Improvement in Alkene Selectivity in the Conversion of Dimethyl Ether into Hydrocarbons by Control of Absorption by Heteropoly Compounds

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In the conversion of dimethyl ether into hydrocarbons over dodecatungstophosphates, the alkene : alkane ratios in the products depend on the ability of these tungstophosphates to absorb dimethyl ether; the alkene selectivity is greatly increased as the contribution of the bulk phase of the catalysts ('pseudo liquid phase') decreases.

Heteropoly compounds readily absorb polar molecules into their structure by expanding the distance between the anions (not by adsorption into micropores).[1,2] As a result, the bulk phases of these compounds are important in some catalytic reactions such as the dehydration of alcohols.[3] This is termed 'pseudo liquid phase' behaviour,[1,2] and we believe that it is a new concept in heterogeneous catalysis. It was confirmed in the dehydration of propan-2-ol over $H_3PW_{12}O_{40}$; the absorption–desorption process was much more rapid than the dehydration reaction and a large amount of propan-2-ol was present in the bulk phase of the catalyst under the reaction conditions.[4]

In this communication, we report on the first extensive study of a catalysed reaction whose selectivity is changed by 'pseudo liquid phase' behaviour. Ono *et al.* reported that heteropolyacids catalysed the conversion of methanol into products which were mainly saturated and aliphatic.[5] We found previously that the selectivity for alkenes increased when organic salts were used.[6] With the aim of elucidating the cause of this effect and also to increase the selectivity for alkenes we carried out the conversion of dimethyl ether (DME) into hydrocarbons over several heteropoly compounds having different absorptivities for DME.

$H_3PW_{12}O_{40}$ (surface area: 5 m^2 g^{-1}) and acidic salts with Na, Cs, and NH_3 [abbreviated as $M_xH_{3-x}PW_{12}$ (M = Na, Cs, and NH_4)] were prepared by a previously described method.[3] The salts with organic bases like 1,3-diazine, 1,4-diazine, 1,3,5-triazine, and 1,4-bis(aminomethyl)benzene (base : anion 1 : 1) were also prepared as described previously,[6] and are abbreviated as 1,3-DA, 1,4-DA, TA, and 1,4-AMB, respectively. For each of these compounds the sorption (or adsorption) of DME was measured at 28 °C by using a quartz spring balance under a pressure of 93 kPa of DME after prior evacuation at 300 °C. Conversions of DME (20.2 kPa) into hydrocarbons were performed in a flow reactor at 290 °C after the catalysts were pretreated at 300 °C. The products were analysed at the stationary state of the reaction (after at least 2 h).

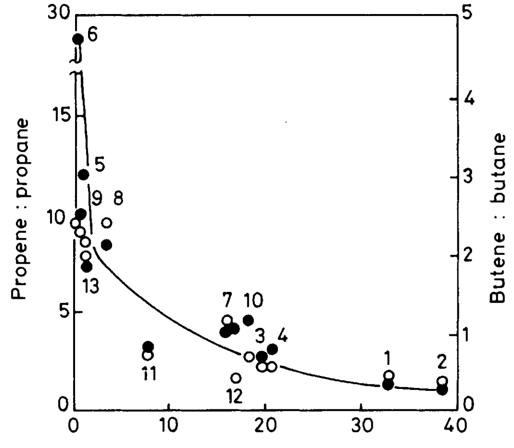

Figure 1. Alkene : alkane ratios in the product hydrocarbons [propene : propane (●); butene : butane (○) in weight] from DME conversion *vs.* absorptivity of the heteropoly catalysts which is expressed in terms of the absorption of DME in surface layer units: (1) H_3PW_{12}, (2) NaH_2PW_{12}, (3) Na_2HPW_{12}, (4) CsH_2PW_{12}, (5) $Cs_{2.5}H_{0.5}PW_{12}$, (6) $Cs_{2.85}$ $H_{0.15}$ PW_{12}, (7) $(NH_4)H_2PW_{12}$, (8) $(NH_4)_2HPW_{12}$, (9) $(NH_4)_{2.5}H_{0.5}PW_{12}$, (10) 1,4-DA, (11) 1,3-DA, (12) 1,4-AMB, (13) TA.

The products were mainly C_1—C_6 hydrocarbons, and the distribution of the carbon number was almost the same for all of the catalysts.[6] Figure 1 shows the changes in alkene : alkane ratio in the C_3- and C_4-hydrocarbons as a function of the absorptivity of the heteropoly compounds. The absorptivities were estimated from the absorptions of DME at 28 °C and are expressed in surface layer units. It was found that the alkene : alkane ratios markedly increased as the absorptivity decreased. The data in Figure 1 were estimated in the range of conversion of DME of 10—30%. In this range, the alkene : alkane ratios changed little; for example, the propene : propane ratio varied from 0.9—1.9 over $H_3PW_{12}O_{40}$. Figure 1 clearly indicates that the absorptivity is an important factor in determining selectivity. It is also of interest that $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and $Cs_{2.85}H_{0.15}PW_{12}O_{40}$ having low absorptivity and high surface areas (100—200 m^2 g^{-1}) showed higher selectivities (C_2—C_4 olefins; 64—70% by weight) than that of $H_3PW_{12}O_{40}$ (C_2—C_4 olefins; 40%) with comparable activities.

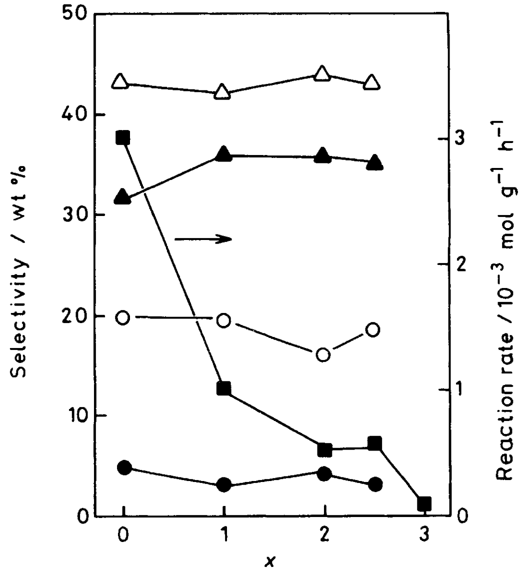

Figure 2. Reaction rate (■) and selectivity for methane (●), C_2—C_4 alkenes (△), C_2—C_4 alkanes (▲), and other, higher hydrocarbons (○) in the conversion of DME over $Na_xH_{3-x}PW_{12}O_{40}$ into hydrocarbons *vs.* the value of x in the heteropoly compound.

Besides the absorptivity, the acidity of the catalyst may be a factor in varying the selectivity. Figure 2 shows the effect of acidity on the selectivity of the conversion and the activity of the catalyst. The product distributions and alkene : alkane ratios for the Na salts were very similar to those with $H_3PW_{12}O_{40}$, while the activity decreased as the Na content increased. Since the acidity (both the amount of acid groups and acid strength) decreased as the Na content increased, and the absorptivity for DME was more or less similar among these Na salts,[3] the result in Figure 2 indicates that the effect of acidity on the selectivity is not significant in this case. Therefore, it may be concluded that the absorptivity of the catalysts is the predominant factor in determining the alkene : alkane ratios. The trend in Figure 1 can be understood as follows: alkenes formed in the bulk of the catalyst near the surface or on the surface (in $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, *etc.*) are readily desorbed, but alkenes produced deep in the bulk of the catalyst (in $H_3PW_{12}O_{40}$, the Na salts, *etc.*) undergo a significant amount of hydrogen-transfer reaction to form alkanes which are then desorbed. The formation of alkanes as secondary products from alkenes was suggested in the conversion of methanol over zeolite catalysts.[7]

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References

1 M. Misono, K. Sakata, Y. Yoneda, and W. Y. Lee, 'Proceedings of the 7th International Congress on Catalysis, Tokyo, 1980,' Kodansha-Elsevier, 1981, p. 1074; ACS/CSJ Chemical Congress, Honolulu, April, 1979.

2 M. Misono, N. Mizuno, K. Katamura, A. Kasai, K. Sakata, T. Okuhara, and Y. Yoneda, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 400.

3 T. Okuhara, N. Hayakawa, A. Kasai, M. Misono, and Y. Yoneda, *J. Catal.*, 1983, **83**, 121.

4 T. Okuhara, T. Hashimoto, M. Misono, Y. Yoneda, H. Niiyama, Y. Saito, and E. Echigoya, *Chem. Lett.*, 1983, 573.

5 Y. Ono, T. Baba, J. Sakai, and T. Keii, *J. Chem. Soc., Chem. Commun.*, 1981, 400.

6 T. Hibi, T. Okuhara, M. Misono, and Y. Yoneda, *Chem. Lett.*, 1982, 1275.

7 C. C. Chang, *Catal. Rev.*, 1983, **25** (1), 1.