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Unprecedented acceleration effects of water on acid-catalyzed reactions over molybdena–zirconia catalysts

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Effects of water on various acid-catalyzed reactions have been studied mainly using MoO_3/ZrO_2. While the reaction rate of gas-phase esterification of acetic acid with ethanol and the dehydration of 2-butanol over $SiO_2–Al_2O_3$ decreased significantly by the addition of water vapor in the feed gas, these reactions over MoO_3/ZrO_2 were found to be greatly enhanced by the presence of water. The enhancement by water was reversible and was remarkable when MoO_3/ZrO_2 was calcined at a temperature range of 773–1073 K. IR spectroscopy of H_2O adsorbed on MoO_3/ZrO_2 suggests that the acceleration effect of water would be due to the generation of acidic sites from water coordinated to Mo species on the surface of MoO_3/ZrO_2.

KEY WORDS: molybdena–zirconia; acceleration by water; dehydration; esterification; hydrolysis; water-tolerant catalysis; acidity.

1. Introduction

Water-participating reactions such as hydration, dehydration, hydrolysis, and esterification are important in the chemical industry [1–3]. Usually liquid acids like sulfuric acid have been utilized because of their economic advantage, in spite of the many disadvantages of corrosion, a large amount of waste, and difficulty of separation. From the viewpoint of environmental protection, development of solid acids, which are active in water or in the presence of water vapor, is keenly desirable. However, it is generally observed that solid acids are severely poisoned by water.

A high-silica H-ZSM-5 has been utilized as only a commercial catalyst for hydration of cyclohexene in a solid–water reaction system [4,5]. The hydrophobic nature of the surface and the specific pore structure are considered to be critical factors for the activity in water. Besides H-ZSM-5, several solid catalysts were reported to be active for acid-catalyzed reactions in water: an acidic salt of heteropolyacid, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ [6–10], heteropolyacid included in a silica matrix [11,12], MoO_3/ZrO_2 [13], zirconium phosphate [14], niobic acid [15,16], lanthanum oxide [17,18], niobium phosphate [19], and polymer resins [20,21]. We found in the present study that, surprisingly, the acid-catalyzed reactions were greatly accelerated by the addition of water over MoO_3/ZrO_2 calcined at 773–1073 K. These results are unprecedented effects of water as far as we know.

2. Experimental

2.1. Materials

Mixed oxides containing zirconia or titania were prepared by an impregnation method. $Zr(OH)_4$ (Nippon Kigennso) or TiO_2 (Aerosil P-25) was impregnated with an aqueous solution such as $(NH_4)_6Mo_7O_{24}\cdot4H_2O$, $(NH_4)_{10}W_{12}O_{41}\cdot5H_2O$, $FeCl_3\cdot6H_2O$, $MnCl_2\cdot4H_2O$, NH_4VO_3, $Ce(NO_3)_3\cdot4H_2O$, and $Y_2(CO_3)_3\cdot2H_2O$ at room temperature. Only $(NH_4)_{10}W_{12}O_{41}\cdot5H_2O$ was dissolved in hot water. The amount of the solution added was 1 cm^3 per 1 g of $Zr(OH)_4$ or TiO_2. After drying, the sample was calcined in air at an elevated temperature for 3 h. The atomic ratio of the metal to Zr or Ti was adjusted to 0.1. As reference, $SiO_2–Al_2O_3$ (reference catalyst from the Catalysis Society of Japan, Al content = 13.8 wt%) and H-ZSM-5 (reference catalyst from the Catalysis Society of Japan, JRC-25-70H, Si/Al = 40) were used after the calcination at 773 K.

2.2. Catalytic reactions

The following three kinds of reaction were examined: (1) hydrolysis of ethyl acetate in excess water; (2) esterification of acetic acid with ethanol; and (3) dehydration of 2-butanol in the presence of water vapor. For the hydrolysis, a 5 wt% aqueous solution of ethyl acetate (30 cm^3, 17 mmol) and 0.8 g of solid catalyst (without any pretreatment) were introduced in the reactor (a three-necked flask, 50 cm^3) at 343 K to start the reaction. In the case of esterification, acetic acid (1 cm^3, 17 mmol) and ethanol (1 cm^3, 17 mmol) were added in the reactor, together with toluene (5 cm^3) as solvent and the solid

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catalyst 0.8 g at room temperature. Then the temperature was raised immediately to 343 K to start the reaction. Dehydration of 2-butanol was performed at 423 K in a flow reactor (Pyrex tube, 10 mm of inside diameter) with a feed gas consisting of 0.9% 2-butanol, 44% H_2O, and He balance. The solid catalyst (50 mg) was pretreated at 573 K in an He flow ($50\,cm^3\,min^{-1}$), and then the gas mixture was fed to the catalyst at a rate of $54\,cm^3\,min^{-1}$ under one atmospheric pressure. The products for these reactions were analyzed with a gas chromatograph (Shimadzu 8A) equipped with columns (PEG 20M for the hydrolysis and esterification, and DOP 30%-Uniport R for the dehydration).

3. Results and discussion

Table 1 shows the catalytic activities of various mixed oxides for hydrolysis of ethyl acetate in excess water. While most of these mixed oxides were less active for this reaction, MoO_3/ZrO_2, MoO_3/TiO_2, and WO_3/ZrO_2 exhibited considerable activity. H-ZSM-5 was more active than these mixed oxides. It was confirmed that the solutions separated from the suspensions of MoO_3/ZrO_2 and WO_3/ZrO_2 were inactive for this reaction. This shows that MoO_3/ZrO_2 and WO_3/ZrO_2 themselves were highly active in the solid state. However, it should be pointed out that the solution from the MoO_3/TiO_2 suspension showed some activity, indicating that active Mo species were released into the solution under the reaction conditions.

In table 2, the catalytic activities of these mixed oxides for gas-phase esterification and dehydration are summarized. It should be emphasized that MoO_3/ZrO_2 calcined at 973 K was superior in activity to H-ZSM-5 and the other solid acids for both reactions. Surprisingly, the high activity of MoO_3/ZrO_2 is due to the acceleration by water (see below).

Table 1
Catalytic activities of various solid acids for hydrolysis of ethyl acetate.

Catalyst[a]	Calcination temp. (K)	Surface area ($m^2 \cdot g^{-1}$)	Conversion[b] (%)
Fe_2O_3/ZrO_2	973	–	1.0
Fe_2O_3/TiO_2	973	–	1.5
V_2O_5/ZrO_2	973	10	3.8
CeO_2/ZrO_2	973	47	3.5
Y_2O_3/ZrO_2	973	–	4.2
Y_2O_3/TiO_2	973	–	7.3
MoO_3/Nb_2O_5	973	–	3.1
MoO_3/TiO_2	773	69	11.4[c]
WO_3/TiO_2	973	47	5.7
MoO_3/ZrO_2	973	72	11.9
WO_3/ZrO_2	1073	47	13.4
MoO_3/ZrO_2	1073	36	12.9
SiO_2–Al_2O_3	773	539	0
H-ZSM-5	773	400	29.4

[a] The atomic ratio in the mixed oxides (except for SiO_2–Al_2O_3 and H-ZSM-5) = 0.1 : 1.

[b] Hydrolysis of ethyl acetate; 5 wt% aqueous solution ($30\,cm^3$) at 343 K for 2 h with 0.8 g of catalyst.

[c] The reaction mainly took place in the liquid phase.

Table 2
Catalytic activities of solid acids for esterification and dehydration.

Catalyst[a]	Calcination temp. (K)	Conversion (%)	
		Esterification[b]	Dehydration[c]
MoO_3/TiO_2	773	15.6	0
MoO_3/ZrO_2	973	48.9	99.7
MoO_3/ZrO_2	1073	46.3	95.7
WO_3/ZrO_2	1073	35.2	98.3
SiO_2–Al_2O_3	773	1.5	25.3
H-ZSM-5	773	43.2	60.3

[a] The atomic ratio in the mixed oxides (except for SiO_2–Al_2O_3 and H-ZSM-5) = 0.1 : 1.

[b] Esterification: acetic acid ($1\,cm^3$) and ethanol ($1\,cm^3$) in toluene ($5\,cm^3$) at 343 K for 2 h with 0.8 g of catalyst.

[c] Dehydration of 2-butanol; in the flow system at 423 K, 2-butanol 0.9%, H_2O 44% in He balance, total flow rate $54\,cm^3\,min^{-1}$, and catalyst 50 mg.

Figure 1 presents the effect of water on the activity for the dehydration of 2-butanol and the influence of the calcination temperature of MoO_3/ZrO_2. It was found that the conversion of 2-butanol was greatly enhanced by the addition of water in the reactant mixture. Furthermore, the acceleration by water was observed only when MoO_3/ZrO_2 was calcined above 773 K. We already reported that MoO_3/ZrO_2 was active for various acid-catalyzed reactions after it was calcined at high temperatures above 773 K [13]. Thus, the water-enhancing effects observed here are probably related to the generation of the active sites of MoO_3/ZrO_2 by the thermal treatment.

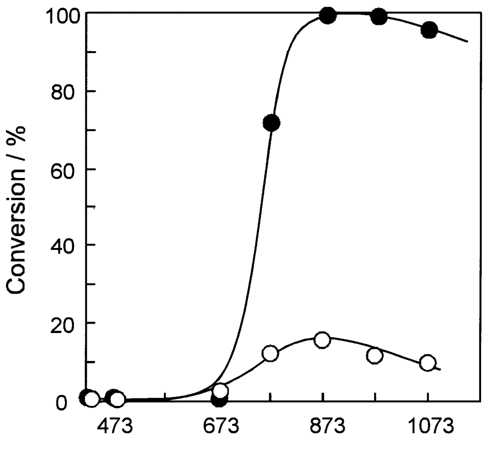

Figure 1. Effects of calcination temperature of MoO_3/ZrO_2 (Mo/Zr = 0.1) on the conversion of dehydration of 2-butanol in the He flow in the absence of water (○) and in the presence of water vapor (44%) (●). Dehydration of 2-butanol was performed at 423 K with 2-butanol 0.9% and He balance (total flow rate: $54\,cm^3\,min^{-1}$).

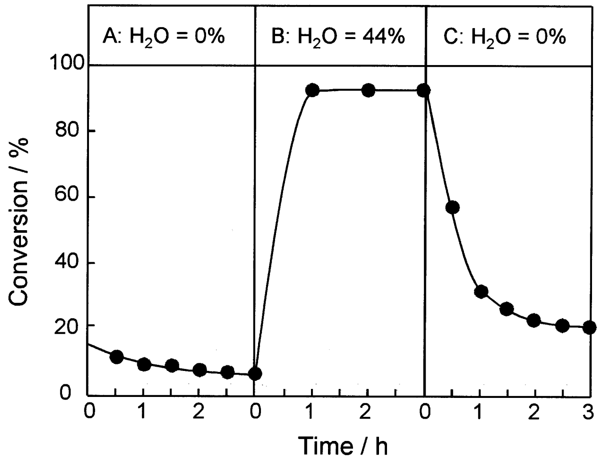

Figure 2. Influence of water on the conversion of dehydration of 2-butanol over MoO_3/ZrO_2 (Mo/Zr = 0.1) calcined at 1073 K. Stage A: in the absence of water; stage B: in the presence of water (44%); stage C: after the cessation of water. Dehydration was performed at 423 K with 2-butanol 0.9% and He balance (total flow rate: $54\,cm^3\,min^{-1}$).

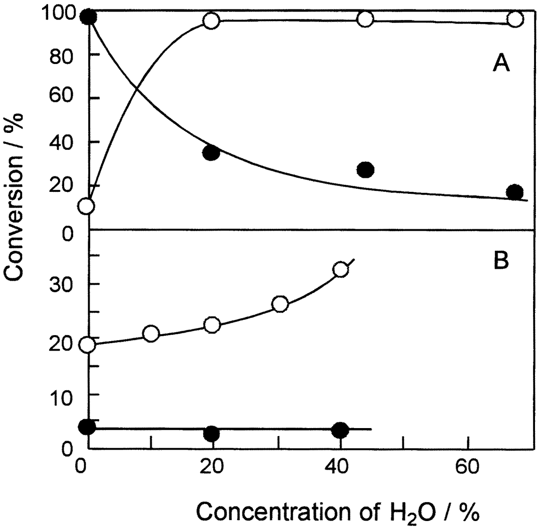

Figure 3. Effects of partial pressure of water on the conversions of dehydration of 2-butanol (A) and gas-phase esterification of acetic acid with ethanol (B) over MoO_3/ZrO_2 (Mo/Zr = 0.1) calcined at 1073 K (○) and SiO_2–Al_2O_3 (●). Dehydration of 2-butanol was performed at 423 K with 2-butanol 0.9% with He balance. Esterification was carried out at 423 K using acetic acid (20%) and ethanol (20%) with He balance.

Figure 2 gives the reversibility of the water-effect for dehydration of 2-butanol over MoO_3/ZrO_2 calcined at 1073 K. In the absence of water (stage A), the conversion was low. When the water vapor (44%) was added to the feed gas, the conversion increased significantly and was kept at its high value for at least 3 h (Stage B). Cessation of the water-supply (Stage C) caused a marked decrease in the conversion. It was confirmed that these changes were reversible for at least several cycles. These unique effects of water on the catalytic activity were not previously reported to our knowledge.

The dependencies of the conversions on the partial pressure of water vapor are shown in figure 3 for dehydration of 2-butanol and esterification of acetic acid and ethanol. The gas-phase esterification was performed at 423 K with a feed of acetic acid (20%), ethanol (20%) and He balance. The addition of water strongly suppressed the dehydration of 2-butanol (figure 3(A)) or gave little effect on the esterification (figure 3(B)) over SiO_2–Al_2O_3. On the other hand, the acceleration by water was clearly demonstrated over MoO_3/ZrO_2.

IR spectroscopy of H_2O adsorption will give information on the active sites. When the H_2O was adsorbed on MoO_3/ZrO_2 at room temperature and was evacuated at 423 K for 1 h, IR peaks at $1628\,cm^{-1}$ ($\delta(H_2O)$) and around $3550\,cm^{-1}$ ($\nu(OH)$) were detected. No clear peaks were observed on ZrO_2 only. Therefore, the peaks due to the adsorbed water are closely related to the Mo species on ZrO_2. It was further revealed that the intensity of the peak at $1628\,cm^{-1}$ after evacuation at 423 K of adsorbed water was small on the inactive MoO_3/ZrO_2, which was calcined at 673 K. Now we speculate that the water molecules coordinate weakly and reversibly to the Mo species of MoO_3/ZrO_2 and act as acidic sites in the presence of water vapor. This idea is consistent with the reversible acceleration of water vapor, as shown in figure 1. The Mo sites having the ability to activate water molecules would be created by interaction between MoO_3 and ZrO_2. In accordance with this idea, Prinetto *et al.* claimed by IR and ESR that Mo species anchor to the ZrO_2 surface via a reaction such as $Mo{-}OH + HO{-}Zr \rightarrow Mo{-}O{-}Zr + H_2O$ and the subsequent reduction of Mo [22]. In addition, Miyata *et al.* inferred the presence of Lewis acid sites on MoO_3/ZrO_2 and the transformation of Broensted acid sites by the presence of water [23].

4. Conclusions

When MoO_3/ZrO_2 was calcined at temperatures higher than 773 K, typical acid-catalyzed reactions such as esterification and dehydration over it were markedly accelerated by the addition of water vapor in the feed gas. This enhancement by water was in contrast to the effects of water over a typical solid acid, SiO_2–Al_2O_3, and other oxides supported on ZrO_2. This unique effect of water found for MoO_3/ZrO_2 is unprecedented in the case of acid-catalyzed reactions over solid acids, and is presumed to be caused by the generation of acidic sites through the reversible coordination of water on Mo ions during the reaction.

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