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Heterogeneous catalysis by heteropoly compounds. An attempt of molecular design of practical solid acid catalysts

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Characteristics of acid catalysis of solid heteropoly compounds (Keggin-type) have been described, with stress in our study for the design of practical catalysts based on those compounds.

Keywords: Heteropoly compounds; acid catalysis; pseudoliquid phase; solid-state NMR; dehydration of alcohols; alkylations

1. Introduction

We know that there are many demands in our society to be solved by the catalytic technology [1], but most of them are not easy to be solved by contemporary catalytic technology. On the other hand, there are many examples which show that, if a catalyst is designed at atomic level, very high efficiency if obtained. Therefore, what we need now is to synthesize new good catalysts that are designed at atomic level and prove that catalysts can cope with the societal demands.

There are several possible ways of the atomic design and synthesis of catalyst. But, if we consider the high site-density, stability, etc. required for practical catalysts, and place stress on the *synthesis* rather then *analysis*, the utilization of well-definable crystalline compounds, such as heteropoly compounds, zeolites, and perovskites, that can be active enough for the practical applications, may be most promising for the mid-term targets.

2. Merits of heteropoly compounds as catalysts

The principal advantages of heteropoly catalysts are [2]:

1) Molecularity of polyanion. This makes possible the molecular design of catalyst and the atomic description of catalytic processes.

2) Catalyst design based on acidic and redox properties. Acidity and oxidizing ability can be controlled in a systematic way.

3) The pseudoliquid and unique coordination (unique basicity) of polyanion often bring about high catalytic activity and selectivity.

Taking advantage of those merits, several large scale processes that utilize heteropoly catalysts have already been commercialized [1]. They are both in acid and oxidation catalysis either in liquid phase or in gas-solid system. The largest is the oxidation of methacrolein (240,000 ton/year).

We have studied several aspects of heteropoly catalysis. But this article will be focused on heterogeneous acid catalysis.

3. Structural characteristics and three types of catalysis of solid heteropoly compounds

As for the structure of solid heteropoly compounds, it is very important to distinguish between primary and secondary structures [2]. The primary structure consists of the heteropoly anion molecules. The secondary structure is the three-dimensional arrangement of the polyanion and cation together with crystallization of water, etc. It was very important for us to realize that the primary structure is rather stable, but the secondary structure is very variable. For example, crystallization of water can be replaced easily by other polar molecules, sometimes accompanying the lattice expansion and contraction. Tertiary structure consists of the shape of the primary particles (crystallites) and their particular aggregation that determines the surface area and the pore structure.

We have shown that there are three different types of catalysis when heteropoly compounds are used as solid catalysts (fig. 1) [2]. In the first cases, reactant molecules are adsorbed on the surface and react there (surface-type). This is the ordinary heterogeneous catalysis. In the second case, reactant molecules go into the bulk (bulk-type (I)). This is not the adsorption in micropores. The present article mainly deals with the acid catalysis of this type. The third one was found in some oxidation reactions at high temperatures (bulk-type (II)). Although the main reaction proceeds on the surface, the redox carriers (protons, electrons) migrate rapidly in the catalyst bulk [3]. In the latter two cases, the catalysis proceeds in a three-dimensional reaction field of solid bulk.

4. Experimental evidence of pseudoliquid phase and its unique catalysis

There are several experimental facts that indicate the presence of pseudoliquid [2]. Two of them will be described.

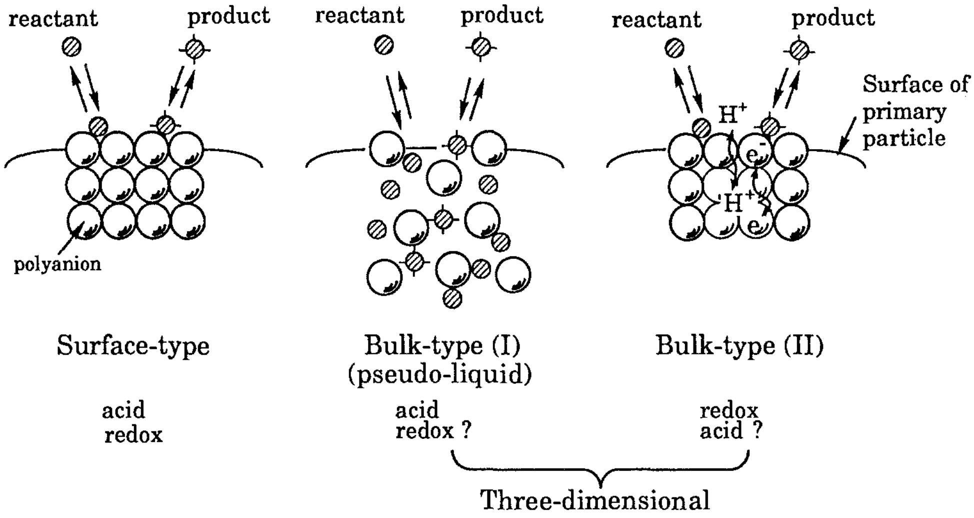


Fig. 1. Three types of catalysis of solid heteropoly compounds.

The first evidence was obtained by a transient response method using isotopically labeled alcohol [4]. The analysis shows:

(1) The amount of alcohol held by the catalyst under the reaction conditions is very large; several molecules per polyanion of the bulk.

(2) The rate of adsorption and desorption is much faster than the rate of dehydration.

The second evidence is the phase transition of the pseudoliquid phase [5]. The rate and the amount of alcohol adsorbed changes correspondingly at a certain partial pressure (fig. 2).

If the reaction takes place in the three-dimensional pseudoliquid phase, not only the active sites on the surface but also those in the bulk whose number is much greater can take part in catalysis. Moreover, the stabilization of alkyl cations in the pseudoliquid phase is inferred by the presence of a methylated polyanion complex.

Due to the two effects, very high activities are often obtained, e.g., in dehydration of alcohols, hydration, etheration and esterification [2].

5. Catalyst design

Catalytic activity and selectivity can be controlled by the acid and adsorption properties. Close correlations between the catalytic activity and the acidity have been demonstrated for several bulk-type reactions [6]. The selectivity depends also on the bulk-type property [7].

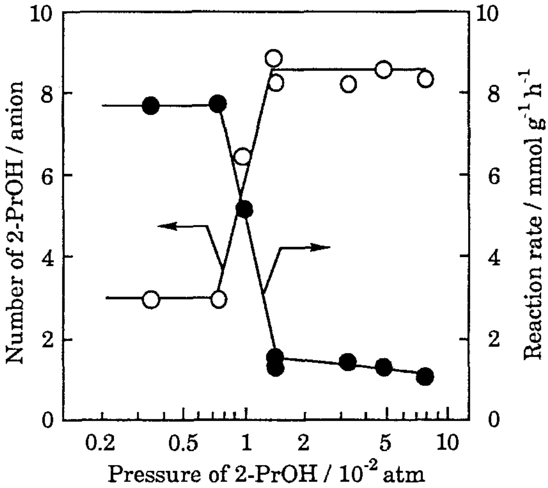


Fig. 2. Pressure dependence of reaction rate and absorption amount for dehydration of 2-propanol over $H_3PW_{12}O_{40}$ at 353 K.

Heteropoly compounds can also be used as solid catalysts in the liquid phase reactions [8,9]. In fig. 3, the catalytic activity for the decomposition of cyclohexyl acetate in xylene is plotted against the extent of Cs substitution for three protons. As the Cs content increases, the catalytic activity decreases at first, but greatly increases when the Cs content is 2.5. The reaction over Cs salts is of surface-type. There is a parallelism between the estimated surface acidity and the catalytic activity of Cs salts for the liquid-solid system (fig. 3) [9] as well as

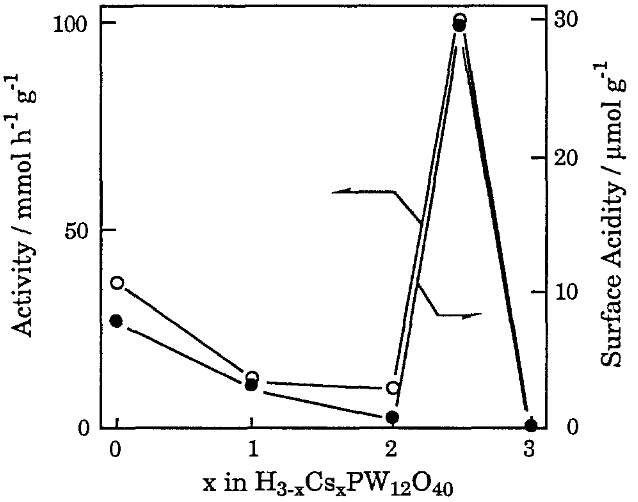


Fig. 3. Surface acidity and catalytic activity for the decomposition of cyclohexyl acetate as a function of Cs content in $H_{3-x}Cs_xPW_{12}O_{40}$.

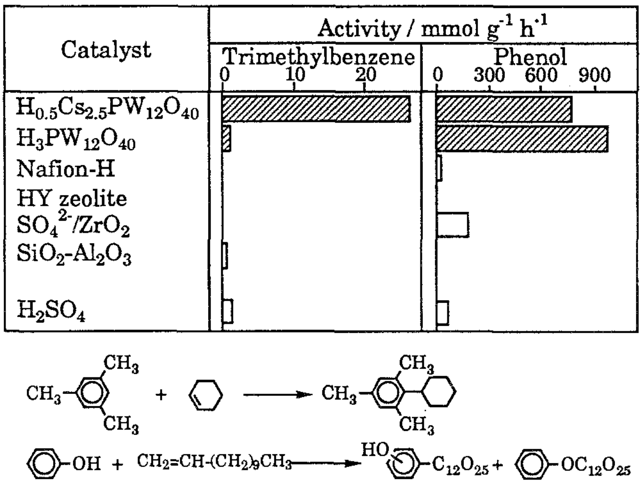


Fig. 4. Catalytic activities of several solid acids for liquid-phase reactions.

for the gas-solid system [10]. The high activity at Cs = 2.5 is due to very fine particles and a high concentration of protons on the surface [11].

The acidic Cs salt was much more active for several alkylation reactions than other solid acids such as zeolites, nafion, and sulfated ZrO_2 that have been reported to be very active, as shown in fig. 4 [12]. It is also remarkable that for the reactions of polar molecules like alkylation of phenol, the free acid is more active than acidic Cs salt. It was indicated that the pseudoliquid behavior exists also in the liquid-solid system.

6. Molecular interactions in pseudoliquid phase

The interactions of water molecules are known. In 29 hydrate, polyanions and clusters of 29 water molecules with protons constitute the ionic crystal. The hexahydrate which is rather stable has diaquoprotons connecting four polyanions. Upon further dehydration, protons move to the most basic bridging oxygen atom, often without change in the lattice structure. The adsorption and desorption of water are very rapid and the equilibrium is rapidly attained. The catalytic activity of $H_3PW_{12}O_{40}$ for butene isomerization was highest when it was hexahydrate. It is remarkable that no deactivation was observed in the case of the hexahydrate.

The next example is pyridine [2]. Heteropoly acids adsorb a large amount of pyridine. After evacuation at 298 K, the number becomes 6 per polyanion and at 403 K it becomes 3. IR shows that uniform pyridinium salt is formed as the latter stage and that the conversion between protonated pyridine dimer and monomer proceeds reversibly. The TPD data of pyridine shows that heteropoly

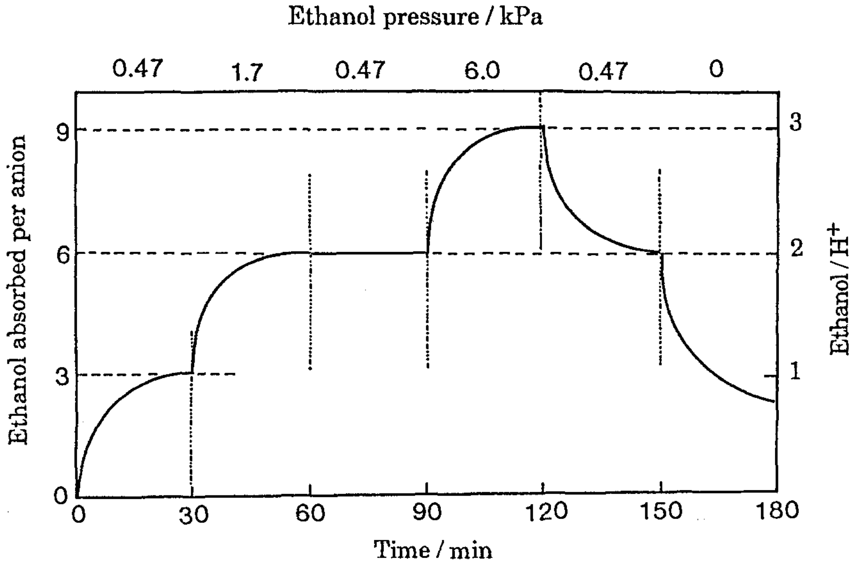
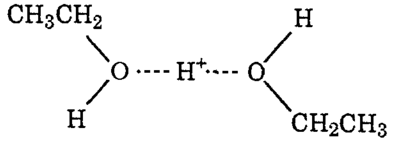


Fig. 5. Changes of the amount of ethanol absorbed in $H_3PW_{12}O_{40}$ at 333 K.

compounds are strong pure protonic acids. It was reported that the amount of pyridine adsorbed depends on the water content of poly acids [13]. We think that this happens because the rate to approach equilibrium greatly depends on the water content.



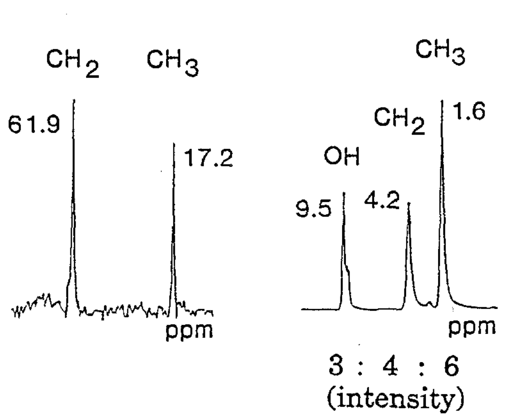


Fig. 6. Solid-state NMR spectra of $H_3PW_{12}O_{40}$ containing ethanol (ethanol/proton = 2).

Similar experiments for ethanol and $H_3PW_{12}O_{40}$ are remarkable as shown in fig. 5 [14]. The amount of ethanol adsorbed changes in a regular way. It is again noted that the number is 3, 6 and 9 per anion (ratio of ethanol to proton; 1, 2 and 3). We attempted to clarify the mode of molecular interactions by using NMR, IR, and X-ray diffraction. Due to the nearly uniform three-dimensional pseudoliquid phase, stoichiometric and spectroscopic studies make sense.

The H NMR spectra obtained by MASNMR are shown in fig. 6 [15]. The intensity ratio as well as the proton to ethanol stoichiometry is in agreement with the dimer species shown in fig. 6. The chemical shifts are close to those in super-acid. The IR spectra and C NMR were consistent with this assignment [16]. To our knowledge, well resolved H NMR of protonated ethanol was first observed for the solid catalyst.

C NMR spectra revealed the presence of protonated monomer, ethoxy and protonated ether in addition to the protonated dimer shown in fig. 6 [15].

7. Mechanism of catalytic dehydration of ethanol

Now it may be interesting to discuss how those ethanol species detected are related to the catalytic dehydration of ethanol, because this heteropoly acid is very active for dehydration of alcohols. C NMR spectra were taken with increasing temperature by using 100% ^{13}C ethanol, to shorten the time for the measurement. The dimer is the only species at room temperature, and as the temperature rises, it is transformed to protonated ethanol monomer and protonated ether, and then to a signal assignable to the ethoxy group.

Combining the thermal desorption of ethanol [6] and the NMR data, a reaction scheme in fig. 7 may be proposed. If this mechanism is true, since the relative composition of the species I, II and III depends on the partial pressure of ethanol, it is expected that at low partial pressure of ethanol ethylene is formed mainly and ether is abundant at high pressure. The experimental results

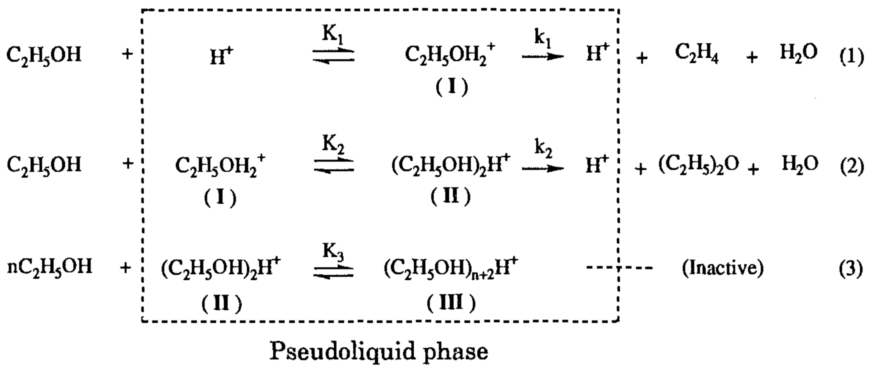


Fig. 7. Mechanism of ethanol dehydration in the pseudoliquid phase.

[17] were in agreement with our expectation. Simulation based on the scheme in fig. 7 reproduced essential features of the experimental results.

8. Future opportunities

As solid catalysts, precise adjustments of acidic, redox and bulk-type properties together with the control of tertiary structure is now possible for the molecular design of catalysts. When heteropoly compounds are used in liquid phase, phase transfer catalysis, new solvents and concentrated solutions are interesting. There are industrial processes utilizing phase transfer systems, e.g., polymerization of THF and epoxidation of olefins.

To change the primary structure is still more interesting. Heteropoly acids described here are limited to those of the Keggin-type. However, there are many other heteropoly acids. Even for the Keggin structure we can substitute one or more of the constituent metal elements with other elements at desired positions. The mixed coordination of Mo and W remarkably accelerates the oxidation of cyclopentene to glutalaldehyde [18]. The combination of poly acids with organometallics is also interesting [19].

Thus, owing to several advantageous properties of heteropoly compounds, the future potential of heteropoly as catalysts may be tremendous.

Acknowledgments

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