Catalytic oxidation of isobutane to methacrylic acid with molecular oxygen over activated pyridinium 12-molybdophosphate

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Isobutane was catalytically oxidized to methacrylic acid with molecular oxygen above 300°C over crystalline particles of pyridinium 12-molybdophosphates which were activated by heat-treatment under a nitrogen stream up to 420°C. During the treatment two third of pyridine were released from the sample and one third remained accompanied by the formation of orthorhombic structure. It was proved by IR studies that the catalyst became a reduced state by this treatment. The reduced state was highly stable even under catalytic oxidation conditions with molecular oxygen. 50% selectivity to methacrylic acid and 22% to acetic acid were achieved at 22% conversion of isobutane. The highly stable reduced state and structure of the activated heteropolymolybdophosphate catalyst seem to be responsible for the high activity for isobutane oxidation and high selectivity to methacrylic acid formation.

Keywords: oxidation, isobutane, methacrylic acid, heteropolymolybdophosphoric acid, pyridine, reduced state, crystal structure, active oxygen

1. Introduction

Because of the global abundance of liquefied petroleum gas (LPG), interest in the potential use of propane and butanes as sources of the corresponding alkenes or their derivatives is increasing [1,2]. In the last decade much progress has been made, and various kinds of catalytic reactions and processes have been proposed, particularly the selective partial oxidation of light alkanes with molecular oxygen in gas phase. The most successful oxidation of lower alkanes is the selective oxidation of *n*-butane to maleic anhydride, which has been successfully demonstrated and commercialized using crystalline V–P–O catalysts [3]. The conversions of methane to methanol, formaldehyde, and higher hydrocarbons (by oxidative coupling of methane (OCM)) have been widely investigated [4,5]. The oxidative dehydrogenation of ethane and propane have also received much attention [6].

Direct synthesis of methacrylic acid via oxidation of isobutane looks most promising. Many patents and papers have already been reported for this reaction [7–12]. Catalysts claimed in the patents are mostly heteropoly compounds based on molybdenum. In addition the catalysts were modified with vanadium, which replaces molybdenum and other metal ions, such as Cu, in the cationic composition. At present, however, the achievements reported are not good enough, reflecting the high difficulty of effective activation of isobutane over solid surfaces. Obviously, the reaction needs multifunctional catalysts since the reaction is a multielectron oxidation. Meanwhile, we reported [13,14] that highly reduced heteropolymolybdophosphoric acids which were formed by the heat-treatment of pyridinium or quinolinium salts of $H_3PMo_{12}O_{40}$ can catalyze the propane oxidation to acrylic acid and acetic acid selectively. And recently we found that this catalyst was also highly active and selective for the oxidation of isobutane to methacrylic acid. In this paper, we report the catalytic performance and the characterization results of the activated pyridinium 12-molybdophosphate catalyst.

2. Experimental

2.1. Catalyst preparation

Stoichiometric pyridinium 12-molybdophosphate was prepared by precipitation; to aqueous solutions of $H_3PMo_{12}O_{40}$ obtained by the recrystallization of commercially available compounds were very slowly added seven times molar amounts of pyridine against Keggin unit at 35–40°C with stirring, followed by further stirring for 30 min, evaporation at 80°C to remove water and excess pyridine molecules, and drying at 120°C for 8 h under a N_2 stream (50 ml min^{-1}). Chemical analyses of the dried sample showed that there were occluded pyridine molecules (0.4 molecules per Keggin unit) in the lattice besides pyridinium ion (3 molecules per Keggin unit). The dried sample was used for the catalytic oxida-

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tion after the heat-treatment in a nitrogen stream at desired temperatures using the reactor described in the following section. The surface area of the heat-treated sample at 420°C was determined to be 12.8 $m^2 g^{-1}$ by the BET method of nitrogen adsorption at liquid nitrogen temperature. Phases of the prepared catalysts were identified by XRD (Rigaku diffractometer RAD-1VB, Cu Kα) measurements. TPD of the occluded and ion-form pyridine from the samples was carried out by heating the dried samples at a ramp rate of 10 K min^{-1} under a He flow (23 ml min^{-1}). Desorption profiles were measured using a thermal conductivity detector and a mass spectrometer. FT-IR spectra (Perkin Elmer, Paragon 1000) were recorded under vacuum at room temperature for the catalysts before and after the heat-treatment using a conventional in situ IR cell. The specimens were prepared by loading the catalysts on KBr disc from catalyst powder suspension in acetone.

2.2. Isobutane oxidation

Isobutane oxidation was carried out at atmospheric pressure in a conventional flow system equipped with a tube reactor (Pyrex, i.d.: 12 mm). The powder catalysts (3 g) diluted with quartz tips (2 g) were loaded in the middle of the reactor. The reactor volume, except the catalyst zone, was minimized to prevent homogeneous gas-phase reactions and decompositions of products. The standard reactant feed for the oxidation was 2.2 mol% of isobutane, 13.7 mol% of oxygen, 33.5 mol% of water, and the remainder nitrogen. The total flow rate was 30 ml min^{-1}. The reaction temperature was varied in the range of 280–340°C. It was confirmed that no reaction took place without catalysts under the above reaction conditions. The feed and products were analyzed with an on-line gas chromatograph operating with two sequential columns, a molecular sieve 13X 1 m, at room temperature for the separation of O_2, N_2, and CO, and Porapak Q 4 m, 65–140°C for hydrocarbons and CO_2 and also with another gas chromatograph with TC-WAX 60 m capillary column for aldehydes and acids.

3. Results and discussion

3.1. Catalytic isobutane oxidation to methacrylic acid

Molybdenum oxide, which is a key component of oxidation catalysts for olefins [15], could be a main component of alkane oxidation catalysts. However, due to its relatively low oxidation ability, molybdenum-based oxide catalysts may need additional functions like surface acidic property. For this purpose, heteropolymolybdic acids and related heteropoly compounds are attractive as catalysts.

We have tested various heteropoly compounds as catalysts for the isobutane oxidation. Typically, non-redox type heteropoly compounds like $H_3PW_{12}O_{40}$ were completely inactive for the isobutane oxidation. The acidic form of 12-molybdophosphate, $H_3PMo_{12}O_{40}$, on the other hand, revealed an activity for isobutane conversion (7%) but yielded mainly complete oxidation products with minor amounts of methacrylic acid (11%) and acetic acid (21%), as reported earlier [8]. The potassium salt of molybdophosphoric acid, $K_3PMo_{12}O_{40}$, was also catalytically inactive. All these results simply indicate that only an acidic property is not satisfactory for the heteropolymolybdophosphate catalyst to be active and selective for the isobutane oxidation. It seems that the reduction–oxidation function of molybdenum oxide (degree of reduction or state of reduction) is also important [16].

Therefore, in order to obtain a reduced heteropolymolybdophosphate, we then attempted to heat-treat pyridinium 12-molybdophosphate. We have tested various treatment temperatures. Non-activated pyridinium salt itself was inactive and a sample activated at a temperature higher than 470°C showed poor catalytic performance, especially a very high selectivity to carbon oxides, due to its lower surface area and lower stability as a catalyst. We found, as a consequence, that pyridinium 12-molybdophosphate after activation of its pale yellow powder form at 420°C in a nitrogen atmosphere for 2 h to dark black green, was a highly efficient catalyst for the selective oxidation of isobutane. Table 1 summarizes the catalytic performance of pyridinium 12-molybdophosphate activated at 420°C for the isobutane oxidation under various reaction conditions. Interestingly, the activated pyridinium 12-molybdophosphate showed a significantly high ability for partial oxidation of isobutane, giving methacrylic acid and acetic acid as the main oxygenated products and small amounts of methacrolein and acrylic acid. Only a trace amount of isobutene was detected. The addition of water in the feed gas was necessary to achieve higher selectivities for both the acids although the conversion of isobutane slightly decreased. As can be seen in table 1, the higher selectivities to the oxygenates were observed under lower reaction temperature and under lower W/F conditions. Very important and characteristic in this catalyst system is the partial pressure effect of oxygen on the conversion and selectivity; the isobutane conversion prominently increased with increasing partial pressure of oxygen although consecutive reactions such as methacrolein to methacrylic acid and methacrylic acid to carbon oxides and C–C bond fission became significant. Under the present best reaction conditions more than 50% selectivity to methacrylic acid and 22% selectivity to acetic acid were achieved at 22% conversion of isobutane over the activated pyridinium 12-molybdophosphate catalyst, which in our knowledge is very superior to other catalysts under the present oxygen-rich reaction conditions.

Figure 1 shows the conversion and selectivity changes

Table 1
Catalytic performance of activated pyridinum 12-molybdophosphate in the selective oxidation of isobutane [a]

Reaction conditions			Conversion i-C_4 (%)	Selectivity (%)				
i-C_4 [b] : O_2 : H_2O : N_2 (mol%)	RT [b] (°C)	W/F (g min ml^{-1})		MAA [b]	AA [b]	AcOH [b]	MAC [b]	COx
2.2 : 7.0 : 33.5 : 57.3	280	0.100	8.4	55.9	1.2	10.9	6.6	25.4
2.2 : 7.0 : 33.5 : 57.3	300	0.100	17.1	52.8	2.5	12.2	13.5	19.0
2.2 : 7.0 : 33.5 : 57.3	340	0.100	47.1	17.9	10.1	32.7	3.5	35.8
2.2 : 13.7 : 33.5 : 50.6	300	0.100	22.2	51.1	4.0	22.0	tr	23.0
2.2 : 20.7 : 33.5 : 43.6	300	0.100	27.8	34.2	7.2	30.2	tr	28.3
2.2 : 13.7 : 33.5 : 50.6	300	0.050	11.5	58.0	3.6	16.5	0.4	21.5
2.2 : 13.7 : 33.5 : 50.6	300	0.033	10.7	50.7	2.6	14.3	13.7	18.7

[a] The catalyst was heat-treated in N_2 flow at 420°C for 2 h; data are collected after 9 h reaction; catalyst weight: 3 g; total flow rate: 30 ml/min.
[b] i-C_4: isobutane; RT: reaction temperature; MAA: methacrylic acid; AA: acrylic acid; AcOH: acetic acid; MAC: methacrolein.

as a function of time on stream in the isobutane oxidation over the activated pyridinium 12-molybdophosphate catalyst. A prominent change of the catalyst at the beginning of the reaction was followed by a stable catalytic performance. The selectivity of this catalyst was rather stable within the duration.

3.2. Characterization of the activated pyridinium 12-molybdophosphate catalyst

It has already been reported that the pyridine treatment brought about higher surface area and a certain structure of the heteropoly acid catalysts [17]. In accordance with the literature, the treated catalysts had surface areas four times higher than those of the non-treated catalysts (3.8 m^2 g^{-1}). However, the drastic changes in catalytic activity and the product distribution by the pyridine treatment as described above could not be explained only by the variation of the surface area, so that we must take an intrinsic change of the catalyst properties by the treatment with pyridine into account.

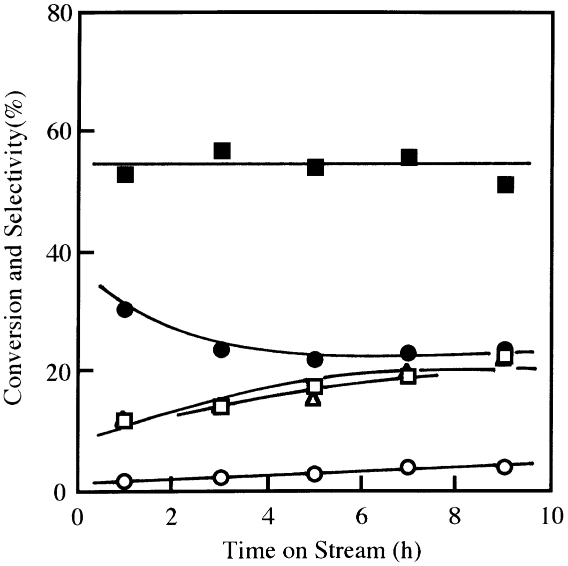

Figure 1. Partial oxidation of isobutane over activated pyridinium 12-molybdophosphate catalyst. Conversion of isobutane (□) and selectivities to methacrylic acid (■), acetic acid (△), acrylic acid (○), and carbon oxides (●) as a function of the time on stream. Reaction conditions: feed composition (mol%), isobutane : O_2 : H_2O : N_2 = 2.2 : 13.7 : 33.5 : 50.6; total flow rate, 30 ml min^{-1}; catalyst weight, 3 g; reaction temperature, 300°C.

We, therefore, conducted TPD, XRD, and FT-IR measurements in order to get an insight into what happens in the pyridinium 12-molybdophosphate sample during the activation in nitrogen atmosphere. Figure 2 shows TPD profiles of the freshly dried pyridinium 12-molybdophosphate sample. Four desorption peaks at about 250, 400, 450, and 520°C were observed in the temperature-programmed region from 100 to 600°C in figure 2 (a). The peak at 450°C was due to the desorption of CO_2 and the other three peaks were of pyridine, as ascertained by mass spectrometry. Very small amounts of CO_2 and water were observed during the pyridine desorption at 520°C, indicating that a small amount of pyridine reacted with the catalyst or decomposed during the desorption, but it was confirmed by elemental analysis that no carbonaceous species remained in the sample heat-treated up to 600°C.

The small desorption peak around 250°C corresponds to the occluded pyridine (0.4 molecules per Keggin unit) during the preparation, which may result in the increased surface area. The two desorption peaks at 400 and 520°C are of pyridines existing in the cationic form in the lattice because of their high desorption temperatures. From the desorption peak areas, the desorptions at 400 and 520°C correspond to two third of pyridinium ion and to one third, respectively. Since the suitable activation temperature was selected to 420°C in terms of the catalytic performance, the pyridinium ions desorbed at 400°C should be eliminated during the heat-treatment, and the pyridinium ion desorbed at 520°C should remain in the lattice. In fact, exactly the same desorption was observed at 520°C for the sample activated at 420°C for 2 h and even for the sample after use for the catalytic oxidation, as shown in figure 2 (b) and (c).

Changes of FT-IR spectra and XRD patterns during the heat-treatment of the pyridinium molybdophos-

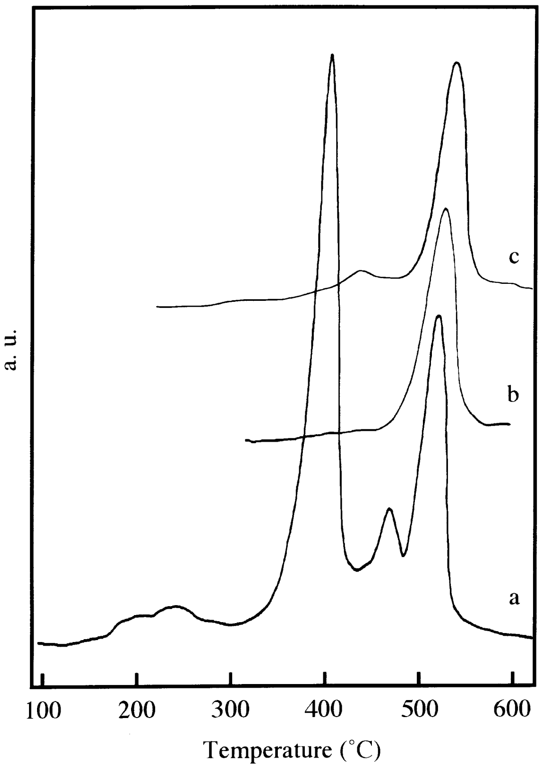

Figure 2. Pyridine TPD from pyridinium 12-molybdophosphate catalysts (a) dried in N_2 at 120°C for 8 h, (b) activated in N_2 at 420°C for 2 h and in He at 300°C for 2 h, and (c) used for the catalytic oxidation (300°C, 10 h) and treated in He at 200°C for 2 h prior to TPD.

phate sample are shown in figures 3 and 4, respectively. Two important points emerged from the FT-IR spectra in the region of pyridinium ion from 1300 to 1700 cm^{-1} and that of metal–oxygen from 600 to 1200 cm^{-1}. First, two peaks were observed at 1531 and 1538 cm^{-1} in the region of the pyridinium ion band. The peak at 1531 cm^{-1} remained after the heat-treatment at 300°C to remove the occluded pyridine but completely disappeared after the heat-treatment at 420°C. On the other hand, the peak at 1538 cm^{-1} did not change at all during the treatment. The results are well coincident with those of TPD shown in figure 2, so that at the present stage we tentatively assume two types of pyridinium ion in the lattice although we do not know the difference. Second, complicated absorptions (965, 973, 985, and 996 cm^{-1}) were observed in the Mo=O band region around 960 cm^{-1} in the spectrum, as shown in figure 3, after the heat-treatment and at the same time the P–O band (1056 cm^{-1}) and the Mo–O–Mo band from 700 to 900 cm^{-1} decreased drastically. This result indicates the formation of reduced molybdenum in the Keggin units in accordance with that CO_2 desorption was observed at 450°C in the TPD of the pyridinium 12-molybdophosphate sample, which formed by the reaction of pyridine with lattice oxygens during the desorption. All these results may allow us to speculate the formation of oxygen-deficient heteropoly anion.

A crystal structure change was also observed during the heat-treatment at 420°C, as shown in figure 4. A poorly crystalline phase obtained on the samples heat-treated at 300°C changed into a different crystal phase

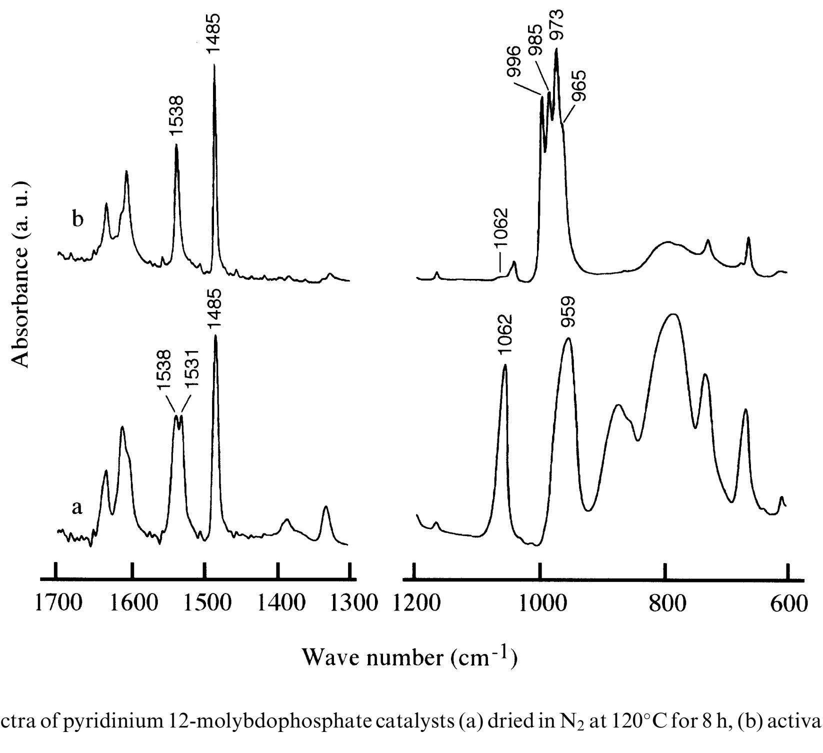

Figure 3. FT-IR spectra of pyridinium 12-molybdophosphate catalysts (a) dried in N_2 at 120°C for 8 h, (b) activated in N_2 at 420°C for 2 h.

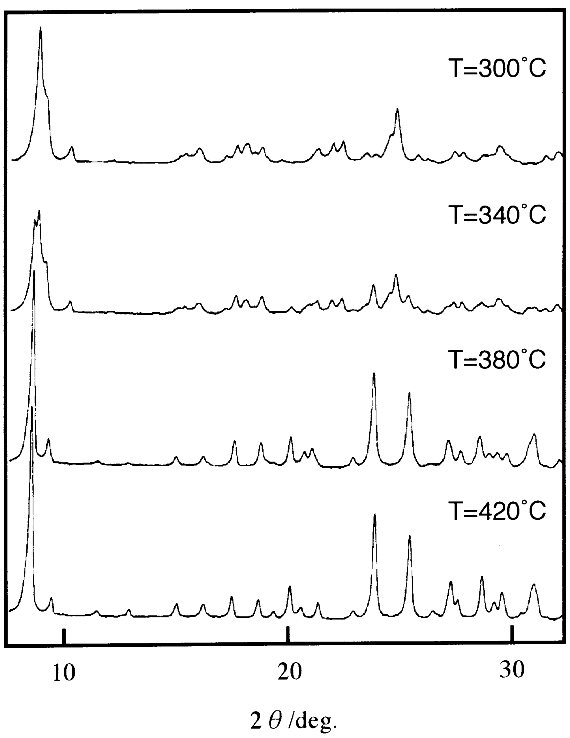

Figure 4. XRD patterns of pyridinium 12-molybdophosphate catalysts heat-treated in N_2 at different temperatures for 2 h each.

with the elimination of two third of the pyridinium ion by the heat-treatment up to 420°C. This phase was classified into the orthorhombic system, which seems to be constructed with pyridinium ions and oxygen-deficient heteropoly anions of reduced molybdenum. Further structural studies are undertaken now.

As a consequence, the highly reduced heteropolymolybdophosphate with oxygen-deficient anions provides sites for activating molecular oxygen and isobutane effectively. Protons formed after the elimination of pyridinium ions may cooperatively act for the activations. Since such reduced state is stable under the catalytic oxidation conditions and the catalytic activity is sustained as far as the pyridinium ions remain in the structure, the role of the pyridinium ions is important.

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