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# SELECTIVE CATALYTIC HYDROGENATION OF PROPARGYL ALCOHOL WITH HETEROPOLY ACID-MODIFIED PALLADIUM

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The Keggin type heteropoly acid was readily reduced with hydrogen in the aqueous phase at 30°C in the presence of Pd(II) or metallic Pd, taking up 1 to 11 molecules of hydrogen per Keggin unit. The palladium catalyst prepared by the $H_2$-reduction of an aqueous solution containing Pd(II) and heteropoly acid was very effective for the aqueous-phase selective semihydrogenation of propargyl alcohol.

The Keggin type heteropoly acid (HPA) has been applied as catalyst to several acid-catalyzed reactions and oxidation processes owing to its dual character of strong acidity and oxidizing ability. We have recently studied the homogeneous catalyses of HPA in order to elucidate its catalytic features at the molecular level.[1~6] We now report a novel attempt of modifying palladium with HPA to effect the partial hydrogenation of an acetylenic compound, together with a unique behavior of HPA when it undergoes $H_2$-reduction in an aqueous phase.

All experiments were performed in a liquid-phase closed system at 30°C under atmospheric pressure. An aqueous solution containing $PdSO_4$, HPA and $H_2SO_4$ (20 ml, pH=1.0 ~ 1.9) was contacted with hydrogen with vigorous stirring. After the completion of hydrogen uptake, 0.1 ml of propargyl alcohol was fed into the solution, and the hydrogenation reaction was initiated under 1.0 atm of hydrogen. A small portion of the solution was withdrawn periodically and analyzed by means of g.l.c.

## Reduction of aqueous HPA with hydrogen

All the HPA tested, $H_3PMo_{12}O_{40}$ (abbreviated as $PMo_{12}$), $H_3PMo_6W_6O_{40}$ ($PMo_6W_6$) and $H_3PW_{12}O_{40}$ ($PW_{12}$), underwent $H_2$-reduction with ease in the presence of Pd(II) ions, and their solutions promptly turned blue ($PW_{12}$) or brownish black ($PMo_{12}$ and $PMo_6W_6$). It has been known that Pd-carbon accelerates the $H_2$-reduction of $PMo_{12}$ and $PMo_6W_6$ in the vapor phase.[7,8] Neverthless it should be noted that even $PW_{12}$, which is insensible to the vapor-phase $H_2$-reduction at lower temperatures,[8] could be readily reduced in the aqueous phase at ambient temperature. It is also interesting that $PMo_6W_6$ and $PMo_{12}$ took up such large amounts of hydrogen as 5 to 11 molecules per Keggin unit (Fig. 1).[9] Some of the hydrogen molecules trapped in HPA appeared fairly mobile: e.g., the hydrogen gas corresponding to 30 to 40% of the total uptake was evolved from the reduced $PMo_{12}$ either on evaccuation at ambient temperature or on heating at 70°C.

Pd-carbon (Pd=5 wt%, Mitsuwa Pure Chemicals Co.) also efficiently catalyzed the $H_2$-reduction of aqueous $PMo_6W_6$ in the same manner as Pd(II). On the other hand, when the Pd that was prepared beforehand by the $H_2$-reduction of aqueous $PdSO_4$ to form large particles of the metal was applied to the $H_2$-reduction of $PMo_6W_6$, the hydrogen uptake noticeably slowed down. It may be, therefore, deduced that aqueous $PMo_{12}$ or $PMo_6W_6$ facilitated the conversion of Pd(II) into such a finely dispersed metal as the palladium on carbon, and thus formed Pd in turn accelerated the $H_2$-reduction of HPA.

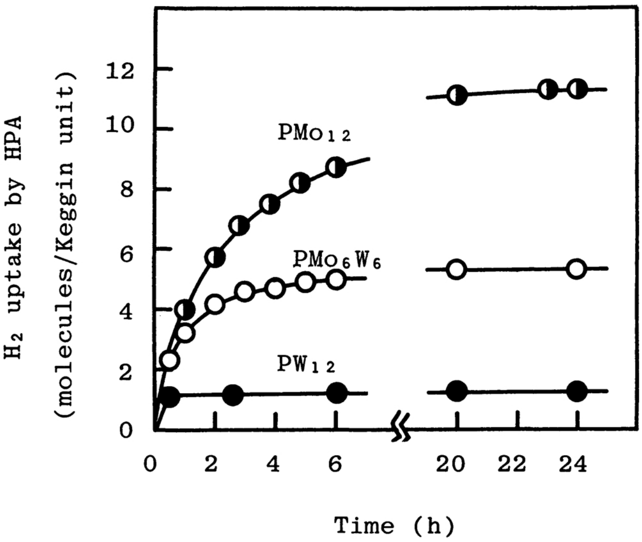

Fig. 1 $H_2$-reduction of HPA in the presence of Pd(II) in the aqueous phase at 30°C and 1.0 atm. $PdSO_4$: $6 \times 10^{-3}$M, HPA: $2 \times 10^{-2}$M.

The reduced $PMo_6W_6$ solution remained homogeneous in appearances, whereas a considerable amount of brown precipitate was separated when $PMo_{12}$ was reduced. In the case of the reduction of $PW_{12}$, metallic palladium was formed obviously. All of the HPA maintained their Keggin structures throughout the reduction treatment, which were ascertained by examining their IR spectra: upon reduction considerable decrease in absorbance were observed with P-O and M-O-M (M=Mo, W) bands.

Hydrogenation of propargyl alcohol

Figure 2 represents a typical reaction pattern of the hydrogenation of propargyl alcohol in the aqueous phase catalyzed by a system that was obtained from the $H_2$-reduction of an aqueous solution containing Pd(II) and $PMo_{12}$ (hereinafter denoted as $[Pd(II)\text{-}PMo_{12}]_{red}$). At an earlier stage of the reaction, allyl alcohol was produced selectively until its yield attained 96 mole %, and followed by further hydrogenation to 1-propanol.

The systems of $[Pd(II)\text{-}PMo_6W_6]_{red}$ and $[Pd(II)\text{-}PW_{12}]_{red}$ also revealed high selectivity, though the latter was less efficient in terms of the reaction rate (Fig. 3). On the other hand, a system $[Pd\text{-}PMo_6W_6]_{red}$ that

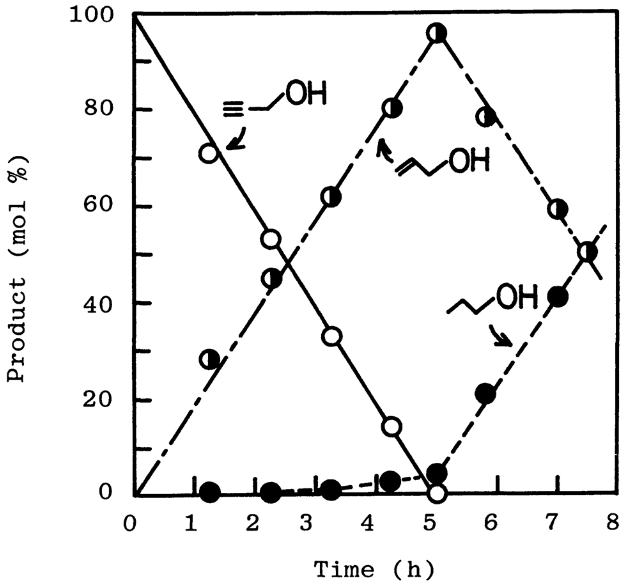

Fig. 2 Hydrogenation of propargyl alcohol by $[Pd(II)\text{-}PMo_{12}]_{red}$ at 30°C. $PdSO_4$: $6 \times 10^{-3}$M, $PMo_{12}$: $2 \times 10^{-2}$M, propargyl alcohol: $8.7 \times 10^{-2}$M.

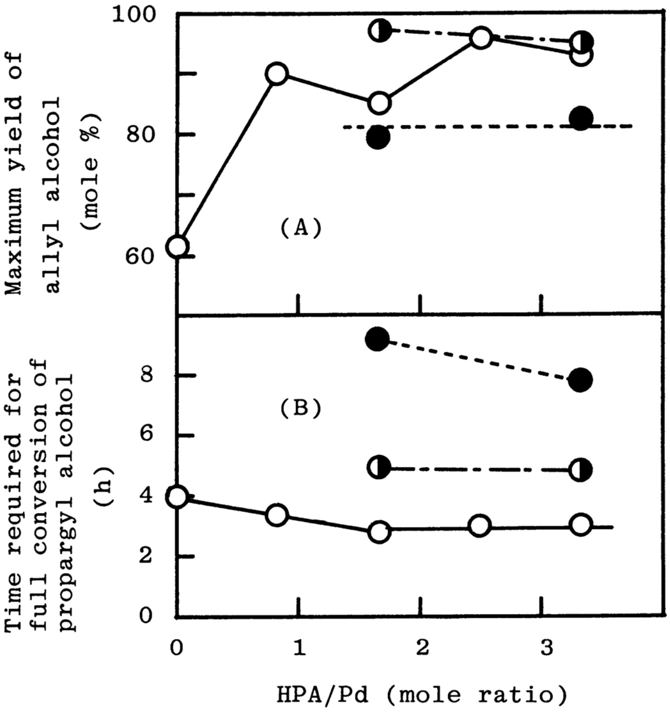

Fig. 3 Dependence of activity and selectivity on HPA/Pd mole ratio in hydrogenation of propargyl alcohol. $PdSO_4$: 6 x $10^{-3}$M, propargyl alcohol: 8.7 x $10^{-2}$M, ○: $[Pd(II)\text{-}PMo_6W_6]_{red}$, ◑: $[Pd(II)\text{-}PMo_{12}]_{red}$, ●: $[Pd(II)\text{-}PW_{12}]_{red}$, at 30°C.

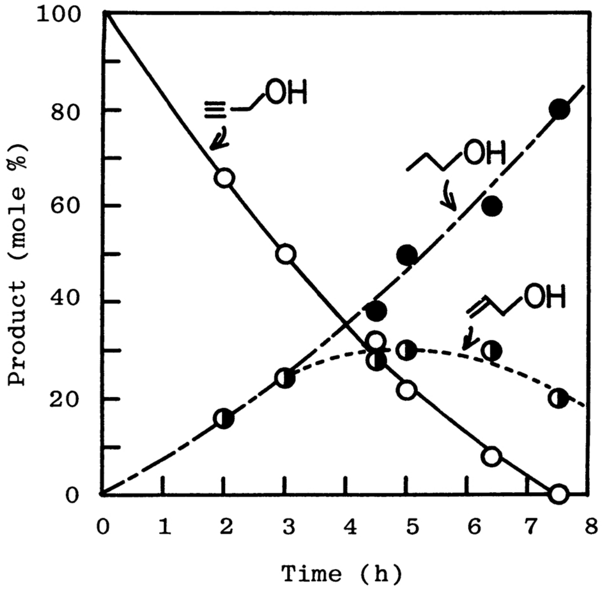

Fig. 4 Hydrogenation of propargyl alcohol by $[Pd\text{-}carbon\text{-}PMo_6W_6]_{red}$ at 30°C.
Pd: 3 x $10^{-3}$M, $PMo_6W_6$: 2 x $10^{-2}$M, propargyl alcohol: 8.7 x $10^{-2}$M.

was obtained by $H_2$-reduction of aqueous $PMo_6W_6$ in the presence of metallic Pd was not effective for the selective semihydrogenation of propargyl alcohol (Fig. 4).

These facts imply that Pd might be subjected to substantial modification with HPA in $[Pd(II)\text{-}HPA]_{red}$ systems, but not in $[Pd\text{-}HPA]_{red}$ systems, to work as a selective catalyst for the semihydrogenation of acetylenic compounds. This modifying effect of HPA suggests a strong coordinative property of the reduced HPA anions on Pd. Among the HPA tested, $PMo_6W_6$ was most effective for the activity of resulting catalyst (Fig. 3B). This is probably because the $[Pd(II)\text{-}PMo_6W_6]_{red}$ system was kept homogeneous during the $H_2$-reduction and the successive hydrogenation reaction.

The variation in pH of the $[Pd(II)\text{-}PMo_6W_6]_{red}$ catalyst system between 1.3 and 1.9 gave little influence on the selectivity as well as on the rate of the semihydrogenation. The effect of the HPA/Pd mole ratio on the selectivity was not so critical in the ratio greater than 1.0, although the reaction rate inclined somewhat to increase until the ratio of about 2 (Fig. 3).

In acetylenic simihydrogenation, Pd loaded on $BaSO_4$ is often applied. Through a separate experiment using a Pd-$BaSO_4$ catalyst which was prepared by a known method[10)] (Fig. 5), the $[Pd(II)\text{-}PMo_{12}]_{red}$ and $[Pd(II)\text{-}PMo_6W_6]_{red}$ systems proved to be comparable to Pd-$BaSO_4$ with respect to both activity and selectivity in the semihydrogenation of propargyl alcohol.

The isopolymolybdate anions which were obtained by the condensation of $MoO_4^{2-}$ ions in an acidic aqueous solution (pH=1.5) were likewise reducible with hydrogen in the presence of Pd(II), and the hydrogen uptake per Mo atom was almost the same as in the system of $[Pd(II)-PMo_{12}]_{red}$. This [Pd(II)-isopolymolybdate]$_{red}$ system was reasonably selective toward the semihydrogenation, giving a maximum yield of allyl alcohol of 90 mole %. But the reaction rate was extremely low: about a third of the rate observed with the $[Pd(II)-PMo_{12}]_{red}$ system at the same concentrations in terms of Pd and Mo. On the other hand, $MoO_4^{2-}$ ions in a basic solution (pH=9.7) took up only 0.03 molecules of hydrogen per Mo atom in the presence of Pd(II), and the resulting $[Pd(II)-MoO_4^{2-}]_{red}$ catalyst system was almost non-selective in the semihydrogenation.

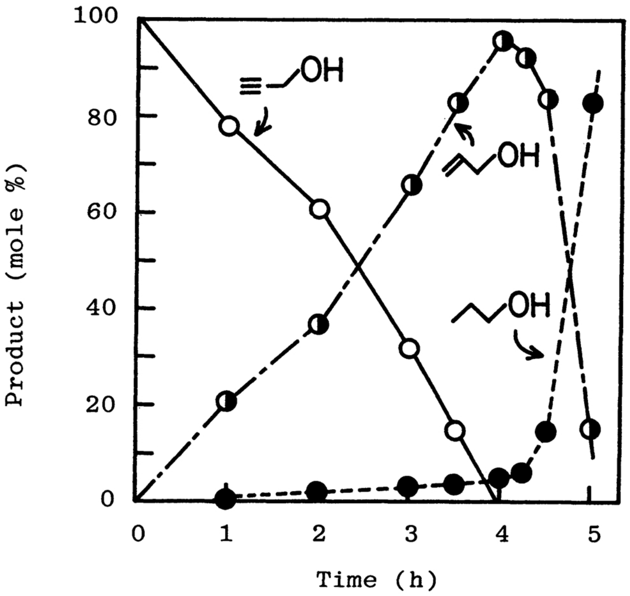

Fig. 5 Hydrogenation of propargyl alcohol by $Pd-BaSO_4$ at 30°C. Pd: $5.3 \times 10^{-3}$M, propargyl alcohol: $8.7 \times 10^{-2}$M.

It is, therefore, concluded that heteropoly anions reveal an excellent modifying effect on palladium in catalytic acetylenic semihydrogenation.

## References

1) Y. Izumi and K. Hayashi, Chem. Lett., 1980, 787.
2) Y. Izumi and K. Urabe, ibid., 1981, 663.
3) K. Matsuo, K. Urabe, and Y. Izumi, ibid., 1981, 1315.
4) K. Urabe, F. Kimura, and Y. Izumi, Shokubai, 22, (1), 10(1980).
5) K. Urabe, K. Fujita, and Y. Izumi, ibid., 22, (4), 223(1980).
6) K. Urabe, F. Kimura, and Y. Izumi, Proc. 7th Intern. Congr. Catalysis, Tokyo, 1980, Kodansha, Tokyo, Elsevier, Amsterdam, 1981.
7) S. Yoshida, H. Niiyama, and E. Echigoya, Shokubai, 22, (4), 220(1980).
8) K. Katamura, T. Nakamura, K. Sakata, M. Misono, and Y. Yoneda, Chem. Lett., 1981, 89.
9) In the absence of HPA, aqueous $PdSO_4$ was reduced with hydrogen taking up 1.5 molecules of hydrogen per Pd atom at pH=1.4. This amount of hydrogen was only 3.8% of the total hydrogen uptake observed in the $H_2$-reduction of $Pd(II)-PMo_{12}$ system.
10) R. Mozingo, "Organic Synthesis", Coll. Vol. III, p.685(1955).

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