

Selective oxidation of isobutane over $H_xFe_{0.12}Mo_{11}VPAs_{0.3}O_y$ heteropoly compound catalyst

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Abstract

Keggin-type molybdophosphoric heteropolyacid catalysts with iron cation partially substituted for proton and arsenic for phosphorus in a bulk form have been synthesized for the selective oxidation of isobutane into methacrylic acid (MAA). It was found that the addition of iron can obviously improve both the conversion of isobutane and selectivity to MAA, while arsenic substitution was mainly in favor of the selectivity to MAA. The best conversion and yield of MAA were 23.9% and 16.7%, respectively, which was obtained at 370 °C with a space velocity of 420 h⁻¹ over $H_xFe_{0.12}PVA_{s0.3}Mo_{11}O_y$ heteropoly compound catalyst. The catalysts were characterized by XRD, SEM, FT-IR, and TPR.

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1. Introduction

Methyl methacrylate (MMA) is an important monomer, which is widely used for producing acrylic plastics or producing polymer dispersions for paints and coats [1]. methacrylic acid (MAA) is the precursor of MMA which have been developed by many commercialized processes until now, but most manufacturers in the world adopted the acetone cyanohydrine (ACH) process first industrially produced by Rohm & Haas Co. in 1933 which have many problems such as high-price feedstock and environmentally unfriendliness. As a substitute method, two-step oxidation of isobutylene has been applied industrially by several Japanese companies (Japan Methacryl Monomer, Mitsubishi Rayon, Kyodo Monomer) [2] for the synthesis of MAA; however, the additional steps as well as the high cost of isobutylene are also industrially undesirable.

An alternative choice is the direct selective oxidation of isobutane that is abundant in the oil producing processes.

Recently the reports on the selective oxidation of isobutane to produce MAA can be found in many patents [3–7] and literatures [2,8–16], among which $H_3PMo_{12}O_{40}$ -based heteropoly compounds were mostly studied and exhibited better activity and selectivity than other systems [17,18]. The substitution or modification of transition metals was found an efficient way to improve the catalytic performance and selectivity to MAA. Unfortunately the MAA yields reported in the previous patents and literatures are all lower than 11.2% [2–17]. It was found difficult for selective oxidation of lower alkanes to attain high yield because of the low activity of reactant and multiple-steps of the reaction mechanism.

This paper introduced a simple preparative route of $H_4PMo_{11}VO_{40}$ -based heteropoly compound catalysts modified with As and Fe. The catalysts were evaluated by the single-step selective oxidation of isobutane to MAA, and

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the conversion of 23.9% and MAA yield of 16.7% were achieved.

2. Experimental

2.1. Catalysts preparation

The catalysts of heteropoly compounds with Keggin structure were prepared according to our previous method [19]. The typical preparation procedure of the catalysts is as follows: a certain amount of P_2O_5 , As_2O_5 , MoO_3 , V_2O_5 were mixed in distilled water and the resultant mixture was refluxed at 80–90 °C for 48–96 h to form a homogeneous yellow solution. Then certain amount of $0.065 \text{ mol dm}^{-3}$ $Fe(NO_3)_3$ solution was added under stirring. The compositions were (a) $H_xFe_{0.12}Mo_{11}PVO_y$, (b) $H_xMo_{11}VPAs_{0.3}O_y$, and (c) $H_xFe_{0.12}Mo_{11}VPAs_{0.3}O_y$. Proper amount of 0.08 mol dm^{-3} KNO_3 or $CsNO_3$ solution was dripped into the (c) solution to produce (d) $H_xKFe_{0.12}Mo_{11}VPAs_{0.3}O_y$ and (e) $H_xCsFe_{0.12}Mo_{11}VPAs_{0.3}O_y$. The final solutions were dried in a water bath at 90 °C. It is necessary to continue grind to avoid the catalyst agglomerating. (c) who uncalcined, calcined at 350, 400 or 450 °C under air atmosphere for 2.5 h to give (c1), (c2), (c3) and (c4), respectively; while (c5) was attained after (c3) reacted for 24 h. The catalysts (a), (b), (d) and (e) were calcined at 400 °C for 2.5 h before reaction or characterization.

2.2. Catalytic reaction

Catalytic reactions were carried out in a stainless steel tubular fix-bed microreactor and the fixed mass of the catalyst was 1.2 g. The products were analyzed online by a 122G gas chromatograph with a porapak-Q column and a FID detector. The CO_x was transformed with a methanation transformer. The typical reaction conditions were: isobutane: O_2 : N_2 = 2:2:3 ml min^{-1} and $T = 370$ °C. All the catalysts were activated at 380 °C for 1 h under 2 ml min^{-1} pure O_2 atmosphere after calcination and before reaction.

2.3. Catalyst characterization

IR spectra of the catalysts were taken on a Perkin Elmer 2000 IR spectrometer by the KBr tablet method. The H_2 -TPR and BET measurements were carried out on a Chembet-3000 BET adsorption instrument and the former was under an atmosphere of mixed H_2 - N_2 containing 15% H_2 (v/v) with a temperature increasing rate of 10 °C min^{-1} and the final temperature of 700 °C. The samples were pretreated at 250 °C under Ar atmosphere for 30 min. The TG-DTA curve of as-prepared (c) was obtained on a PCT-IA differential thermal balance with a heating rate of 10 °C min^{-1} . The surface structure of the catalysts were studied by SEM on a KYKY-2800 SEM instrument. X-ray diffraction (XRD) patterns were measured by a BRUKER D8 Advance diffractometer using Cu

$K\alpha$ radiation ($\lambda = 1.54056$ Å). The 2θ angles were scanned from 5° to 70° at a rate of 2° min^{-1} .

3. Results and discussion

3.1. Characterization of the catalysts

The catalysts were characterized by FT-IR spectra, TG-DTA curves, TPR, SEM and XRD patterns and their results are shown in Figs. 1–5. Fig. 1 shows the IR spectra of the catalysts, where all the catalysts but (c4) have four strong absorption peaks between 1065 and 790 cm^{-1} which can be attributed to heteropoly anion of the Keggin structure. The vibration of V–O bond is marked by the very strong absorption of Mo–O bond [20]. Compared with those of (a) $H_xFe_{0.12}Mo_{11}PVO_y$, all the four characteristic absorption peaks of (c3) $H_xFe_{0.12}Mo_{11}VPAs_{0.3}O_y$ shift by the addition

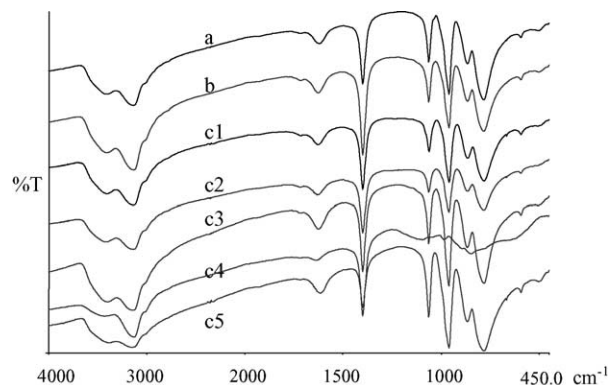


Fig. 1. IR spectra of the catalysts. (a) $H_xFe_{0.12}Mo_{11}PVO_y$, (b) $H_xMo_{11}VPAs_{0.3}O_y$, (c) $H_xFe_{0.12}Mo_{11}VPAs_{0.3}O_y$: (c1), (c2), (c3), (c4) is (c) no calcined, calcined at 350, 400 and 450 °C respectively, (c5): after reaction of (c3).

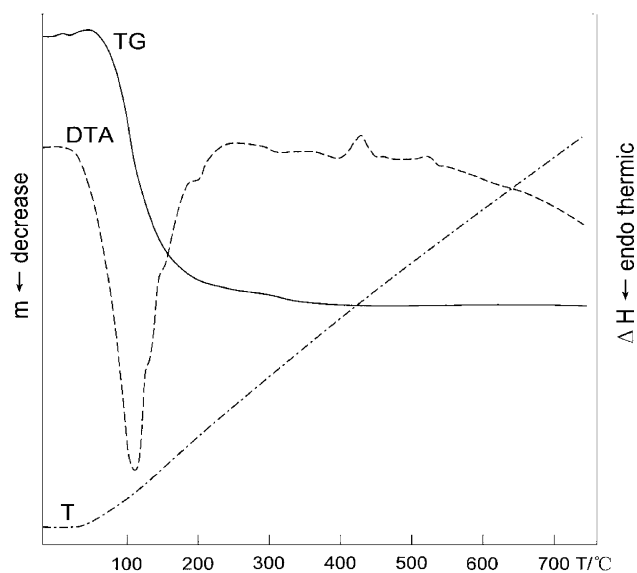


Fig. 2. TG-DTA curve of $H_xFe_{0.12}Mo_{11}VPAs_{0.3}O_y$.

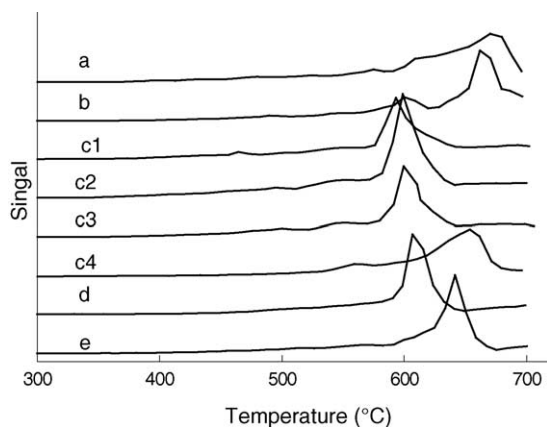


Fig. 3. TPR spectra of the catalysts. (a) $H_xFe_{0.12}Mo_{11}PVO_y$, (b) $H_xMo_{11}VPAs_{0.3}O_y$, (c) $H_xFe_{0.12}Mo_{11}VPAs_{0.3}O_y$: (c1), (c2), (c3), (c4) is (c) no calcined, calcined at 350, 400 and 450 °C, respectively, (d) $H_xKFe_{0.12}Mo_{11}VPAs_{0.3}O_y$, (e) $H_xCsFe_{0.12}Mo_{11}VPAs_{0.3}O_y$.

of As; $\nu(P-O_a)$ and $\nu(Mo=O_t)$ blue shift 1 and 1.8 cm^{-1} ; $\nu(Mo-O_b-Mo)$ and $\nu(Mo-O_c-Mo)$ red shift 4.9 and 24.4 cm^{-1} . The large red shift of $\nu(Mo-O-Mo)$ suggests that As has partly entered the first structure of Keggin anion which influences the M–O bond. The four characteristic absorption peaks of (b) have similar wavenumbers to those of (c3); the Keggin anion structure is well conserved after the catalyst (c) has been calcined at 350 or 400 °C, while after calcined at 450 °C the characteristic absorption peaks standing for the Keggin anion structure disappear and at the same time, the catalytic activity disappear, which shows that the active species of the catalyst is the Keggin structure component. The vibration of $\nu(Mo-O_b-Mo)$ and $\nu(Mo-O_c-Mo)$ in (c5) compared with that of (c3) is weak after reaction because Mo^{6+} has been partly reduced to Mo^{5+} [21], but the main Keggin structure is well reserved.

The TG–DTA curves of as-prepared catalyst (c) $H_xFe_{0.12}Mo_{11}VPAs_{0.3}O_y$ shown in Fig. 2 exhibit an endothermic peak at 95 °C accompanying great weight loss, which shows the existence of much lattice water. Another exothermic peak at 432 °C without weight loss indicates that the catalyst begins to decompose at 400 °C and is completely decomposed at 450 °C which indicates the catalyst can keep the Keggin structure in the course of catalytic reaction. The

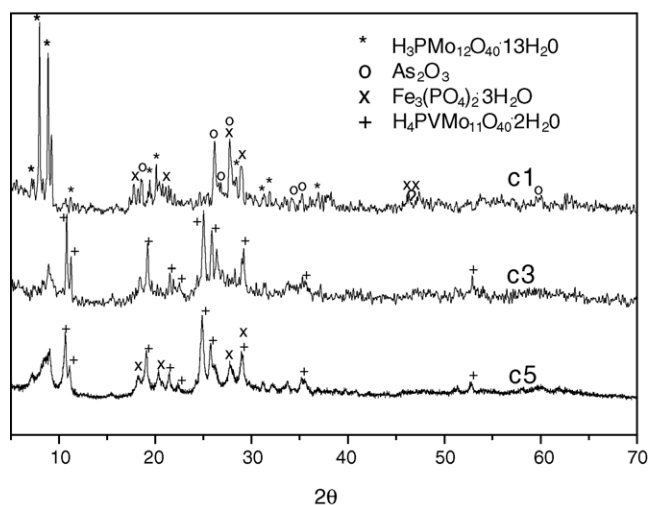


Fig. 5. X-ray diffraction patterns of the catalyst (c) $H_xFe_{0.12}Mo_{11}VPAs_{0.3}PO_y$. (c1) as-prepared, (c3) calcined at 400 °C, (c5) after reaction.

catalyst will lose its activity if the Keggin structure is destroyed owing to over-temperature calcination.

The TPR results of the catalysts are shown in Fig. 3, from which one main reduction peak within the range of 590–680 °C can be observed. It is evident that the addition of As increases the catalytic oxidation ability. Catalyst (c) is easier to be reduced than catalyst (a) probably because As and P have the close electronegativity value but the 4d orbit of As is easier to form $As \leftarrow O$ feedback bond than the 3d orbit of P to form $P \leftarrow O$ bond, resulting in the increase in counter-polarization to Mo^{6+} . Compared with catalyst (b), the main reduction peak of catalyst (c) is lower by about 80 °C showing that the addition of Fe^{3+} may occupy the counter-charge position and improves the ability of the catalyst. One possible reason is that the oxygen-spilling between Fe^{3+} and heteropoly anion can speed up the oxygen transfer usually thought as the rate determining step, leading to decrease in the reduction temperature of lattice oxygen [22] as well as increase in the catalytic activity.

Catalyst (c3) has one main reduction peak at 600 °C and two small ones at 496 and 550 °C. Compared with the reduction peak of catalyst (c3), the main reduction peak of catalyst (d) and catalyst (e) modified by K or Cs respectively shift to high temperature and the two small reduction peaks weaken visibly for Cs-modified catalyst (e), while they are almost

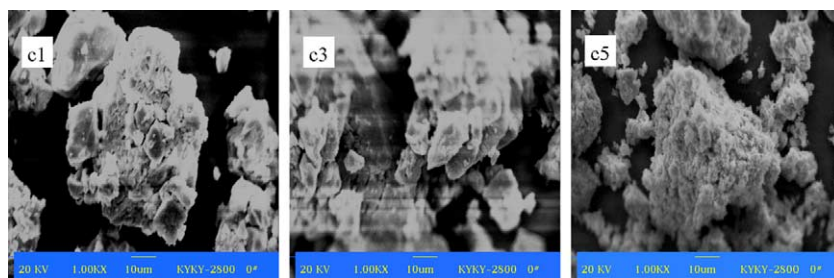


Fig. 4. SEM photographs of the catalyst (c) $H_xFe_{0.12}Mo_{11}VPAs_{0.3}PO_y$. (c1) as-prepared, (c3) calcined at 400 °C, (c5) after reaction.

invisible for K-modified catalyst (d), suggesting that the addition of alkali can obviously weakens the oxidation ability of the catalysts.

The reduction peaks at lower temperature are weak for uncalcined catalyst (c1), and the lowest ones are found for catalyst (c4) calcined at 450 °C, whose main reduction peak shifts from 600 to 654 °C and weakens considerably, meaning that proper calcination is in favor of the enhancement of oxidation ability of the catalyst and that the calcination at a higher temperature will lead to a great decrease in oxidation ability due to the destruction of the Keggin structure.

Fig. 4 is the SEM photographs of catalyst (c) treated under different conditions. The surface of both as-prepared catalyst (c1) and catalyst (c3) calcined at 400 °C are smooth, and so they have low surface area of 10.5 and 6.8 m² g⁻¹, respectively, showing no remarkable effect of appropriate calcination on the catalyst surface structure but some reduction of surface area. In contrast, catalyst (c5) reacted for 24 h becomes flocculent, so the surface area of the catalyst improves to 12.1 m² g⁻¹.

Fig. 5 shows the XRD patterns of catalysts (c1), (c3) and (c5), from which different crystal species and the conversions are observed. For catalyst (c1), the strong characteristic peaks of the Keggin structure of H₃PMo₁₂O₄₀ are found, and the characteristic peaks of Fe₃(PO₄)₂·(H₂O)₃ demonstrate that the As atoms have partly entered the heteropoly anion and substituted P atoms, in accordance with the IR results above. When catalyst (c1) is calcined at 400 °C and activated under pure oxygen (catalyst c3), the characteristic peaks of H₃PMo₁₂O₄₀ disappear and the strong characteristic peaks of H₄PMo₁₁VO₄₀ emerge, which indicates that V has entered into the heteropoly anion and formed the structure to fit the catalytic oxidation of isobutane during the process of calcination and activation. Compared with that of catalyst (c3) before reaction, the crystal structure of the heteropoly compound after the reaction is found greatly changed. The characteristic peaks of Fe₃(PO₄)₂·(H₂O)₃ emerge again and the peaks of H₄PMo₁₁VO₄₀ are a little weaker, demonstrating that the active species are mainly composed of Keggin structure heteropoly compound and that the existence of other species such as Fe₃(PO₄)₂·(H₂O)₃ is highly necessary for the improvement of catalytic performance.

Table 3
The effect of the alkali metals on catalytic properties

Catalysts	Reaction temperature (°C)	Isobutane conversion (%)	Yield (%)				
			MAL	AcOH	AA	MAA	CO _x
H _x Fe _{0.12} Mo ₁₁ VPAs _{0.3} O _y	370	23.9	0.98	2.8	0.95	16.7	2.47
H _x KFe _{0.12} Mo ₁₁ VPAs _{0.3} O _y	360	25.7	0.54	1.6	0.47	4.1	19.0
	370	28.3	0.21	2.0	0.46	3.5	22.1
H _x CsFe _{0.12} Mo ₁₁ VPAs _{0.3} O _y	350	17.5	0.96	2.1	0.35	10.2	3.89
	370	22.1	0.85	3.0	0.61	7.9	9.7

MAL: methacrolein; AcOH: acetic acid; AA: acrylic acid; MAA: methacrylic acid; gas velocity: *i*Bu:O₂:N₂ = 2:2:3 ml min⁻¹. All the data were collected after reaction for 4 h to reach equilibrium.

Table 1
The properties of catalyst H_xFe_{0.12}Mo₁₁VPAs_{0.3}O_y

Reaction time (h)	Isobutane conversion (%)	Yield (%)				
		MAL	AcOH	AA	MAA	CO _x
1	29.4	0.71	3.8	1.15	12.7	11.0
4	23.9	0.98	2.8	0.95	16.7	2.47
8	23.8	1.10	2.6	0.86	16.3	2.94
24	23.8	1.04	2.0	0.93	15.6	4.23

MAL: methacrolein; AcOH: acetic acid; AA: acrylic acid; MAA: methacrylic acid. Reaction temperature: 370 °C, gas velocity: *i*Bu:O₂:N₂ = 2:2:3 ml min⁻¹.

3.2. Catalytic activity for the isobutane oxidation

3.2.1. The activity test of the catalyst

Selective oxidation of isobutane to MAA over the catalyst H_xFe_{0.12}Mo₁₁VPAs_{0.3}O_y was tested and the results are summarized in Table 1. From Table 1 one can find that steady catalytic activity and selectivity to MAA can be obtained after 4 h. The best results are attained at after 4 h, when the conversion of isobutane is 23.9% and the yields of MAA, methacrolein (MAL), acetic acid (AcOH), acrylic acid (AA) and CO_x are 16.7%, 0.98%, 2.8% and 0.95% and 2.47%, respectively, which are obviously higher than those reported in previous literatures.

3.2.2. The influence of the counter-charge cations

The effect of the Fe content on the catalytic performance was systemically investigated and summarized in Table 2. It is found that the conversion of isobutane and the selectivity

Table 2
The effect of the content of Fe on catalytic properties of H_xFe_bMo₁₁VPAs_{0.3}O_y

<i>b</i>	Isobutane conversion (%)	Yield (%)				
		MAL	AcOH	AA	MAA	CO _x
0	16.4	1.4	0.8	0	3.6	10.6
0.8	20.6	1.3	2.1	0.70	8.9	7.6
1.2	23.9	0.98	2.8	0.95	16.7	2.47
1.6	19.3	1.1	1.9	0.37	9.2	6.7

MAL: methacrolein; AcOH: acetic acid; AA: acrylic acid; MAA: methacrylic acid. Reaction temperature: 370 °C, gas velocity: *i*Bu:O₂:N₂ = 2:2:3 ml min⁻¹. All the data were collected after reaction for 4 h to reach equilibrium.

Table 4

The effect of the content of As on catalytic properties of $H_xFe_{0.12}Mo_{11}VPAs_aO_y$

a	Isobutane conversion (%)	Yield (%)				
		MAL	AcOH	AA	MAA	CO _x
0	31.2	0.50	4.9	1.06	6.7	18.0
0.2	24.1	1.25	3.2	0.90	12.0	6.75
0.3	23.9	0.98	2.8	0.95	16.7	2.47
0.4	23.2	1.44	1.8	0.68	9.8	9.48

MAL: methacrolein; AcOH: acetic acid; AA: acrylic acid; MAA: methacrylic acid. Reaction temperature: 370 °C, gas velocity: $iBu:O_2:N_2 = 2:2:3 \text{ ml min}^{-1}$. All the data were collected after reaction for 4 h to reach equilibrium.

to MAA increase greatly from 16.4% and 22.2% to 23.9% and 69.9%, respectively, with proper Fe modification. The improvements of both the activity and the selectivity by Fe modification of molybdophosphoric acid catalyst have been proved by Martin and the reason may be the Fe^{3+}/Fe^{2+} redox couple intervening in the oxidation–reduction of the bulk acid by charge transfer between the Fe^{3+} and the Mo^{5+} of the Keggin anion [23].

It can be observed from Table 3 that the addition of K or Cs caused a sharp decrease in the MAA yield even though the addition of K can slightly improve the activity of catalyst, which is different from the previous studies in the selective oxidation of isobutane over heteropoly compound [2,8–17]. The Cs-substitution has a negative effect on the activity of catalyst and increases split products such as AcOH and AA though it increases the surface area from 6.8 to 20.1 $\text{m}^2 \text{g}^{-1}$. The addition of K reduces all organic product yields. The optimal reaction temperature with Cs or K modified catalyst decrease to 350 and 360 °C, respectively.

3.2.3. The influence of As content

The influence of the As content on the catalytic activity and selectivity to MAA has been tested. The results are summarized in Table 4. It is found that the addition of As obviously decreases catalytic activity and that the appropriate As modification can efficiently enhance the selectivity to MAA by restraining the split products. The optimal yield of MAA is achieved at the As content $a = 0.3$ with conversion of 23.9% and selectivity to MAA of 69.9%.

3.2.4. The influence of the temperature of calcination

The effect of calcination temperature was tested and the results are listed in Table 5. It is found that the catalytic activity and selectivity to MAA are greatly affected by the calcination temperature. An appropriate enhancement of calcination temperature makes for the improvement of catalytic performance. The catalyst calcined at 400 °C and activated under 2 ml min^{-1} pure O_2 atmosphere at 380 °C for 1 h exhibits the highest activity of 23.9% and the best selectivity of 69.9%. The conversion of isobutane is only 20.3% and the selectivity to MAA is 56.7% when the catalyst has been calcined at 350 °C and activated under the same conditions. Because of

Table 5

The effect of calcination temperature on catalytic properties of $H_xFe_{0.12}Mo_{11}VPAs_{0.3}O_y$

Calcination temperature (°C)	Isobutane conversion (%)	Yield (%)				
		MAL	AcOH	AA	MAA	CO _x
350	20.3	0.86	2.9	0.29	11.5	4.75
400	23.9	0.98	2.8	0.95	16.7	2.47
450	4.8	0	0	0	0	4.8

MAL: methacrolein; AcOH: acetic acid; AA: acrylic acid; MAA: methacrylic acid. Reaction temperature: 370 °C, gas velocity: $iBu:O_2:N_2 = 2:2:3 \text{ ml min}^{-1}$. All the data were collected after reaction for 4 h to reach equilibrium.

the destruction of the Keggin structure testified by the above IR and TG–DTA results, the catalyst calcined at 450 °C shows very low activity and no selectivity to MAA, which indicates that the existence of the Keggin structure is necessary for catalytic oxidation of isobutane to synthesize MAA on this catalyst.

4. Conclusions

$H_4PMo_{11}VO_{40}$ -based heteropoly catalysts modified by transition metals were synthesized by a simple chemical process and used for the selective oxidation of isobutane. The conversion of isobutane is 23.9% and the selectivity to MAA reaches 69.9% under optimal conditions over the catalyst $H_xFe_{0.12}Mo_{11}VPAs_{0.3}O_y$ which are improved obviously compared with those in previous literatures. The modifying iron as $Fe_3(PO_4)_2 \cdot (H_2O)_3$ and counter-cation in the Keggin structure are responsible for the improvement of catalytic ability of both conversion and selectivity to MAA. In addition, the modification with As only makes for the enhancement of selectivity to MAA. The addition of K or Cs causes a negative effect on the yield of MAA and the addition of K improves the isobutane conversion.

Acknowledgements

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