Partial Oxidation of Propane to Acrylic Acid over Reduced Heteropolymolybdate Catalysts

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Propane was catalytically oxidized to acrylic acid and acetic acid with molecular oxygen at 360 °C over heteropolymolybdophosphoric acids which were treated with pyridine in the catalyst preparation. Under presently optimized reaction conditions 24% selectivity to acrylic acid and 15% to acetic acid were achieved at 12% conversion of propane. A reduced state of the catalyst generated by heat-treatment of the pyridine-treated heteropoly acid is important for the selectivities.

Selective conversions of propane using gas-phase oxidations with molecular oxygen over heterogeneous catalysts are currently very important issues.[1] It is the ammoxidation of propane that researches and developments have been most prominent among various propane conversion processes. Naturally, the achievements of selective oxidation of propane to oxygenates such as acrolein and acrylic acid have also been desired increasingly and eagerly. At present, however, the achievements reported so far are not far-enough, reflecting high difficulties of effective activation of propane over solid surface. Vanadium oxide seems to be suitable for this purpose because it has generally high oxidation ability for organic compounds. In fact, many kinds of vanadium-based complex oxide catalysts have been investigated. Molybdenum oxide, which is a key component of oxidation catalysts of olefins, has also high oxidation ability, which is, however, lower than that of vanadium oxide. Therefore, for the propane oxidation, molybdenum-based oxide catalysts may need an additional function like surface acidic property. Heteropolymolybdic acids and related heteropolycompounds are attractive as catalysts for the propane oxidation.[2] Here in this letter, we wish to report our recent findings that heteropolymolybdophosphoric acid treated with pyridine can catalyze the propane oxidation to acrylic acid and acetic acid.

Heteropoly compounds tested in the present study as catalyst are listed in Table 1. $H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$ were obtained by the recrystallization of commercially available compounds. $(NH_4)_3PMo_{12}O_{40}$ and $K_3PMo_{12}O_{40}$ were prepared with $(NH_4)_6Mo_7O_{24}H_2O$, H_3PO_4, and KNO_3.[3] $H_4PMo_{11}VO_{40}\cdot 29H_2O$ was prepared according to the literature.[4] Pyridine-treated heteropolycompounds, denoted by (Py) for each treated catalyst as shown in Table 1, were prepared by precipitation method; to the aqueous solutions of corresponding heteropoly acids were added the desired amounts of pyridine at 35~40 °C with stirring, followed by filtration, washing with water, and drying at 120 °C for 8h under 5% O_2/N_2 stream. The pretreatment conditions and reaction conditions for the propane oxidation were set out in the footnote of the table. It was confirmed that no homogeneous gas-phase reaction took place under the conditions. Surface area was determined by BET method (nitrogen adsorption at liq. N_2 temperature). FT-IR spectra were recorded at room temperature for the catalysts after the catalytic reaction.

The $H_3PW_{12}O_{40}$ catalyst was completely inactive for the propane oxidation (Table 1). An acidic form of molybdophosphate, $H_3PMo_{12}O_{40}$ catalyst, on the other hand, revealed an activity for propane conversion and yielded propene, the oxidative dehydrogenation product, and acids, acrylic acid and acetic acid. Potassium salt of molybdophosphoric acid, $K_3PMo_{12}O_{40}$ catalyst was inactive. The set of these results simply indicates that an acidic property and reduction-oxidation functions of molybdenum oxide are responsible for the heteropolymolybdophosphate catalyst

Table 1. Comparison of the catalytic performances of various heteropolyacids and heteropolycompounds in the propane oxidation[a]

Catalyst	Surface Area / $m^2 \cdot g^{-1}$	Conversion / %		Selectivity / %				$I_{P\text{-}O}$ / $I_{Mo=O}$ [b]
		C_3H_8	O_2	C_3H_6	Acrylic Acid	Acetic Acid	$CO+CO_2$	
$H_3PW_{12}O_{40}$ [c]	5.9	0	0	-	-	-	-	0.9
$H_3PW_{12}O_{40}(Py)$ [d]	n.d.[g]	0	0	-	-	-	-	1.0
$H_3PMo_{12}O_{40}$ [c]	3.8	1.6	3.7	61.1	1.3	4.1	33.3	0.8
$H_3PMo_{12}O_{40}$* [c]	3.8	0.9	2.7	73.0	1.3	10.6	11.8	0.9
$H_3PMo_{12}O_{40}(Py)$ [d]	12.8	8.5	51.7	tr	21.1	8.9	69.5	0.3
$H_3PMo_{12}O_{40}(Py)$* [d]	12.8	7.5	43.7	tr	28.5	15.3	55.0	0.3
$H_3PMo_{12}O_{40}(Py)$* [d,e]	12.8	0.8	3.8	tr	35.0	14.4	38.7	0.3
$K_3PMo_{12}O_{40}$ [c]	n.d.[g]	0	0	-	-	-	-	1.0
$(NH_4)_3PMo_{12}O_{40}$* [d]	15.2	4.5	28.8	15.9	5.6	26.2	49.2	0.8
$H_4PMo_{11}VO_{40}$ [c]	2.3	0.9	2.3	90.6	2.2	3.3	3.7	0.6
$H_4PMo_{11}VO_{40}(Py)$ [f]	8.0	2.1	6.3	50.8	7.4	10.7	30.3	0.5

[a] Data are collected after 7 h reaction. Reaction temperature : 340 °C, catalyst weight : 3 g, total flow rate : 50 ml·min^{-1}. Reactant : C_3H_8 / O_2 / N_2 = 20.4 / 10.0 / 69.6 (mol%) [* C_3H_8 / O_2 / H_2O / N_2 = 20.4 / 9.9 / 19.9 / 49.8 (mol%)]. [b] $I_{P\text{-}O}$ and $I_{Mo=O}$ are the absorption intensities of ν [P-O] (1064 cm^{-1}) and ν [Mo=O] (962 cm^{-1}) in the FT-IR spectra of the catalysts after the reaction, respectively. [c] Pretreatment condition : 380 °C, 2 h under 20% O_2 / N_2 flow. [d] Pretreatment condition : 420 °C, 2 h under N_2 flow, followed by 380 °C, 2 h under 20% O_2 / N_2 flow. [e] Catalyst weight : 0.5 g. [f] Pretreatment condition : 430 °C, 2 h under N_2 flow, followed by 380 °C, 2 h under 20% O_2 / N_2 flow. [g] Not determined.

to be active for the propane oxidation. The catalyst substituted with vanadium, $H_4PMo_{11}VO_{40}$, a well-known catalyst for aldehyde oxidations to acids, gave a similar product distribution to the $H_3PMo_{12}O_{40}$ catalyst but the activity was rather poor.

In order to obtain higher conversion of propane in the above catalyst system, we then attempted to enlarge the surface area of the active $H_3PMo_{12}O_{40}$ catalyst by the treatment with pyridine during the catalyst preparation. It has already been well known that the pyridine treatment brought about higher surface area of heteropoly acid catalysts.[5] The pyridine treatment was performed on the $H_3PMo_{12}O_{40}$, $H_3PW_{12}O_{40}$, and $H_4PMo_{11}VO_{40}$ catalysts and their catalytic activities and selectivities were summarized in Table 1. In accordance with the literatures,[5] the treated catalysts had surface areas of four time higher than that of the non-treated catalysts and accordingly these treated catalysts, except $H_3PW_{12}O_{40}$(Py), showed higher conversion of propane. The conversion of propane was pronouncedly enhanced by the treatment of $H_3PMo_{12}O_{40}$ catalyst. Unexpectedly, this catalyst gave a significantly different product distribution, where acrylic acid and acetic acid were main oxygenated products and only a trace amount of propene was formed. When propane was allowed to react in the presence of water over the catalyst, the higher selectivities for both acids were achieved although the conversion of propane slightly decreased. Such drastic change of the product distribution was observed even at a low conversion of propane under a short contact time, so that it may result from either the variation of the surface area or intrinsic change of catalyst properties accompanied with the change of surface area by the treatment with pyridine. To investigate the direct effect of surface area, various $H_3PMo_{12}O_{40}$(Py) catalysts which were prepared by changing the amount of pyridine for the treatment and accordingly have different surface areas, were tested for the propane oxidation. The added amount of pyridine was always larger than that for producing the stoichiometric pyridinium salt, $(C_6H_5NH)_3PMo_{12}O_{40}$. Reaction rate of propane per surface area, conversion, selectivity and surface area were illustrated in Figure 1, and the reaction conditions were indicated in the legend of this figure. The surface area and the conversion increased with increasing amount of pyridine. On the other hand, the reaction rate and selectivity to each product were almost constant during the change of the surface area. This independency on the surface area clearly revealed that the pyridine treatment caused a variation of intrinsic property of the $H_3PMo_{12}O_{40}$ catalyst.

Table 1 also listed the catalytic performance data of $(NH_4)_3PMo_{12}O_{40}$ catalyst which has a surface area similar to $H_3PMo_{12}O_{40}$(Py) catalyst. The ammonium salt catalyst was active but gave the broad product distribution. This result also supports that the pyridine-treatment results in certain intrinsic change of the $H_3PMo_{12}O_{40}$ catalyst. We compared reduced state of the catalyst after the reaction by using the ratio of the IR absorption intensities as shown in the last column of Table 1. We can see a trend that the lower the ratio (in other words, the higher the reduced state[6]), the higher the yield of the acids. Obviously, the pyridine treatment has an effect on the catalysts to be able to keep highly reduced states during the propane oxidation. Since it was observed by FT-IR that pyridine still remained in the $H_3PMo_{12}O_{40}$(Py) catalyst even after the reaction for 8 h (0.8 pyridine per Keggin unit by chemical analysis), we now conclude that pyridine molecule of which amount is small enough not to neutralize the acid remains in the lattice of the heteropolymolybdophosphate and stabilizes the reduced state, which may be necessary for the formation of acrylic acid by the propane oxidation.

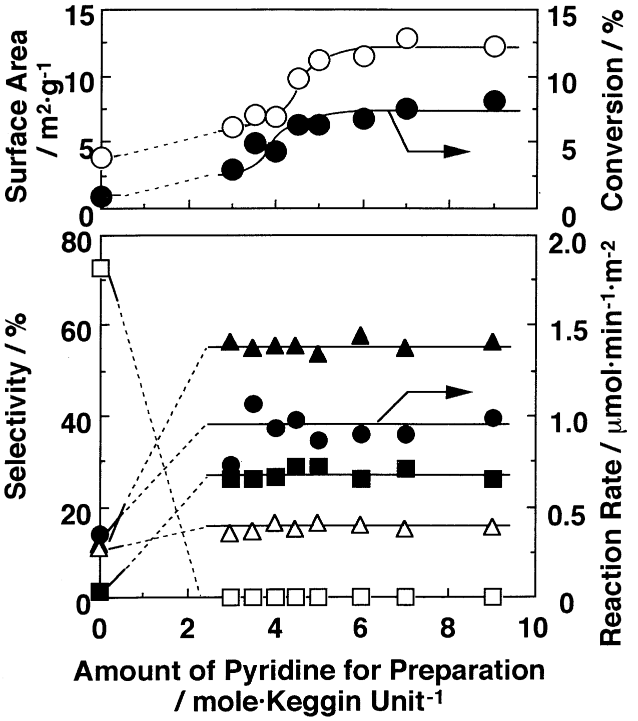

Figure 1. Propane oxidation over $H_3PMo_{12}O_{40}$(Py) catalysts treated with pyridine during the preparation and their surface area. Reaction temperature : 340 °C, catalyst weight : 3 g, total flow rate : 50 ml·min^{-1}, reactant : $C_3H_8/O_2/H_2O/N_2$=20.4 / 9.9 / 19.9 / 49.8 (mol%). Pretreatment conditions : 420 °C, 2 h under N_2 flow, followed by 380 °C, 2 h under 20% O_2 / N_2 flow. ● : C_3H_8, ■ : acrylic acid, △ : acetic acid, □ : C_3H_6, ▲ : $CO+CO_2$.

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