July, 1985] NOTES *Bull. Chem. Soc. Jpn.*, *58*, *2155—2156 (1985)*

Heteropoly Acids Supported on Acidic Ion-exchange Resin as Highly Active Solid-acid Catalysts

Toshihide Baba,* Yoshio Ono,† Tadao Ishimoto, Shun-ichi Moritaka, and Seiichi Tanooka
Department of Industrial Chemistry, Kochi Technical College, Monobe, Nankoku, Kochi, 783
†*Department of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo, 152*

(Received December 12, 1984)

Synopsis. Heteropoly acids supported on a macroreticular acidic ion-exchange resin shows much higher activity than those supported on activated carbon for the synthesis of methyl *t*-butyl ether and the esterification of acetic acid with 1-pentanol. This high activity can plausibly be attributed to the interaction of heteropoly anions with substrates which are protonated by the protons of the acidic resin.

Heteropoly acids are very effective as catalysts for a variety of acid-catalyzed reactions.[1–4] They can be used as homogeneous as well as heterogeneous catalysts. In order to use them as solid-acids, however, it is desirable to support them on an appropriate carrier, since their surface areas are small. Izumi *at al.*[5] have reported that heteropoly acids supported on silica gel or activated carbon exhibit high catalytic activities for the alkylation of benzene with ethylene, the esterification of acetic acid with ethanol, and the dehydration of 2-propanol. It has also been reported that heteropoly acids and their salts supported on silica or activated carbon are effective in forming methyl *t*-butyl ether (MTBE) from isobutene and methanol in the vapor phase.[6–8] Here, we wish to report that heteropoly acids supported on an acidic ion-exchange resin become very active catalysts for some acid-catalyzed reactions, namely, MTBE synthesis and esterification.

The catalysts were prepared as follows. Heteropoly acid was dissolved in water, and a macroporous acidic resin, Amberlyst-15, was added to the solution. The suspension was kept overnight and then dried by evaporation. The reactions were carried out with a continuous-flow reactor operating at atmospheric pressure. The catalyst was packed in a reactor of silica tubing (10 mm i.d.) placed in a vertical furnace. Liquid reactants were delivered by means of a motor-driven syringe and vaporized in the preheating zone of the reactor containing 10 cm^3 of quartz chips. Isobutene was fed through a flowmeter. The products were analyzed by means of gas chromatography.

Table 1. Catalytic activities of heteropoly acids supported on Amberlyst-15 and activated carbon

Catalyst	Isobutene conversion/%	Selectivity to MTBE/%
$H_4SiW_{12}O_{40}$/Amberlyst-15	42.0	99.7
$H_3PW_{12}O_{40}$/Amberlyst-15	38.7	99.8
$H_3PMo_{12}O_{40}$/Amberlyst-15	18.0	100
Amberlyst-15	11.0	100
$H_4SiW_{12}O_{40}$/activated carbon	2.1	100

Reaction conditions: 323 K, $W/F = 0.50$ g h mol^{-1}, isobutene pressure, 25.3 kPa; methanol pressure, 25.3 kPa; 30 wt% heteropolyacids supported.

In Table 1, the catalytic activities of heteropoly acids (30 wt%) supported on Amberlyst-15 are compared with those of dodecatungstosilicate (TSA) supported on activated carbon and Amberlyst-15 itself. Every heteropoly acid supported on Amberlyst-15 was much more active than Amberlyst-15 itself, TSA supported on the resin being most active. It is also worthy of note that TSA on Amberlyst-15 is far more active than TSA on activated carbon. In all cases, the catalytic activities did not change with time on stream for at least 8 h. The selectivity to MTBE is very close to 100%. The other detectable products are isobutene dimers. No formation of dimethyl ether was observed in any case.

The dependence of the isobutene conversion and the selectivity to MTBE on the amount of supported TSA on Amberlyst-15 is illustrated in Fig. 1. The isobutene conversion increased with the increase in the supported amount and reached a maximum at 30 wt%, where the selectivity to MTBE was 99.7%. The catalysts with less activity showed a 100% selectivity.

The dependence of the isobutene conversion to MTBE on the contact time for the reaction over Amberlyst-15, TSA(30 wt%) on Amberlyst-15, and TSA(30 wt%) on activated carbon, is shown in Fig. 2. The relative activity of the three catalysts was estimated from the rate of the reaction at lower contact times as follows; TSA/activated carbon: Amberlyst-15:TSA/Amberlyst-15=1:13:33. In every case, the isobutene conversion increased with the contact time and approached to a constant value

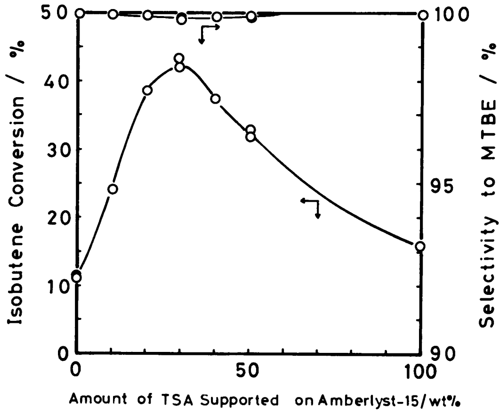

Fig. 1. Change in isobutene conversion and selectivity to MTBE with supported amount of TSA on Amberlyst-15. Reaction conditions: 323 K, $W/F = 0.50$ g h mol^{-1}, isobutene pressure 25.3 kPa, methanol pressure 25.3 kPa, nitrogen pressure 50.7 kPa.

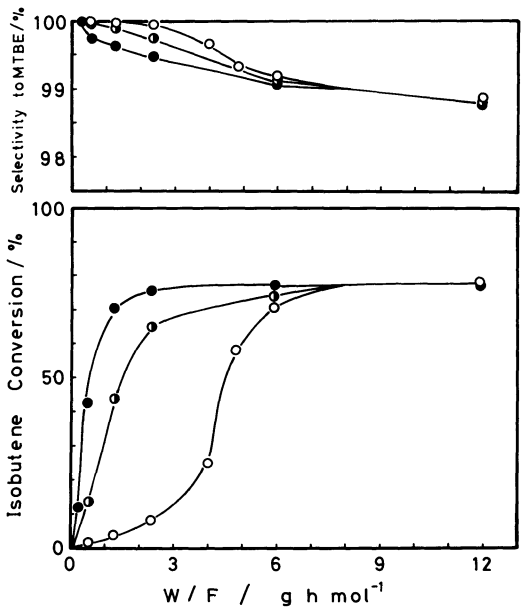

Fig. 2. Effect of contact time on isobutene conversion and selectivity to MTBE. (●): TSA (30 wt%) supported on Amberlyst-15, (○): Amberlyst-15, (◑): TSA (30 wt%) supported on activated carbon. Reaction conditions: 323 K, isobutene pressure 25.3 kPa, methanol pressure 25.3 kPa, nitrogen pressure 50.7 kPa.

because of the limitation by the thermo-dynamic equilibrium.

The reaction temperature was varied in the range of 323—373 K. The highest yield, 57%, was obtained at 333 K. The decrease in the MTBE yield at higher temperatures is due to the limitation by the thermodynamic equilibrium. The selectivity to MTBE was 100% at and below 333 K, but it dropped at higher temperatures as a result of the dimerization of isobutene.

To further test the efficiency of heteropoly acid supported on the ion-exhange resin, the esterification of acetic acid with 1-pentanol to form pentyl acetate in the vapor phase was carried out at 378 K over Amberlyst-15, TSA supported on Amberlyst-15, and TSA supported on activated carbon. As is shown in Fig. 3, the catalytic activity did not change with time on stream in any cases. Heteropoly acid supported on Amberlyst-15 showed a much higher activity for the esterification than the resin itself and also than that supported on activated carbon. Thus, the 1-pentanol conversion over Amberlyst-15 (13.6%) was increased up to 22.4% by supporting TSA(30 wt%) on the resin. The selectivity to pentyl acetate was 100% in every case.

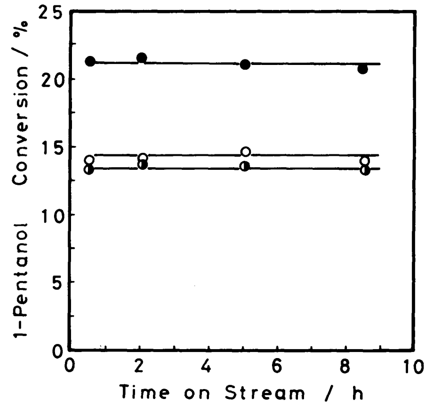

Fig. 3. Change in 1-pentanol conversion in the esterification from acetic acid and 1-pentanol. (●): TSA (30 wt%) supported on Amberlyst-15, (◑): Amberlyst-15, (○): TSA (30 wt%) supported on activated carbon. Reaction conditions: 378 K, $W/F=9.33\times10^{-2}$ g h mol^{-1}, acetic aicd pressure 15.1 kPa, pentyl alcohol pressure 15.1 kPa, nitrogen pressure 70.7 kPa.

Izumi and his coworkers1,8) found that heteropoly acids show a much higher catalytic activity for many reactions as homogeneous catalysts than do sulfuric acid or *p*-toluenesulfonic acid and attributed the higher activity to the interaction of heteropoly anions and substrates or protonated substrates. For example, they postulated the existence of a protonated butene-heteropoly anion complex in the hydration of 1-butene.1)

The interaction between the heteropoly anion and substrate (or protonated substrate) should be important also in the reactions over hereropoly acids supported on carriers. In the case of heterogeneous systems, it seems of the utmost importance that protons and heteropoly anions exist in close proximity. Protons originating from heteropoly acids naturally satisfy this condition. In addition, in the heteropoly acid/ion-exchanger system, protons originating from the ion-exchanger also can interact with supported heteropoly anions, and they exhibit a higher activity than those of the resin not supported by the anions. This may explain the high activity of heteropoly acid–acid resin composite catalysts.

References

1) Y. Izumi, K. Matsuo, and K. Urabe, "The Chemistry and Uses of Molybdenum, Proceedings, 4th International Conference on Catalysis," Section V-B, Golden (1982), p. 289.

2) M. Misono, "The Chemistry and Uses of Molybdenum, Proceedings, 4th International Conference on Catalysis," Section V-B, Golden (1982), p. 302.

3) I. V. Kozhevnikov and M. I. Matveev, *Applied Catal.*, **5**, 135 (1983).

4) Y. Ono, M. Taguchi, Gerile, S. Suzuki, and T. Baba, "Stud. Surface Sci. Catal.," ed by B. Imelik *et al.*, Elsevier, Amsterdam (1984), in press.

5) Y. Izumi, R. Hasebe, and K. Urabe, *J. Catal.*, **84**, 402 (1984).

6) A. Igarashi, T. Matsuda, and Y. Ogino, *J. Jpn. Pet. Inst.*, **22**, 331 (1979).

7) T. Matsuda, A. Igarashi, and Y. Ogino, *J. Jpn. Pet. Inst.*, **23**, 30 (1980).

8) Y. Ono and T. Baba, Proc. 8th International Congress on Catalysis, Berlin, Vol. 5, Verlag Chemie, Weinheim (1984), p. 405.

9) Y. Izumi, K. Matsuo, and K. Urabe, *J. Mol. Catal.*, **18**, 299 (1983).