THE IMPORTANT ROLE OF THE BULK OF 12-TUNGUSTOPHOSPHORIC ACID IN THE CATALYTIC DEHYDRATION OF ALCOHOLS TO OLEFINS

Toshio OKUHARA, Atsushi KASAI, Nobukiyo HAYAKAWA,[1]
Makoto MISONO[*], and Yukio YONEDA
Department of Synthetic Chemistry, Faculty of Engineering,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

Organic compounds containing oxygen and nitrogen like alcohols and pyridine were readily incorporated into the bulk of heteropoly acids, while hydrocarbons such as butenes and benzene were adsorbed only on the surface. It was found in the dehydration of ethanol over $H_3PW_{12}O_{40}$ that ethylene was yielded predominantly from absorbed ethanol in the bulk, whereas diethyl ether was formed on the surface.

It is known that heteropoly compounds, which have both acidic and oxidative properties, catalyze many kinds of reactions such as dehydration of alcohols,[2] Friedel-Crafts type reaction,[3] oxidative dehydrogenation[3] and partial oxidation of organic compounds.[2,5] Recently, it has been reported that $H_3PW_{12}O_{40}$ catalyzes the conversion of methanol into hydrocarbons[6] and that $H_3PMo_{12}O_{40}$ is effective as an oxidant in the catalytic oxidation of 1-butene with Pd-salts.[7] We already reported that heteropoly acids such as $H_3PMo_{12}O_{40}$ and $H_3PW_{12}O_{40}$ were almost pure Brönsted acids.[8] The latter exhibited the most strong acidity among heteropoly acids having the Keggin structure, and was more active than SiO_2-Al_2O_3 by a factor of about 2000 for the dehydration of 2-propanol.[2,9]

In view of the fact that the organic molecules like acetone, alcohols and pyridine are readily absorbed into the bulk of heteropoly acids, we pointed out the possibility that reactions take place in the bulk near the surface.[5a,10] Some evidence to support this idea has recently been presented.[11] In the present communication, we wish to report new evidence which demonstrates clearly the role of the bulk in the catalytic reactions.

Two samples of $H_3PW_{12}O_{40}$ were used in this work. One was synthesized by a conventional method.[12] The other sample was obtained from Nippon Muki Kagaku Ltd. and was purified by extraction with diethyl ether and recrystallization from water. These two samples exhibited the same IR spectrum and catalytic behavior. The surface area of the sample evacuated at 300°C was about 5 m^2/g as measured by BET method. Absorption (and/or adsorption) was measured by use of a quartz spring balance for pyridine, benzene, toluene and 2-propanol, and by a volumetric method for NH_3, ethylene, 1-butene, methanol, and ethanol. The catalytic dehydration of ethanol was carried out in a circulating system (188 ml) connected to an on-line gas-chromatograph. The activities for the isomerization of butenes and the dehydration of 2-propanol were determined by use of pulse and flow method, respectively.

Table 1.   Absorption(adsorption) of
various gases into(on) $H_3PW_{12}O_{40}$ [a]

gas	Numbers of ab(ad)sorption molecule/K.U.[b]
Pyridine	6.0
Ammonia	3.2
2-Propanol	6.3
Ethanol	6.2
Methanol	2.2
Benzene	0.1 (0.8)[c]
Toluene	0.04 (0.4)
1-Butene	0.2 (1.1)
Ethylene	0.03 (0.05)

a) $H_3PW_{12}O_{40}$ was pretreated by evacuation at 130°C.
b) Irreversible absorption at r.t.
c) The values in parentheses mean the surface coverage.

Fig. 1   Thermal desorption of ethanol from $H_3PW_{12}O_{40}$.
$H_3PW_{12}O_{40}$(0.6 g) was pre-evacuated at 130°C.

The amounts of irreversible absorption (or adsorption) of various gases into (or on) $H_3PW_{12}O_{40}$ are listed in Table 1.   Alcohols, pyridine and NH_3 were readily incorporated into the bulk of $H_3PW_{12}O_{40}$, the number of absorbed molecules per Keggin unit (K. U.) was ca. 3 for NH_3 and 6 for pyridine and alcohols except methanol.   In contrast with this, hydrocarbons like ethylene, 1-butene, benzene and toluene were adsorbed only on the surface.   Since absorption of gases into the bulk of ordinary solid oxide does not take place, heteropoly acids are unique in the high ability of absorption.[5a]

We attempted in this work to elucidate the roles which the molecules incorporated into the bulk play in the catalytic reactions.   First, thermal desorption was carried out in order to examine the reactivity of ethanol absorbed in $H_3PW_{12}O_{40}$.   A typical result is shown in Fig. 1.   Ethylene began to appear near 70°C, and its amount reached a maximum at 75 - 100°C.   Heating above 130°C yielded various hydrocarbons such as ethane, propene, propane, methane and n-butane.   These hydrocarbons seem to be formed by the reaction of ethylene in the bulk, probably by the decomposition of oligomers formed from ethylene, because only a very small amount of hydrocarbons besides ethylene was observed on thermal desorption from $H_3PW_{12}O_{40}$ which had been kept in contact with ethylene (183 mmHg) at 200°C for 1.5 h.

When diethyl ether (400 mmHg) was introduced over $H_3PW_{12}O_{40}$ at room temperature, diethyl ether was readily absorbed into the bulk (4.8 molecules per K. U.).   By subsequent thermal desorption, it was desorbed mainly as diethyl ether in the temperature range from 25 to 130°C and ethylene appeared at 100 - 160°C.   However, diethyl ether was scarcely detected during the thermal desorption of ethanol absorbed in $H_3PW_{12}O_{40}$.   These findings indicate that ethanol was not converted to diethyl ether in the bulk during the thermal desorption.

Figure 2 shows the time course of the catalytic dehydration of ethanol over $H_3PW_{12}O_{40}$ at 100°C.   In contrast to thermal desorption, catalytic reaction yielded diethyl ether in preference to ethylene.   When the pressure of ethanol was increased abruptly during the catalytic reaction (indicated by an arrow in Fig. 2), the formation of diethyl ether was accelerated in proportion to the second order of the
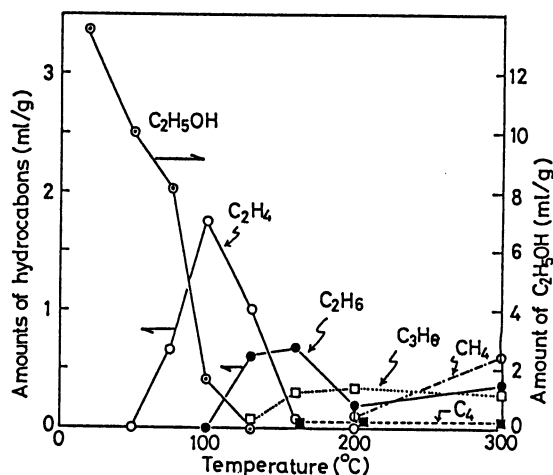
ethanol pressure.   On the contrary,
the rate of ethylene formation was not af-
fected by the change in the ethanol pres-
sure.   The amount of ethanol plus ethylene,
which were collected for 30 min after the
run by an trap kept at -196°C keeping the
catalyst at 100°C was greater than those
in the gas phase owing to the desorption
of these compounds from the bulk.   The
amount of $C_2H_5OH(a)$ was 0.5~1.0 per K.U.,
and was shown by dotted lines in Fig. 2.
Diethyl ether recovered after the run was
almost equal to that existed in the gas
phase, indicating that no diethyl ether
was produced from the bulk as in the case
of thermal desorption of ethanol.   There-
fore, the formation of diethyl ether under
the reaction conditions must have occurred
only on the surface acid sites.

Fig. 2   Dehydration of ethanol over
$H_3PW_{12}O_{40}$ at 100°C.
$H_3PW_{12}O_{40}$ (0.3 g) was
pre-evacuated at 130°C

$C_2H_5OH(a)$: ethanol held by the
catalyst (calculated)

Large difference in the pressure depend-
ence between ether and ethylene formation
cannot be explained if the two reactions
take place on the same sites.   Little dependence of the rate of ethylene formation
on ethanol pressure may reasonably be understood if one assumes that ethylene
formation predominantly occurred in the bulk of $H_3PW_{12}O_{40}$ and that the active sites
for ethylene formation in the bulk were already saturated by ethanol.

Based on these results, we propose the following scheme for the dehydration of
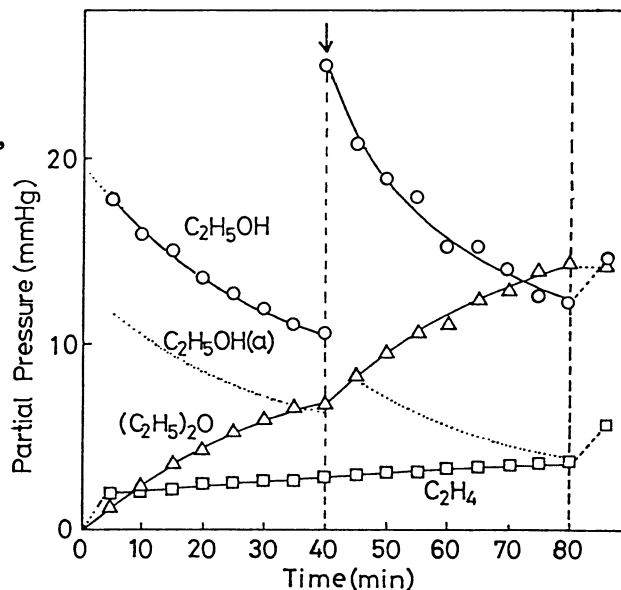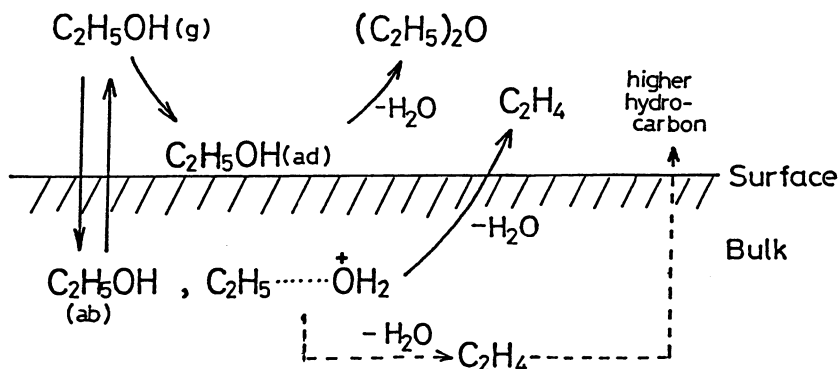

ethanol.   Two types of ethanol may be present in the bulk.   One is weakly bonded and
desorbed easily as ethanol at low temperature (<100°C), and the other is probably
protonated and is converted to ethylene at about 100°C.   Other hydrocarbons formed
at high temperature are yielded by the secondary reaction of ethylene in the bulk
as shown in the scheme.

Since butenes were not absorbed into the bulk, the isomerization of butenes
must occur on the surface.   If so, the increase in the surface area of $H_3PW_{12}O_{40}$ by

dispersing on SiO_2 should increase the rate of this reaction in proportion to the surface area of $H_3PW_{12}O_{40}$. On the other hand, the rate of dehydration of alcohols would not increase so effectively, since these reactions proceed not only on the surface but in the bulk. Figure 3 shows the changes of the rates for the isomerization of cis-2-butene and the dehydration of 2-propanol over $H_3PW_{12}O_{40}$ supported on SiO_2.

The rates of both reactions normalized to the weight of $H_3PW_{12}O_{40}$ increased by dispersion on SiO_2, but the extents of the increase were quite different. The isomerization of cis-2-butene was accelerated by a factor of about 20 at low loading levels of $H_3PW_{12}O_{40}$ compared with the unsupported $H_3PW_{12}O_{40}$, while only 4 times acceleration was observed for the dehydration of 2-propanol.

Fig.3   Activities of $H_3PW_{12}O_{40}$ supported on SiO_2 for isomerization of cis-2-butene and dehydration of 2-propanol.
● : Isomerization of cis-2-butene at 50°C
○ : Dehydration of 2-propanol at 100°C

This result also supports the idea the bulk(at least the bulk near the surface) of heteropoly acids takes part directly in the catalytic reactions like dehydration of alcohols.
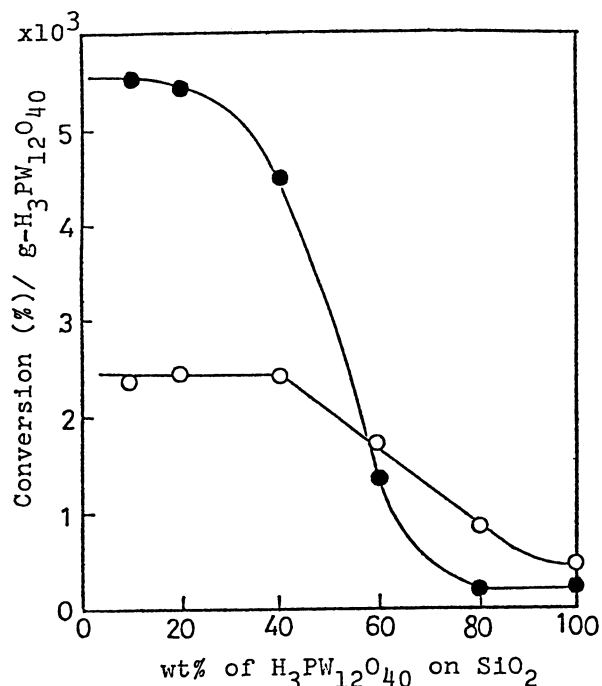
References

1) On leave from the Sumitomo Chemical Industry Co. Ltd.
2) M.Otake and T.Onoda, Shokubai, 17, 13(1975); 18, 169(1976).
   A.Igarashi, T.Matsuda and Y.Ogino, J. Japan Petrol. Inst., 22, 331(1979).
   T.Matsuda, A.Igarashi and Y.Ogino, J. Japan Petrol. Inst., 23, 30(1980).
3) R.T.Sebulsky and A.M.Henke, Ind.Eng.Chem.,Process.Res.Devel., 10, 272(1971).
   K.Nomiya, S.Sasa and M.Miwa, Bull.Chem.Soc.Jpn., 53, 2089(1980).
   K.Nomiya, H.Saijo and M.Miwa, Chem.Lett., 1980, 1075.
4) M.Otake and T.Onoda, 7th Intern.Congr.Catalysis, Tokyo, 1980, preprints B 3.
5) a)M.Misono, K.Sakata, Y.Yoneda and W.Y.Lee, 7th Intern.Congr.Catalysis, Tokyo, 1980, preprints B 27.
   b)T.Ohara, Shokubai, 19, 157(1977).
6) Y.Ono, T.Mori and T.Keii, 7th Intern.Congr.Catalysis, Tokyo, 1980, preprints C 12.
7) K.I.Matveev, E.G.Zhizhina, N.B.Shitova, L.I.Kuznetsova, Kinet.Katal., 18, 380 (1977).
   K.Urabe, F.Kimura and Y.Izumi, 7th Intern.Congr.Catalysis, Tokyo, 1980, preprints C 14.
8) M.Furuta, K.Sakata, M.Misono and Y.Yoneda, Chem.Lett., 1979, 31.
9) T.Okuhara, N.Hayakawa, A.Kasai, M.Misono and Y.Yoneda, Shokubai, 22, 226(1980).
10) K.Sakata, K.Konishi, M.Misono and Y.Yoneda, Shokubai, 21, 307(1979).
   K.Sakata, M.Misono and Y.Yoneda, Chem.Lett., 1980, 151.
11) Y.Saito, N.Yoneda, H.Niiyama and E.Echigoya, 46th Catalysis Society Meeting, Sendai, A-3P07(1980).
12) "Inorganic Syntheses," ed by H.S.Booth, McGraw-Hill(1939), Vol. 1.