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Dehydration of Alcohols on/in Heteropoly Compounds

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The dehydration of methanol, ethanol, 1-propanol, and 1-butanol were studied using 12-tungstophosphates as acid catalysts, Even "neutral" salts displayed acid-catalytic properties. A good correlation between acidic strength of the salts and their catalytic activity was established. However, several abnormal acid-catalytic behaviors were observed, namely, change of activity with process time, conversion vs *W/F* relationship, and reactivity sequence of various alcohols. In particular, the alcohols reactivity under high partial pressures was found in the order: MeOH > EtOH > 1-PrOH > 1-BuOH, while a reverse sequence was obtained under low partial pressures of alcohols. These results were reasonably interpreted in view of a pseudo-liquid phase catalysis model.

1. INTRODUCTION

Heteropoly acids and their metal salts are well known acidic and oxidative catalysts. Many potential applications have been proposed for these compounds, such as hydration of olefins (*1*), methanol conversion to hydrocarbons (*2*), oxyhydration of propene to acetone (*3*), methanol/ammonia conversion to methylamines and HCN (*4*), modified Wacker-type reaction (*5*), synthesis of MTBE (*6, 17*), and others (*7*). Most of the reactions proceed not only on the acidic form of these compounds, but also on "neutral" salts, even if the reaction is an acid-catalyzed one (*8*). In this context, it is of great importance, both practical and scientific, to study the catalytic behavior of metal salts of heteropoly acids. Several advantages are also expected by salt formation, which may lead to a bifunctional or multifunctional catalysis (*3, 9*) and a greatly improved thermal stability in some of the metal salts (*8, 10*).

As far as acid-site formation in "neutral salts" is concerned, several possibilities have been pointed out. Niiyama *et al.* have postulated that the Lewis acidity of metal cation constitutes the origin of acidic properties, while the Brønsted ones are a result of hydrolysis, in the presence of water. Recent studies, by means of photoacoustic IR spectroscopy, have revealed that these salts may also contain protons in the solid lattice (*23*). Ono *et al.* have reported for salts of reducible metal cations that cation reduction by hydrogen also leads to Brønsted acid-site formation (*11*). Misono *et al.* have suggested that the nonstoichiometry of cation/polyanion results in acidic properties (*12*). These considerations partially explain the results; however, more information is necessary for a better understanding of the acidic properties of metal salts.

A remarkable characteristic of heteropoly compounds is their ability to easily absorb polar substances, such as alcohols, ether, and nitrogen-containing bases. Catalytic reaction also takes place in the solid lattice, known as "pseudo-liquid phase catalysis" (*13*). Based on this concept, a kind of "molecular sieving effect" may be expected. This is not due to molecular size effect, as found for zeolites, but to polarity of these compounds, suggesting us many

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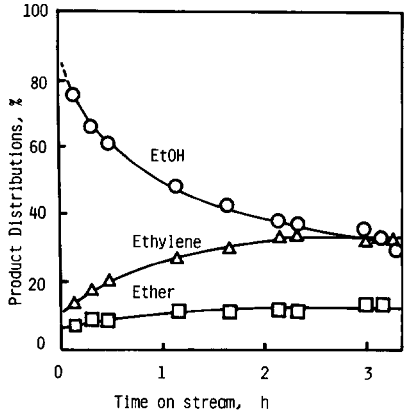

FIG. 1. Time course of ethanol dehydration on CaPW. Reaction temperature = 523 K; W/F = 15.6 g-cat h/mol; EtOH concn = 25% (balance He); pretreatment in He stream, at 400°C, for 30 min.

potential applications of these compounds.

In this paper, the acid-catalytic behaviors of 12-tungstophosphates for the dehydration of alcohols are reported. This reaction is a widely employed "test reaction" for acidic catalysis, and hence, general information regarding typical solid acid catalysts was available. Some of the abnormal behaviors found in this work can be ascribed to absorptive properties of the catalysts, while other can be satisfactorily interpreted in view of a pseudo-liquid phase catalysis model.

2. EXPERIMENTAL

2.1 Catalyst Preparation

Commerically available (Wako Pure Chemicals, reagent grade), 12-tungstophosphoric acid, abbreviated as HPW, was used as a starting material. Metal salts were prepared by double decomposition of acid and metal carbonates or nitrates, according to the procedure described by Tsigdinos (*15*). Details were given in a previous report (*8*). Prior to use, the catalyst was activated in a He stream for 30 min at 400°C.

2.2 Reaction

The dehydration of alcohols was carried out in a conventional flow type reactor under atmospheric pressure. Alcohols were fed using a syringe-type microfeeder at a concentration of 25% (mol) in helium flow, and W/F, based on the total gas flow, was 15.6 g h/mol, unless otherwise noted.

2.3 Acid Strength Measurement

The acid strength of the catalyst was determined by using Hammett indicators (*14*). For this purpose, the catalyst was pretreated in a helium stream at 400°C for 30 min, cooled to room temperature, immersed in an indicator/benzene solution, and then subjected to visual inspection. The following indicators (pK_a) were used: anthraquinone (−8.2), benzalacetophenone (−5.6), dicinnamalacetone (−3.0), benzenazodiphenylamine (+1.5), and dimethylyellow (+3.3).

3. RESULTS

Figure 1 shows the activity change of CaPW during the reaction. The total activity increased with time on stream and established a stationary value after 3 h. The selectivity ratio, ethylene/ether, did not change significantly. Most of the catalysts, including transition metal salts, showed similar behaviors. The only exceptions were MgPW and BaPW, whose stationary activities were attained from the beginning. The results reported here concern only the stationary state of the catalysts, while in some runs water pretreatment was effected in order to shorten the transition period.

The effect of various catalyst pretreatments on the activity of CaPW is given in Fig. 2. Hence, the selectivity did not change significantly was avoided in the illustration. While H_2 and isobutene pretreatment had not any effect, water pretreatment resulted in a stationary activity just from the beginning.

The plots of ethanol overall conversion against the contact time for a series of alkaline earth metal salts are shown in Fig. 3. No distinct difference was found among used catalysts, regarding the dependence of selectivity upon W/F. BaPW, SrPW, and

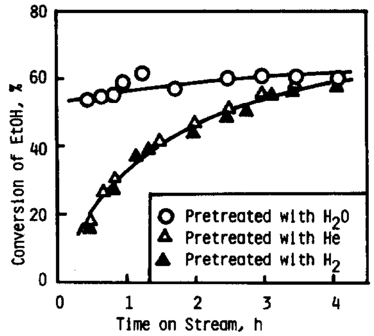

FIG. 2. Activity change with time on stream, showing the effect of various pretreatments. Reaction temperature = 523 K; *W/F* = 15.6 g-cat h/mol; EtOH concn = 25% (balance He); catalyst CaPW.

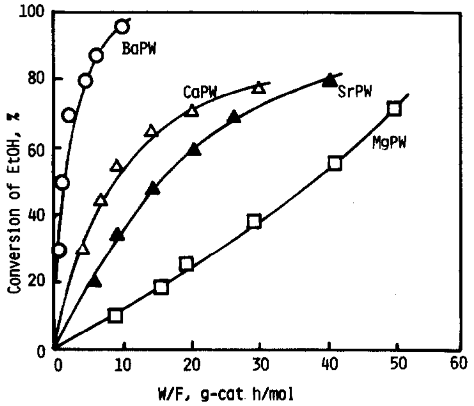

FIG. 3. Effect of contact time on ethanol overall conversion on various alkaline earth metal salts. Reaction temperature = 523 K; EtOH concn = 25%.

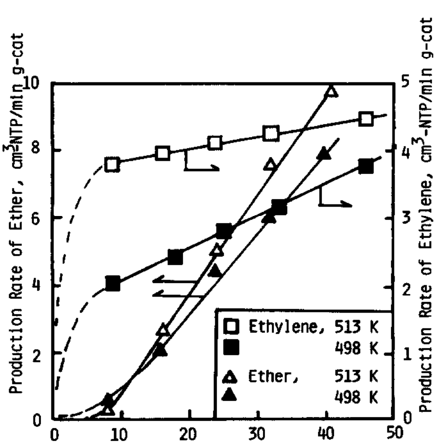

FIG. 4. Effect of ethanol inlet concentration on the rate of ethylene and ether production. Catalyst = BaPW; *W/F* = 10.5 g-cat h/mol.

CaPW showed convex curves, characteristics of a positive order reaction, while MgPW a concave one, as a result of a negative reaction order with respect to reactant concentration, or due to some acceleration effect of the product(s). Later discussion (4.2) reveals that only the latter is the case.

Figure 4 shows the effect of EtOH concentration on the production rate of ethylene and ether. The rate of ethylene formation displayed a nearly zero-order dependency, while that of ether a second-order dependency upon partial pressure of ethanol.

In Fig. 5 the dehydration of methanol (MeOH), ethanol (EtOH), 1-propanol (PrOH), and 1-butanol (BuOH) were plotted against partial pressures of each alcohol. The olefin/ether ratio varied from MeOH to BuOH depending on the length of carbon chain. In this context, dimethyl ether was the sole product in MeOH dehydration, while only traces of ether were found in the dehydration of PrOH and BuOH. The overall rate of alcohol conversion was calculated from the amount of [olefin + 2 ether] produced from each alcohol. The alcohols relative reactivity was

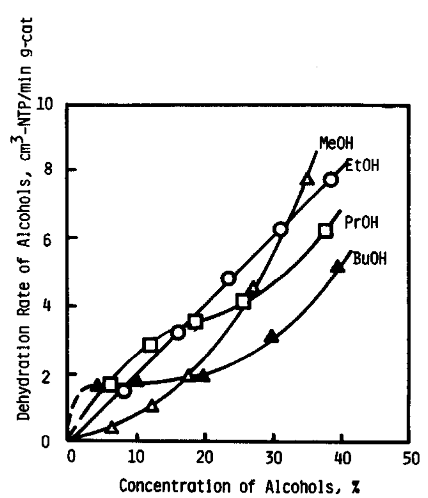

FIG. 5. The total rate of dehydration of various alcohols, as a function of inlet concentration. Catalyst = BaPW; reaction temperature = 483 K; *W/F* = 31.6 g-cat h/mol.

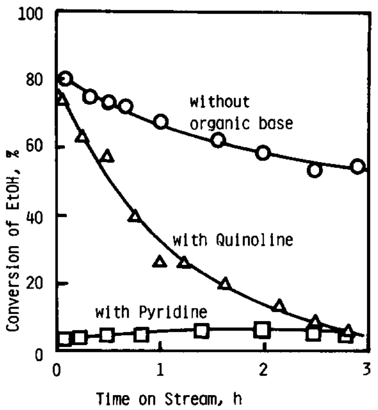

FIG. 6. Effect of organic bases on ethanol dehydration. Catalyst MgPW; reaction temperature = 553 K; reactant mixture (mol): 24% ethanol, 3% organic base, (He balance); W/F = 15.6 g-cat h/mol.

found to increase in the order: BuOH > PrOH > EtOH > MeOH under low partial pressures, in agreement with the known reactivity sequence in acid-catalyzed dehydration of alcohols [for example, (*16*)], while a reverse sequence, i.e., MeOH > EtOH > PrOH > BuOH, was obtained under higher partial pressures of alcohols, indicating a pseudo-liquid phase catalysis, which will be discussed later.

The effect of organic bases was also investigated (Fig. 6). For the sake of experimental convenience, a catalyst of lower activity was used, otherwise higher reaction temperatures should be employed to prevent possible condensation of quinoline. Pyridine showed a remarkable influence on the catalytic activity, which caused a significant decrease of conversion (less than 5%) just after the introduction. The effect of quinoline was similar, in the sense that it also suppressed the catalytic activity, but different in that the poisoning rate was much slower. Using the value of W/F and molar concentration of organic bases, the amount of organic base introduced in the catalyst bed in the first hour was calculated to 1.9 mmol, being larger than the catalyst amount (0.5 mmol), indicating that the observed slow rate of "poising" was not due to the small doses of organic base compared to the number of acid sites.

Figure 7 correlates the acid strength with the catalytic activity of heteropoly compounds. A reasonably good correlation was found. It should be noted, however, that the activity measurements have been done after the stationary state had been established, while the acidic strength ones prior to the reaction. The acidic properties undoubtedly changed by the contact of produced water. To our opinion, however, it is not unreasonable to assume a parallelism between initial and stationary activity, becase most of the catalysts have shown similar activity change profiles with process time.

Figure 8 shows the transient behaviors of the reaction, when alcohol feed stopped, after the stationary activity had been estab-

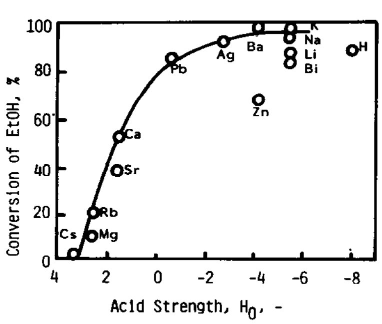

FIG. 7. Relationship between catalytic activity and acid strength of the catalysts. Reaction condition: temperature = 523 K; EtOH concn = 25%; W/F = 15.6 g-cat h/mol.

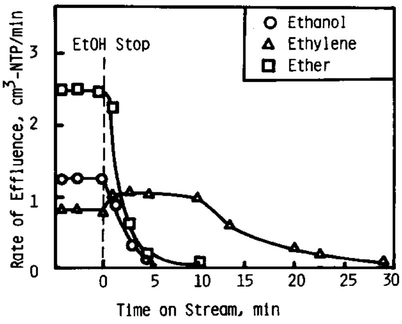

FIG. 8. Transient behaviors of effluent products from the catalyst bed, after the ethanol feed stoppage. Catalyst BaPW; reaction temperature = 498 K; W/F = 14.6 g-cat h/mol; EtOH concn = 22.6% → 0.

lished. Ether formation reduced rapidly while the ethylene one lasted for a long time. The integrated amount of ethylene produced in this case was about 1 mmol/g-cat, larger than the expected one from surface area calculations (several m^2/g).

4. DISCUSSION

Before discussing the present results, it is worth noting the general characteristics of alcohol dehydration and absorptive properties of heteropoly compounds. Some of the catalytic behaviors are quite analogous to those of typical solid acid catalysts, while some others may be, at first glance, different but can be explained in terms of the adsorptive and absorptive properties of heteropoly compounds or, in other words, pseudo-liquid phase catalysis.

It is generally accepted that dehydration of alcohols takes place on either Brønsted or Lewis acid sites. The alcohols reactivity decreases in the order: MeOH < EtOH < PrOH < BuOH, and EtOH < iso-PrOH < tert-BuOH (*17*), which can be interpreted in view of the relative stability of corresponding carbeniun ions or affinity of each alcohol to protons. On the other hand, ether formation is often observed in the dehydration of small alcohols, and the ratio of ether/olefin in the products is found to increase in the order: MeOH > EtOH > PrOH > BuOH. One of the plausible mechanism for ether formation is so-called "Rideal–Eley mechanism," in which the reaction occurs between gas-phase alcohols and adsorbed (as carbenium or oxonium ion) species (*18*).

The ability of heteropoly compounds to adsorb polar substances, such as alcohols, ethers, organic bases, etc., into their solid lattice, constitutes one of the striking features of these compounds. Readness of absorption in case of alcohols increases in the order: MeOH > EtOH > PrOH > BuOH, which is related to the polarity and bulkiness of each alcohol. Water is also absorbed into the lattice, promoting in this way the enhancement of the absorption rate of a second molecule (*19*).

4.1 Reactivity of Alcohols on/in Heteropoly Compounds

There is no doubt that the reaction proceeds via an acid-catalyzed mechanism. This fact is clearly demonstrated in Figs. 6 and 7, which are conventional procedures to examine the role of acidic sites. However, several unexpected performances were found, different from a "normal" acidic catalysis.

The STY (space time yield) vs partial pressure relationship for a series of alcohols (Fig. 5) differs from one alcohol to another. Consequently, the reactivity sequence varies with reaction conditions, and a "normal" behavior in terms of an acid catalysis, under low partial pressures can be observed. At higher pressure region, however, the reverse sequence is resulted, which can be reasonably interpreted in the way that follows.

Hence, MeOH is the alcohol most readily absorbed into the solid lattice, the number of available sites for MeOH dehydration is larger than that for BuOH, especially under a high partial pressures region. On the other hand, absorption of PrOH and BuOH do not take place significantly until pressures higher than 0.3 atm are employed. Abnormal curves observed for PrOH and BuOH can be considered as the coupling effect of a Langmuir type dependency at low-pressure regions and a parabolic one at higher pressures. The latter one is often observed during the absorption of polar substances into heteropoly compounds. It is understood that the surface catalysis predominates under low partial pressures, prevailing "intrinsic" reactivity sequence, while pseudo-liquid phase catalysis becomes important under high partial pressures giving rise to an "absorbability" sequence.

Participation of absorbed alcohol in the catalysis is also indicated in Fig. 8. The catalyst holds a quite large amount of alcohol, larger than that one expected from surface adsorption.

These considerations can also explain the different features of poisoning effects found for pyridine and quinoline. If it is assumed that the rate of absorption into solid lattice is in the order: pyridine > EtOH > quinoline, then EtOH does not have any chance to react when pyridine/EtOH mixture is fed, because every site will be occupied by pyridine before EtOH arrival. Quinoline, on the other hand, is not so readily incorporated into solid lattice, because of its lower polarity and larger molecular size. Consequently, in the presence of quinoline, EtOH has the chance to react first and poisoning effects appears as a slow rate process.

4.2 Activity Increase during the Reaction

As we have already reported (*19*), the water coexistence remarkably enhances the absorption of alcohols, explaining in this way the apparent activity increase with process time as given in Fig. 1. In the initial stage of the reaction, the catalyst does not contain so much water, while as the reaction proceeds, water is produced which in turn enhances the rate of alcohol incorporation. That means, the number of available sites for the reaction increases with time.

In collaboration with Okuhara *et al.*, the authors have pointed out that the mathematical treatment of pseudo-liquid phase catalysis is analogous to catalysis in porous particle (*20*). Based on this concept, the importance of diffusion process can be examined by evaluating the "effectiveness factor."

The generalized Thiele modulus, ϕ_s, introduced by Wagner and developed by Weisz *et al.* (*21*), can be written as follows:

$$\phi_s = (R^2/D)r_{obs}(1/C_s), \qquad (1)$$

where r_{obs} is the observed rate of reaction per unit volume of catalyst which may involve the effect of diffusion; R and D are particle radius and effective diffusivity, respectiviely; C_s is reactant concentration at the interface of solid (or pseudo-liquid) phase, which is the most distinct difference between the present analysis and that for conventional gas–porous solid catalysis. In this approach, any knowledge concerning kinetic expression is unnecessary.

In the following calculation, we made appeal at the value of $R^2D = 830$ (s) reported by Okuhara *et al.* (*20*) and an experimentally obtained rate of reaction, $r_{obs} = 4.5 \times 10^{-6}$ (mol/cm^3 s). C_s can be roughly calculated from transient response data, which indicate 1 mmol of alcohol absorbed/g catalyst, resulting in $C_s = 3 \times 10^{-3}$ mol/cm^3. In this context, $\phi_s = 1.2$ and the effectiveness factor becomes equal to 0.9. This value indicates that the reaction is close to a kinetically controlled regime, but diffusion still has an effect. One should expect a smaller value of diffusivity in the beginning, due to the lack of absorbed water, than that in later stage, but we must not forget the calculations always contain uncertainties to a considerable extent. We can say, however, it is *not unreasonable* to consider that diffusion process affects the global rate. In this case, water produced during reaction reduces the mass transfer resistance and hence, it enhances global rate of reaction.

A second explanation, but of minor importance to our opinion, for the increase of catalytic activity with time is that, produced water takes part in the formation of Brønsted acid sites, which are more active for the dehydration reaction than Lewis ones are. We have already pointed out the possibility:

$$M^{n+}(H_2O)_{m+1} \rightarrow [M(OH)]^{(n-1)+}(H_2O)_l + H^+ + (m-l)H_2O \qquad (2)$$

for the formation of Brønsted acid sites in the presence of water (*8*). This was further supported by Baba *et al.* (*11*), for nonreducible metal salts. The process may be important in the very beginning; however, we consider inadequate an attribution of the observed slow increase of the activity to hydrolysis process, which may be very fast.

Baba *et al.* have also reported a similar activity profile vs process time, in acid-catalyzed MeOH conversion to hydrocarbons on/in CuPW and AgPW. This is due to reduction of Cu^{2+} or Ag^+ to zero valent metals either by hydrogen or methanol which accompanies the formation of Brønsted acid sites, according to the following reaction:

$$Ag^+ + 1/2H_2 \rightarrow Ag^0 + H^+. \qquad (3)$$

But this is not the case of the present study, because nonreducible metal cations were employed and besides this, no effect of H_2 and isobutene pretreatment was observed (Baba *et al.* have found that H_2 prereduction resulted in a higher and stable activity just from the beginning).

The concave curve found for conversion vs. *W/F* relationship (Fig. 3 for MgPW) can be also attributed to water participation, whose effect becomes significant at a higher conversion region.

4.3 Mechanism of Ether and Ethylene Formation

It is widely accepted that the dehydration of alcohols proceeds via parallel/successive reaction paths, namely,

$$ROH \rightarrow ROR \rightarrow R'. \qquad (4)$$

Independent experiments for testing the effects of *W/F* on the yields of ethylene and ether in EtOH dehydration indicated a typical characteristic expected from Eq. (4). That is to say, the yield of ether attains a maximum at a certain *W/F* value.

In a previous report (*22*), we have proposed that ether formation may occur via a bimolecular mechanism, between chemically activated alcohol and physically sorbed one, while olefin formation takes place via an unimolecular one, represented by:

$$\begin{aligned} &ROH_{gas} \rightarrow ROH_{sorb.} \\ &ROH_{sorb.} \xrightarrow{H^+} (ROH_2)^+ \rightarrow \\ &\qquad R^+ + H_2O \rightarrow R' \\ &R^+ + ROH_{sorb.} \rightarrow ROR + H^+. \qquad (5) \end{aligned}$$

The distinct difference between the kinetic performances of ethylene and ether formation, as given in Fig. 4, can be explained by this mechanism. Ether formation must be proportional to the amount of physically sorbed alcohol, which has a nearly second-order dependency upon gas phase pressure of ethanol (*22*), while the rate of ethylene formation is proportional to the amount of ROH_2^+, which is independent of ethanol gas phase pressure, because of strong acidic properties of the catalyst.

Transient response data given in Fig. 8 can also be interpreted in view of the above mentioned mechanism. A point worth noting in Fig. 8 is that while ether formation decreases exponentially after the stoppage of ethanol feed, ethylene formation keeps a stationary value which starts to decrease 15 min after the stoppage, when the ether formation completely ceases to occur. This is a clear indication of the two important roles of sorbed alcohol, first as a ROH_2^+ or R^+ supplier "reservoir" and second as a direct participant for ether formation via a Rideal–Eley like mechanism.

Quantitative analysis of transient response data will be given elsewhere.

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