Michael addition in the pseudoliquid phase of heteropoly compounds

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Abstract

Catalytic behaviors of various Keggin- and Dawson-type heteropolyacids for the Michael addition of alcohols to cyclohexenone have been investigated and the results were compared with those of other acid catalysts. The heteropolyacids, particularly $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$, showed much higher catalytic activities than $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, H-ZSM-5, and SO_4^{2-}/ZrO_2 and high selectivities (ca. 100%). Quantitative analysis revealed that both cyclohexenone and alcohol molecules were absorbed in the catalyst bulk phase at the early stage of the reaction and their amounts remained nearly constant during the reaction. Furthermore, the reaction rates of various heteropolyacids were approximately in proportion to the quantity of reactants absorbed in the catalyst phase, showing that the reaction proceeded in the pseudoliquid phase. The catalyst bulk phase gradually turned from a solid to a very viscous liquid lump, but this was called pseudoliquid in the present work from its appearance and the quantities of absorbed (or dissolved) molecules. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Heteropoly compound; Michael addition; Psuedoliquid phase; Cyclohexenone; Alcohol

1. Introduction

Heteropoly compounds have been successfully applied as catalysts to various reactions, by taking advantage of not only their controllable acid and redox properties but also the pseudoliquid behavior and soft basicity of heteropolyanion [1]. Due to the pseudoliquid behavior, where all of the polyanions and protons in the solid bulk can take part in catalysis, high catalytic activity and unique selectivity are often observed. For example, the solid $H_3PW_{12}O_{40}$ was several to hundreds times more active than a silica–alumina catalyst for several gas–solid phase reactions [1]. The pseudoliquid behavior

was also found for liquid–solid phase reactions [2]. The activity of $H_3PW_{12}O_{40}$ (surface area < 5 m^2 g^{-1}) is twice that of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (> 100 m^2 g^{-1}) in the case of pinacol rearrangement, while the latter is much more active for alkylation which proceeds on the surface, reflecting the surface acidity.

As for the basicity of heteropolyanion, it has been reported that hydrations of propene and isobutylene in homogeneous solution are catalyzed very efficiently by heteropolyacids owing to the stabilization of protonated intermediates through the complexation with polyanion [3,4]. A role of basicity in the stabilization of alkyl cation intermediates was indicated also for the heterogeneous catalysis, to explain the much higher activities of solid heteropoly compounds

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than zeolites and sulfated zirconia for the alkylation of aromatic compound (acid–base bifunctionality) [5].

We chose in this study, as the extension of our ongoing study on heteropoly catalysis, the Michael addition to make clearer the characteristics of the catalysis of heteropolyacids and to find new possible catalytic reactions. Michael addition is one of the important reactions to form carbon–carbon bonds in organic syntheses [6,7]. This reaction which is ordinarily the 1,4 addition of carbanion to conjugated double bond is promoted by basic (sometimes Lewis acid) catalysts and often accompanied by several side reactions such as 1,2-addition and condensation to polymerized products. To avoid side reactions, very mild conditions or usage of silyl compounds are usually recommended.

Hence it may be very interesting to explore the potential applicability of heteropoly catalysts to Michael addition, as the pseudoliquid behavior, uniform protonic acidity, etc., may function favorably in this reaction. In the present study, the reactions of polar molecules, that is, cyclohexenone and several alcohols (Eq. (1)) were chosen, since earlier studies show that polar molecules are absorbed into the pseudoliquid phase.

$$R = iso\text{-Pr, Me, Et, } t\text{-Bu, Bn}$$
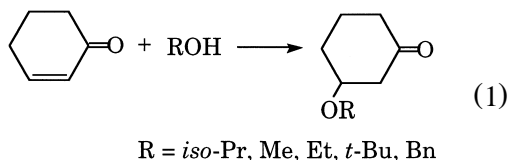
2. Experimental

2.1. Catalysts

$H_3PW_{12}O_{40}$ (HPW), $H_3PMo_{12}O_{40}$ (HPMo), and $H_4SiW_{12}O_{40}$ (HSiW) were purchased from Nippon Inorganic Color and Chemical. These were purified by the extraction with diethyl ether and recrystallization as previously described. Infrared spectra of these heteropoly-

acids were in agreement with those in the literature [8]. $H_4GeW_{12}O_{40}$ (HGeW) and $H_6P_2W_{18}O_{62}$ (Dawson structure) were prepared according to the literature [9,10]. For comparison with these heteropolyacids, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ ($Cs_{2.5}$, prepared according to the literature [5,11]), SO_4^{2-}/ZrO_2 (prepared also according to the literature [12]), H-ZSM-5 (prepared from Na-ZSM-5, Tosoh), $AlCl_3$ (Wako Junyaku), $TiCl_4$ (Wako Junyaku) and $Ti(OH)_4$ (Tokyo Chem.) were used. $AlCl_3$, $TiCl_4$ and $Ti(OH)_4$ were used without further purification. Heteroporiacids (including $Cs_{2.5}$), SO_4^{2-}/ZrO_2 and H-ZSM-5 were pretreated respectively at 150°C, 370°C and 535°C, in N_2 flow for 2 h before use.

2.2. Catalytic reactions

The Michael addition of alcohol to cyclohexenone was carried out in a two-neck flask in the atmosphere of argon. Typical reaction conditions were 2 h, at room temperature, using cyclohexane (30 ml) as solvent. In the case of $AlCl_3$ and $TiCl_4$, the reactions were carried out at $-78°C$ and $-20°C$ and with dichloromethane and acetonitrile as solvent, respectively. All reactants purchased from Tokyo Chem. were used without further purification. The reaction was started by adding the catalyst (typically: heteropolyacids 0.5 g and other catalysts 0.2 g) to a mixture of cyclohexenone (20 mmol) and alcohol (20 mmol). After a certain period of reaction the mixture was analyzed with a gas chromatograph (FID, capillary column, PEG-200, 30 m) and with ^{1}H-NMR.
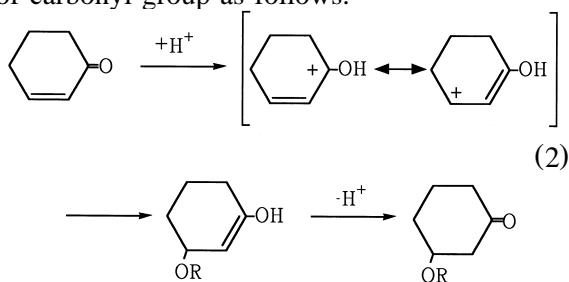
3. Results

3.1. Addition of isopropanol to cyclohexenone catalyzed by HPW

3.1.1. Time course and material balance

The reaction (Eq. (1); $R = (CH_3)_2CH$)) took place smoothly in the presence of HPW at 300 K. The only product detected by ^{1}H-NMR was

the 1,4-adduct, β-isopropoxycyclohexenone. The reaction probably proceeds via protonation of carbonyl group as follows.

$$ (2) $$

During the reaction, the reactants in cyclohexane solution decreased and the product appeared gradually, as shown by solid squares in Fig. 1. The catalyst was present as agglomerates of powder in the early stage and turned into a very sticky liquid-like lump in about 10 min. Approximately, the volume of the catalyst phase was 0.5 cm^3 (powder) and that of sticky lump 1 cm^3. No catalyst was detected in solution as confirmed by the absence of UV–vis absorption at 267 nm. This means that the amount of polyanion was less than 0.1% of the polyanion present in the reaction system. In accordance with this, the reaction did not proceed in the solution after the solution and catalyst phases were separated.

When the material balance in the solution was checked, a significant deficit was found. So the catalyst phase (powder or viscous liquid lump) was separated by dissolution into water and analyzed by gas chromatography. Results are also shown in Fig. 1. Total amounts of cyclohexenone and 1,4-adduct(β-isopropoxycyclohexenone in the reaction system are shown by solid squares, and those in the catalyst phase by open circles. It was found that cyclohexenone was rapidly absorbed in the catalyst phase in the early stage of the reaction and the amount in this phase remained almost constant during the reaction. In addition, a small amount of the product was retained in the catalyst phase. The results for isopropanol, which are not shown in this figure, were very similar in quantity and rate to those of cyclohexenone. Quantities of 2.7-mmol cyclohexenone and 2.5-mmol isopropanol which amounted to about 15% of the quantities initially added to the system and are six times larger than the number of polyanions in molar ratio. It is interesting that this ratio is comparable with the ratio previously observed in the case of catalytic dehydration of alcohols in the gas–solid system (three to seven, depending on the reaction conditions) [13,14]. It is also to be noted that the absorption was faster than the reaction.

The ^{1}H-NMR spectra of the sticky catalyst phase exhibited the signals of the two reactant molecules (6.1 and 7.4 ppm for CH=CH of
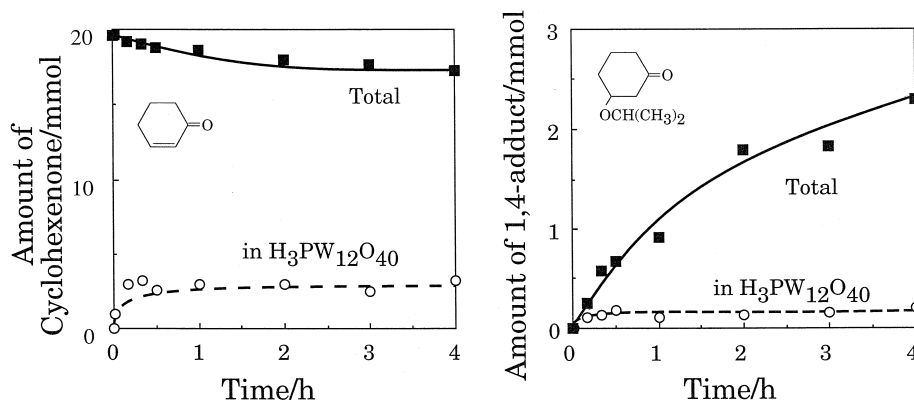

Fig. 1. Time courses of cyclohexenone and 1,4-adduct in the reaction of cyclohexenone with isopropanol. ■; total amounts in the reaction system, ○; the amount in the catalyst phase.

cyclohexenone and 4.2 (CH) and 8.5 ppm (OH) of isopropanol). These assignments were made with reference to the spectra of neat liquid samples of the two reactants or solid NMR spectra of ethanol in psuedoliquid phase of HPW [15]. In addition, a very small amount of the 1,4-product, β-isoproxycyclohexenone, was detected in the catalyst phase. If these are all taken into consideration, a material balance better than 98% was obtained.

The results described above such as faster absorption–desorption than the reaction and the absence of reaction in solution indicate that the reaction proceeded in the catalyst phase, that is, pseudoliquid phase.

### 3.1.2. Comparison of HPW with other acid catalysts

Results obtained by using other acid catalysts are compared with HPW in Table 1. As for the catalytic activity, the amounts of 1,4-adduct formed divided by the weight of catalyst are given in parentheses. For HPW and $Cs_{2.5}$, the product detected by ^{1}H-NMR was only the 1,4-adduct and material balances were good, indicating that the selectivity was almost 100%. SO_4^{2-}/ZrO_2 showed a very low activity, a trace amount of the 1,4-adduct being observed, and the reactant remained almost intact. H-ZSM-5 was inactive. In the case of $Ti(OEt)_4$, no 1,4-adduct was obtained, but a small amount of ethanol. $AlCl_3$ and $TiCl_4$ were very active, but gave low selectivities probably due to side reactions like condensation. In these cases, several peaks were detected in the products in gas chromatography, but the assignments were not made.

Therefore, the superior performance of HPW may be obvious; its activity was moderate, but at least 10 times more active than $Cs_{2.5}$, and the selectivity was nearly 100%. It was found in an experiment that the same reaction took place at a comparable rate in a homogeneous solution system which was obtained by increasing the amounts of the reactants. According to our experiences, the rate in the pseudoliquid phase relative to that in homogenenous solution seems to vary with the type of reaction. A comparative study concerning this point is now in progress.

3.2. Addition of isopropanol to cyclohexenone catalyzed by other heteropolyacids

Results of the reaction catalyzed by several heteropolyacids are shown in Fig. 2. The selectivities were nearly 100% except for HPMo, for which polymerized products were detected and the selectivity was 77%. The catalytic activity was the highest with HSiW and the following order of catalytic activity was obtained.

$$HSiW > HPW > HPMo > HGeW$$
$$> H_6P_2W_{18}O_{62} \qquad (3)$$
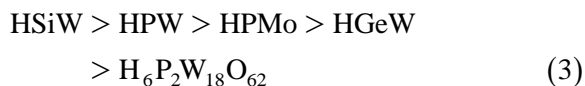
The acid strengths of these heteropolyacids are reported [1] to be in the order of

Table 1
Michael addition of isopropanol to 2-cyclohexen-1-one catalyzed by various catalysts

Catalysts	Catalyst, amount g^{-1}	Product, mmol[a]	Conversion, %	Selectivity, %
HPW	0.5	1.7(3.4)	8	98
$Cs_{2.5}$	0.2	0.06(0.29)	0.9	100
SO_4^{2-}/ZrO_2	0.1	0.03(0.2)	trace	(100)
H-ZSM-5	0.1	0(0)	0	–
$Ti(OEt)_4$	0.2	0(0)	0	–
$AlCl_3$	0.2	0.9(4.5)	18	27
$TiCl_4$	0.2	2.0(8.5)	16	63

Reaction temperature; 300 K, except for $AlCl_3$ (193 K) and $TiCl_4$ (253 K).
[a] Figures in parentheses are the amount of product per 1 g.

$$HPW > HPMo > HSiW > HGeW$$
$$= H_6P_2W_{18}O_{62} \tag{4}$$
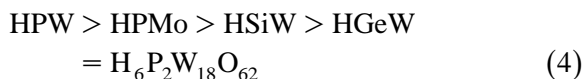
and the softness of the polyanion [1] is presumably

$$HSiW > HGeW > HPW > HPMo. \tag{5}$$

The order of catalytic activity (Eq. (3)) does not follow either of the latter two orders. It is noted however that Eqs. (3) and (5) agree with each other except for HGeW. As indicated by the results in Fig. 1, the reaction appeared to proceed in the catalyst phase (solid or sticky liquid). So the quantity of reactant molecules present in the catalyst phase during the reaction was measured for each catalyst by the same method as used to obtain the data in Fig. 1. The analysis was made of the catalyst phase after 2 h from the start of the reaction in separate experiments. The quantities absorbed were comparable for the two reactants as in the case of HPW. In Fig. 3, the amounts of 1,4-product produced in the entire reaction system (mostly in the major solvent phase), that are shown in Fig. 2 are plotted against the quantities of cyclohexenone and isopropanol detected in the catalyst phase. A good correlation is noted between the rate of formation of the 1,4-adduct in the entire system and the amounts of the reactant molecules absorbed in the catalyst phase; the rate increases as the reactants absorbed are greater.

The absorption of reactants in the catalyst phase may be controlled by several factors such

Fig. 3. Dependence of the amount of products on the amounts of reactants absorbed in the pseudoliquid phase. ■; Cyclohexenone, ○; Isopropanol.

as the acid strength, soft basicity of polyanions, etc. Probably, the reaction rate is determined by the combination of these properties, but quantitative discussion is not possible at present. Nonetheless, it is very probable from the correlation seen in Fig. 3 that the reaction proceeds in the catalyst phase and the absorption property has a great influence on the catalytic activity.

In the early stage of the reaction, the catalyst phase was solid and this is a pseudoliquid phase. The solid became a viscous liquid lump in the later stage. We proposed previously the pseudoliquid behavior for the gas–solid and liquid–solid reaction systems where the catalysts were always solid. So the catalyst phase in the present study may not be the same pseudoliquid as we proposed previously [1]. However, the numbers of absorbed molecules in the catalyst phase
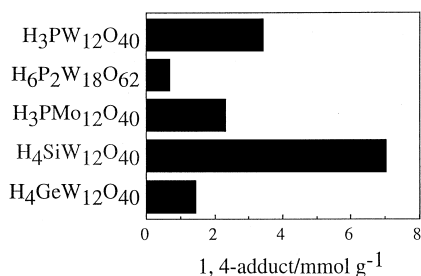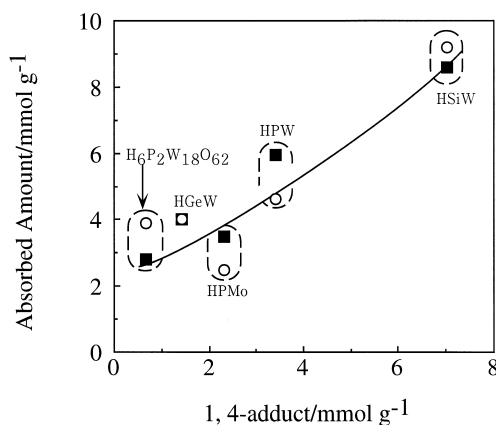

Fig. 2. Comparison of various heteropolyacid catalysts for the reaction of cyclohexenone with isopropanol. Solvent: cyclohexane, reaction temp.: r.t. time: 2 h.
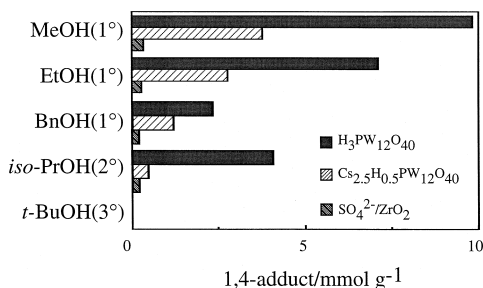

Fig. 4. Comparison of the reactivity of various alcohols.

for the present case are comparable with those found for alcohol dehydration catalyzed by solid heteropolyacids [13,14], as described above, and the reaction rate did not change much with the change in the appearance of the catalyst phase. Therefore, the term pseudoliquid phase is used tentatively in this paper for both cases.

3.3. Michael addition of various alcohols to cyclohexenone

Fig. 4 shows the results of the reaction with several alcohols catalyzed by HPW, $Cs_{2.5}$ and SO_4^{2-}/ZrO_2. In the case of surface-type catalysis, that is, SO_4^{2-}/ZrO_2 and $Cs_{2.5}$, the relative reactivity of alcohols was primary > secondary > tertiary, in agreement with the known trend [16]. On the other hand, the relative reactivity of isopropanol and benzyl alcohol was reversed for HPW. This indicates that it is more difficult for bulky benzyl alcohol (cross-section of molecule; 33.7 $\mathring{A}^2$) than for isopropanol (27.5 $\mathring{A}^2$) to be absorbed in the pseudoliquid phase. Our previous studies showed that the basicity and the bulkiness of molecules are the two major factors to control the rate of absorption [17]. In fact, the quantity taken in the catalyst phase was 1.4 mmol g^{-1} for benzyl alcohol which was considerably smaller than that of isopropanol, 4.6 mmol g^{-1}.

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