. Catal. 14 (1969) 107.
[7] M.T. Aronson, R.J. Gorte and W.E. Farneth, J. Catal. 98 (1986) 434.
[8] M.T. Aronson, R.J. Gorte and W.E. Farneth, J. Catal. 105 (1987) 455.
[9] M.A. Makarova, C. Williams, V.N. Romannikov, J.M. Thomas and K.I.J. Zamaraev, J. Chem. Soc. Faraday I Sept 1989, accepted.
[10] C. Williams, M.A. Makarova, L.V. Malysheva, E.A. Paukshtis, J.M. Thomas and K.I. Zamaraev, in preparation.