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Article

Selective Oxidation of Propane over CsFePVAsMo Heteropoly Compound Catalyst

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Both the partially reduced and non-reduced multi-component heteropoly compound catalysts with Keggin structure were prepared and used for the selective oxidation of propane. The catalysts were characterized by IR, H_2-TPR, NH_3-TPD, SEM and XRD. The addition of Cs increased the selectivity of acrylic acid and acetic acid. The selective oxidation performance was greatly improved with the addition of As. Among all of the tested catalysts, the catalytic performance of the $Cs_{1.8}Fe_{0.16}H_xPVAs_{0.4}Mo_{11}O_{40}$ (non-reduced) was the best and the maximum yield of acrylic acid reached 16.42%.

Keywords　heteropoly compound, partially reduced, selective oxidation, propane, acrylic acid

Introduction

As a kind of important and versatile material in organic chemical industry,[1] acrylic acid can be produced by many ways. Among them, the selective oxidation of propane is always attractive because it has potential application as a source of cheap raw material.[2-8] The catalytic function of heteropoly compounds in solid state has induced a lot of studies because their redox and acidic properties can be controlled at atomic/molecular level.[9-12] A great deal of research has been done to oxidize propane to acrylic acid (AA) by heteropoly compound catalyst systems. Mizuno previously reported that $Cs_{2.5}Fe_{0.08}H_{1.26}PVMo_{11}O_{40}$ showed high catalytic activity for oxidation of propane.[13] In the reaction conditions: $T=300$—400 ℃ and $C_3H_8/O_2/N_2=30/40/30$, the best performance (13% yield of acrylic acid at 48% of propane conversion) was observed with $Cs_{2.5}Fe_{0.08}H_{1.26}$-$PVMo_{11}O_{40}$. It is interesting that the partially reduced heteropoly compounds showed higher selectivity to acrylic acid for oxidation of propane.[14] Jiang reported that over the $H_xCu_{0.6}Cr_{0.6}PMo_{10}V_2As_{0.6}O_{40}$ (partially reduced), the maximum conversion of propane and the maximum yield of acrylic acid reached 38% and 14.8%, respectively.[15]

In our present work, we reported the catalytic performance and properties of both the partially reduced and non-reduced CsFeHPVAsMoO heteropoly compound catalysts for the selective oxidation of propane. The catalytic performance of the partially reduced catalyst was compared with that of the non-reduced catalyst. The catalytic performance and properties of these catalysts were modified with the addition of As and Cs. The roles of promoters Cs and As were discussed.

Experimental

Catalyst preparation

Four catalysts of heteropoly compounds (HPC) with Keggin structure were prepared according to literature.[16] The typical procedure is shown as follows. A certain amount of P_2O_5, As_2O_5, MoO_3, V_2O_5 and Fe or $Fe(NO_3)_3$ was mixed by molar ratio ($P:V:As:Mo:Fe=1:1:0.4:11:0.16$) with water and refluxed at 70—80 ℃ for 48—72 h to form a homogeneous solution. Among them, one was partially reduced HPC and the others were non-reduced HPC. The partially reduced heteropoly acid was prepared using Fe as the reductant. The color of the partially reduced heteropoly acid solution was blue, but the color of the non-reduced heteropoly acid solution was red. Then an aqueous solution of cesium carbonate (0.08 mol•dm^{-3}) was added into the heteropoly acid solution while being stirred at 60 ℃. The resulting suspension was evaporated to dry in a water bath. The four catalysts are designated as $1^{\#}$, $2^{\#}$, $3^{\#}$ and $4^{\#}$, corresponding to $Cs_{1.8}Fe_{0.16}H_xPVAs_{0.4}Mo_{11}O_{40}$ (partially reduced), $Cs_{1.8}Fe_{0.16}H_xPVAs_{0.4}Mo_{11}O_{40}$, $Cs_{1.8}Fe_{0.16}H_xPVMo_{11}O_{40}$, and $Fe_{0.16}H_xPVAs_{0.4}Mo_{11}O_{40}$, respectively.

Characterization

IR spectra of the catalysts were taken on a Perkin Elmer 2000 IR spectrometer (Perkin Elmer Co.) by KBr

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tablet method.

Specific surface area, temperature-programmed reduction (TPR) and temperature-programmed desorption (TPD) were measured by a Chembet-3000 Adsorption Instrument (Quantachrome Co.). In the H_2-TPR experiments, the sample (*ca.* 30 mg) was exposed to a 20 mL•min^{-1}, 15% H_2/N_2 flow, and heated at a rate of 10 ℃•min^{-1}. The final temperature was 650 ℃. NH_3-TPD experiments were performed under a 20 mL•min^{-1}, NH_3 (pure) flow for 1.5 h at 80 ℃, then swept with a 20 mL•min^{-1} N_2 (purity: 99.99 vol%) flow at a temperature rate of 10 ℃•min^{-1}. The specific surface area experiments were carried out under an atmosphere of mixed He-N_2 containing 20% (mol/mol) N_2.

The patterns of scanning electron microscopy (SEM) of both the $Cs_{1.8}Fe_{0.16}H_xPVAs_{0.4}Mo_{11}O_{40}$ (before and after reaction 12 h) and the $Fe_{0.16}H_xPVAs_{0.4}Mo_{11}O_{40}$ were obtained on a KYKY-2800 SEM meter (Chinese Academy Science Instrument).

X-ray powder diffraction (XRD) was measured by a BRUKER D8 Advance diffractometer using Cu Kα radiation ($\lambda = 1.54056 \times 10^{-7}$mm). The 2θ angles were scanned from 5° to 70° at a rate of 2 (°)•min^{-1}.

Catalytic testing

The synthesized catalysts were tested for the partial oxidation of propane in a tubular fixed-bed microreactor-gas chromatography. The weight of catalyst was 1.2 g. Before each reaction, the catalysts were treated in a nitrogen stream (10 mL•min^{-1}) for 1 h at 320 ℃. The products were analyzed online by a gas chromatograph (GC102N) equipped with a porapak-Q column (6×2000 mm^2), a FID detector and a N-2000 workstation. The conversion and yield data were collected after reacting 2—3 h, when nearly steady state was obtained for each catalyst.

Results and discussion

The analysis of the catalysts structure

The IR spectra of the catalysts are shown in Figure 1. Four strong absorption peaks near 1063, 956, 870 and 789 cm^{-1}, which are attributed to the vibration of P—O bond, Mo=O bond and Mo—O—Mo bonds of different locations, respectively, showed that these four catalysts all contained heteropoly anions of the Keggin structure. The vibration of V—O bond could not be seen because of the very strong absorption of Mo—O bond.[15] It was evident that the Keggin anion structure was well conserved in catalysts containing Cs^+ counterions. The partially reduced catalyst showed no evident difference from the other three catalysts.

The specific surface area data of the four catalysts are shown in Table 1. It was shown that the four catalysts all had small specific surface area. But the specific surface area of the catalysts containing Cs^+ was much bigger than that of the catalysts containing no Cs^+, so the activity of the catalysts containing Cs^+ was improved greatly. After reaction for 12 h, the specific surface area of the catalysts decreased drastically.

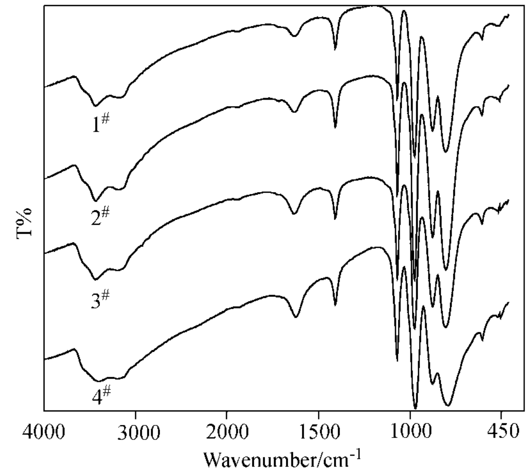

Figure 1 IR spectra of four catalysts: (1#) $Cs_{1.8}Fe_{0.16}H_xPVAs_{0.4}$-$Mo_{11}O_{40}$ partially reduced; (2#) $Cs_{1.8}Fe_{0.16}H_xPVAs_{0.4}Mo_{11}O_{40}$; (3#) $Cs_{1.8}Fe_{0.16}H_xPVMo_{11}O_{40}$ and (4#) $Fe_{0.16}H_xPVAs_{0.4}Mo_{11}O_{40}$.

Table 1 The specific surface area (m^2•g^{-1}) of the catalysts

Catalyst	Specific surface area/(m^2•g^{-1})
1# $Cs_{1.8}Fe_{0.16}H_xPVAs_{0.4}Mo_{11}O_{40}$ partially reduced	20.01
2# $Cs_{1.8}Fe_{0.16}H_xPVAs_{0.4}Mo_{11}O_{40}$ before reaction	21.99
3# $Cs_{1.8}Fe_{0.16}H_xPVMo_{11}O_{40}$	20.30
4# $Fe_{0.16}H_xPVAs_{0.4}Mo_{11}O_{40}$	1.39
5# $Cs_{1.8}Fe_{0.16}H_xPVAs_{0.4}Mo_{11}O_{40}$ after reaction	3.87

The electron microscopy study has been focused on the samples of $Fe_{0.16}H_xPVAs_{0.4}Mo_{11}O_{40}$, $Cs_{1.8}Fe_{0.16}H_x$-$PVAs_{0.4}Mo_{11}O_{40}$ (before reaction), and $Cs_{1.8}Fe_{0.16}H_x$-$PVAs_{0.4}Mo_{11}O_{40}$ (after reaction). The micrograph (Figure 2a) shows that the particle size of 4# catalyst was 8 to 20 μm, the surface of 4# catalyst was much smoother than that of other two catalysts. The micrograph of 2# catalyst (Figure 2b) was different from that of 4# catalyst. With the addition of Cs, the particles of 2# catalyst became smaller, with the particle size of 5 to 10 μm. On the particles, the rich and tiny surface could be observed. The particles had infinite and meticulous texture, which meant that the active component of the catalyst became much more dispersed, so it showed the best catalytic performance. After the reaction for 12 h, the sintering phenomenon was observed over 2# catalyst and the particles aggregated and became bigger, so the specific surface area of 2# catalyst became smaller. The same result can also be seen from the data of specific surface area of the catalysts.

Figure 3 shows the XRD patterns of the catalysts. The cell parameters of 2# sample (after reaction) is as

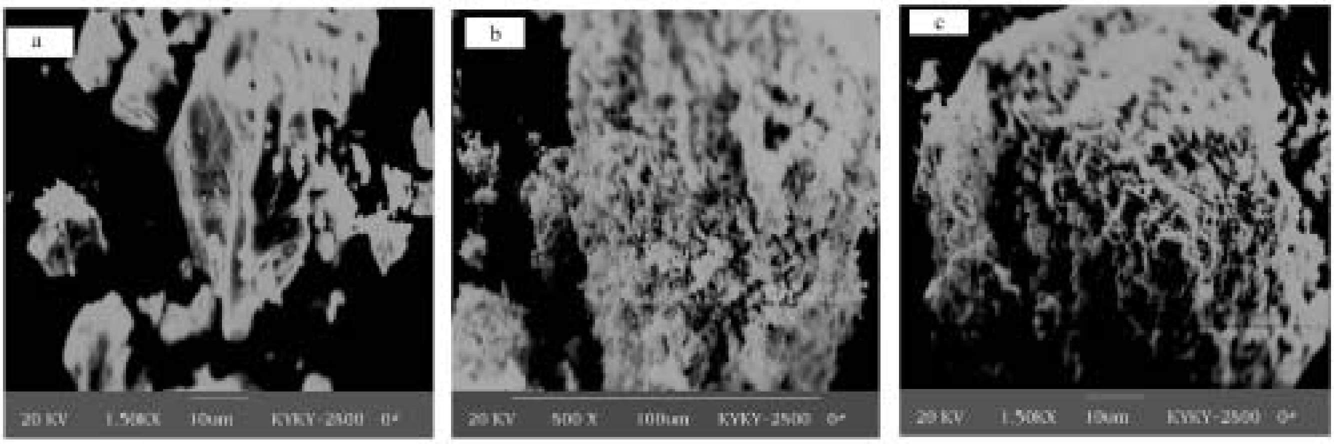

Figure 2 SEM graphs of (a) $Fe_{0.16}H_xPVAs_{0.4}Mo_{11}O_{40}$ ($4^{\#}$), (b) $Cs_{1.8}Fe_{0.16}H_xPVAs_{0.4}Mo_{11}O_{40}$ ($2^{\#}$) before reaction and (c) $Cs_{1.8}Fe_{0.16}H_xPVAs_{0.4}Mo_{11}O_{40}$ ($2^{\#}$) after reaction.

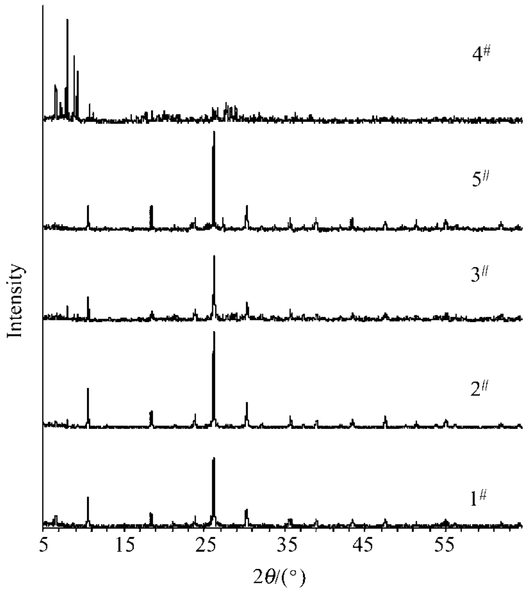

Figure 3 X-ray diffraction patterns of the catalysts: ($1^{\#}$) $Cs_{1.8}Fe_{0.16}H_xPVAs_{0.4}Mo_{11}O_{40}$ partially reduced; ($2^{\#}$) $Cs_{1.8}Fe_{0.16}H_xPVAs_{0.4}Mo_{11}O_{40}$ before reaction; ($3^{\#}$) $Cs_{1.8}Fe_{0.16}H_xPVMo_{11}O_{40}$; ($4^{\#}$) $Fe_{0.16}H_xPVAs_{0.4}Mo_{11}O_{40}$ and ($5^{\#}$) $Cs_{1.8}Fe_{0.16}H_xPVAs_{0.4}Mo_{11}O_{40}$ after reaction.

follows: cubic system $a=b=c=11.756\times10^{-7}$ mm, $\alpha=\beta=90°$, $V=1.62472\times10^{-18}$ mm^3. The XRD pattern of $4^{\#}$ sample was completely different from the other samples of containing Cs counterions. $4^{\#}$ sample was mainly composed of two acid phases, the $H_xAsV_nMo_{12-n}O_{40}\cdot yH_2O$ and $H_xPV_nMo_{12-n}O_{40}\cdot yH_2O$. According to literature report,[17,18] both $H_xAsV_nMo_{12-n}O_{40}\cdot yH_2O$ and $H_xPV_nMo_{12-n}O_{40}\cdot yH_2O$ have the triclinic crystal structure. With the addition of the Cs^+, the protons were substituted for the Cs^+, and a new cubic phase, which corresponds to $Cs_4PVMo_{11}O_{40}\cdot xH_2O$, was detected. In $1^{\#}$, $2^{\#}$ and $3^{\#}$ samples, the cubic phase was all observed. Comparing the XRD pattern of $2^{\#}$ sample after reaction with that before reaction, the catalyst crystal structure showed no distinctive difference. According to Langpape's studies,[20] acid phase is the catalytically active one, and the pure cesium salt is inactive. Why dose $2^{\#}$ sample show the best activity for propane oxidation? It is conceivable that with the addition of cesium cations, both the solid cesium salt and a hydrated acid phases are produced in the compound. Because the cesium salt is a big cationic heteropolyacidic salt so its solubility in the water is very small. It is also conceivable that during the preparation, the cesium salt is precipitated firstly and then the acid covered the salt particles.[20] But the acid film was too thin to be detected by X-ray diffraction. It is possible that the supported acid has the larger specific surface areas than the pure acid phases. This was proved by the specific surface area data.

The analysis of oxidative ability and acidic property of the catalysts

H_2-TPR measurements The TPR curves of the four catalysts are shown in Figure 4. It was shown that all of the four catalysts had a consumption peak of H_2 in the range of temperature 570—650 ℃. Their apex temperatures were near 615, 583, 634, 580 ℃ respectively. $2^{\#}$ and $4^{\#}$ catalysts had consumption peak of H_2 in the range of lower temperature. Especially the starting temperature of the $2^{\#}$ catalyst reduced by H_2 was near 410 ℃, which meant that it was more reducible than the others. It was evident that the addition of As increased the catalyst oxidative ability, while the oxidative activity did not vary with the addition of Cs. Comparing the partially reducted catalyst ($1^{\#}$) with the non-reduced catalyst ($2^{\#}$), the reduction peak shifted to higher temperature, starting around 600 ℃, and the apex was around 615 ℃. The catalyst oxidative ability decreased. According to the report by Mao,[16] the redox reaction in the range of lower temperature may be attributed to the redox procession between the HPC with higher assembly structure and the hydrogen, while the reduction peaks appearing at higher temperature may be attributed to the decomposition procession of the HPC from higher assembly structure to the lower assembly one until the oxides eventually. So $2^{\#}$ catalyst had the best catalytic activity in the partial oxidation of propane.

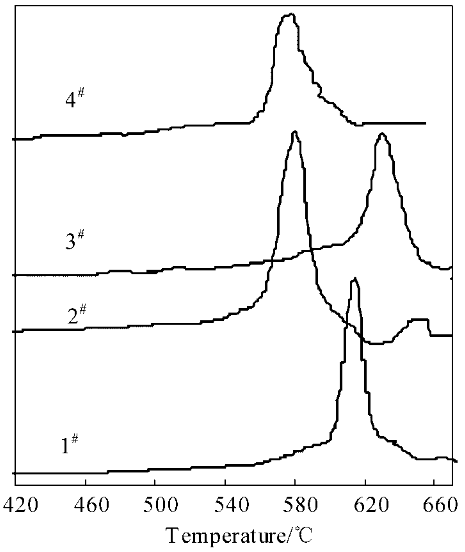

Figure 4 The TPR of four catalysts: ($1^{\#}$) $Cs_{1.8}Fe_{0.16}H_x$-$PVAs_{0.4}Mo_{11}O_{40}$ partially reduced; ($2^{\#}$) $Cs_{1.8}Fe_{0.16}H_xPVAs_{0.4}Mo_{11}$-$O_{40}$; ($3^{\#}$) $Cs_{1.8}Fe_{0.16}H_xPVMo_{11}O_{40}$ and ($4^{\#}$) $Fe_{0.16}H_x PVAs_{0.4}Mo_{11}O_{40}$.

NH_3-TPD measurements To examine the acidic property of the four catalysts, NH_3-TPD was carried out and the profiles are shown in Figure 5. All of the four catalysts had a desorbed peak of NH_3 in the range of 170—370 ℃. The integral areas of TPD profiles of $1^{\#}$, $2^{\#}$, $3^{\#}$ and $4^{\#}$ catalysts were 280, 482, 589, 2249 respectively. Over $1^{\#}$ catalyst, the integral area was smaller, which shows that only a small amount of NH_3 was desorbed and the acidity of $1^{\#}$ catalyst was lower. Over $2^{\#}$ catalyst, the amount of desorbed NH_3 was about 1.7 times as much as that of $1^{\#}$ catalyst. It showed that the acidity of the catalyst decreased when the catalyst was partially reduced. The acidity of $3^{\#}$ catalyst was almost the same as that of $2^{\#}$ catalyst, which indicated that the acidity had no distinct change with the addition of As. Over $4^{\#}$ catalyst, the amount of desorbed NH_3 was about 4.6 times that of $2^{\#}$ catalyst, which shows that the acidity of $2^{\#}$ catalyst was lower. Because H^+ in the catalyst was replaced by Cs^+, the acidity of the heteropoly compound catalysts decreased gradually, which was in accordance with the result in literature.[19]

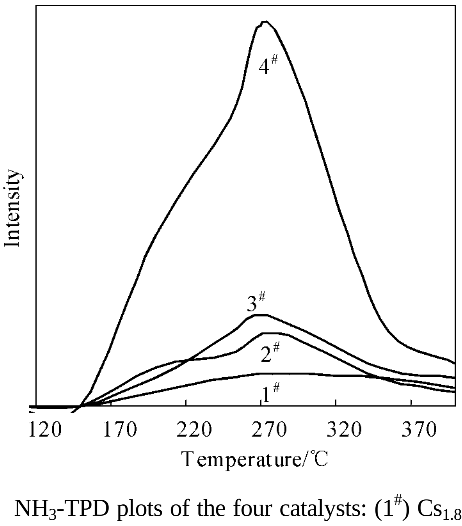

Figure 5 NH_3-TPD plots of the four catalysts: ($1^{\#}$) $Cs_{1.8}Fe_{0.16}H_x$-$PVAs_{0.4}Mo_{11}O_{40}$ partially reduced; ($2^{\#}$) $Cs_{1.8}Fe_{0.16}H_xPVAs_{0.4}Mo_{11}$-$O_{40}$; ($3^{\#}$) $Cs_{1.8}Fe_{0.16}H_xPVMo_{11}O_{40}$ and ($4^{\#}$) $Fe_{0.16}H_xPVAs_{0.4} Mo_{11}O_{40}$.

Catalytic activity for the propane oxidation

Effect of As and Cs Table 2 shows the results of the oxidation of propane catalyzed over the four catalysts respectively. The presence of As increased the oxidative activity. The TPR profiles also confirmed this fact. Because the radius of As is bigger than that of P, the addition of As would make some distortion of the Keggin structure and lower the symmetry of the crystal, so the activity of the catalyst increased greatly. The presence of Cs could increase the selectivity to acrylic acid. According to Mizuno,[21] the substitution of Cs^+ for H^+ can increase the specific surface area. Cesium cations can also increase the thermal stability of the heteropolyanion.[22] It has already been reported that the presence of Cs cations makes the catalyst more hydrophobic.[19] So when the Cs was added to the catalyst, the catalyst should have a tendency to expel polar molecules, such as acetic acid (HOAc) and acrylic acid (AA), and make their desorption easier, then increase the selectivity to AA (S_{AA}) and HOAc. But, it is interesting that the partially reduced catalyst did not exhibit the best catalytic performance, which was contrary to the report.[15] It may be due to the different mechanism of the propane oxidation over the different catalysts.

Table 2 Comparison of the catalytic activity of four catalysts for the selective oxidation of propane[a]

Catalyst	Conversion/%	Y_{AL}	Y_{HOAc}/%	Y_{AA}/%	S_{AA}/%
$1^{\#}$	26.82	0.44	5.40	10.37	38.66
$2^{\#}$	35.27	0.56	7.77	16.42	46.55
$3^{\#}$	19.89	0.33	3.04	5.09	25.59
$4^{\#}$	31.09	0.49	2.52	4.02	12.93

[a] AL: acrolein, HOAc: acetic acid, AA: acrylic acid, Y: yield, S_{AA}: selectivity of AA. ($1^{\#}$) $Cs_{1.8}Fe_{0.16}H_xPVAs_{0.4}Mo_{11}O_{40}$ partially reduced; ($2^{\#}$) $Cs_{1.8}Fe_{0.16}H_xPVAs_{0.4}Mo_{11}O_{40}$; ($3^{\#}$) $Cs_{1.8}Fe_{0.16}H_xPV$-$Mo_{11}O_{40}$; ($4^{\#}$) $Fe_{0.16}H_xPVAs_{0.4}Mo_{11}O_{40}$. Catalyst weight: 1.2 g, $T=420$ ℃, $C_3H_8 : O_2 : N_2=1 : 3 : 6.4$ (mol/mol), space velocity $=960\ h^{-1}$.

Effect of temperature Figure 6 (a) shows the temperature effect on the conversion and yield over $1^{\#}$ catalyst. The conversions of propane were 10.87%, 11.5%, 19.89%, 26.82% and 29.54% at 300, 340, 380, 420, and 440 ℃, respectively, and increased as reaction temperature went up. The yield of AA (Y_{AA}) gradually increased with a rise in reaction temperature and the maximum yield of AA was 10.37% around 420 ℃. The maximum yield of HOAc (Y_{HOAc}) was about 6.88% at 400 ℃. The temperature dependency of the conversion and yield for $2^{\#}$ catalyst is shown in Figure 6 (b). The yields of AA at 300, 340, 380, 420, and 440 ℃ were 2.45%, 4.67%, 10.18%, 16.42% and 11.26%, respectively and the maximum yield was obtained around 420 ℃. The maximum yield of HOAc was about 10.47% at 380 ℃. The yields of AA and HOAc greatly decreased above 420 ℃. For 1$^{\#}$ and 2$^{\#}$ catalysts, the maximum yield of AA was obtained at 420 ℃, then decreased with a rise in reaction temperature. The decrease of yields of AA and HOAc was mainly due to the successive oxidation of the products at high temperature. Usually, the heteropoly compounds suffer from the lower thermal stability during the reaction, compared with the composite oxides. It is interesting that both of the catalyst show their best catalytic performances under 420 ℃, which is in the range of the decomposition temperature of the heteropoly compounds. It meant that the partially destroy of the heteropoly catalysts may benefit their catalytic performances, which was confirmed by our previous studies.[23]

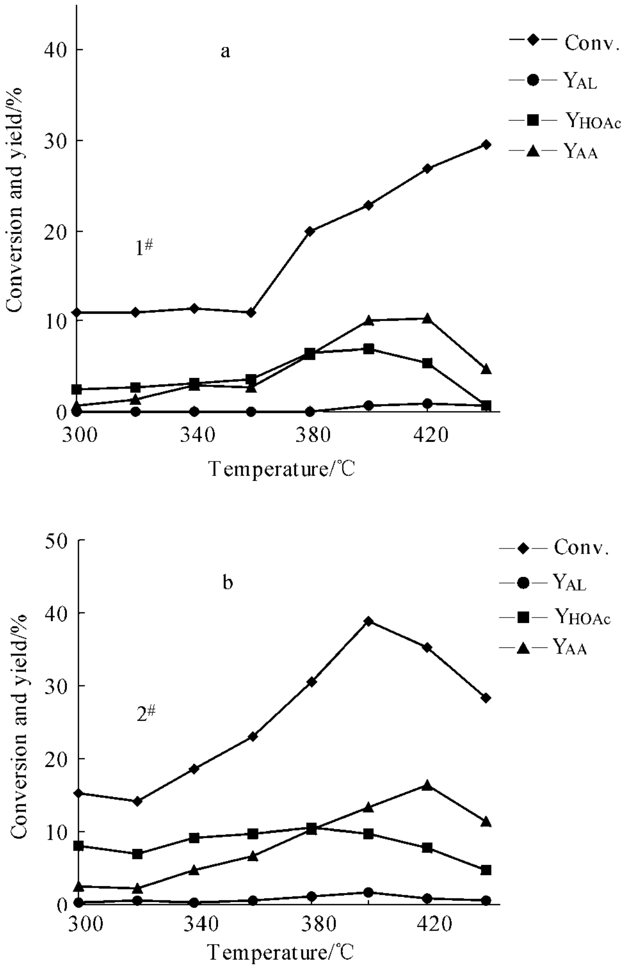

Figure 6 Effect of the reaction temperature on the selective oxidation of propane. Reaction conditions: C_3H_8 : O_2 : N_2=1 : 3 : 6.4 (mol/mol), space velocity=960 h^{-1}. (1$^{\#}$) $Cs_{1.8}Fe_{0.16}H_xPVAs_{0.4}Mo_{11}O_{40}$ partially reduced; (2$^{\#}$) $Cs_{1.8}Fe_{0.16}H_xPVAs_{0.4}Mo_{11}O_{40}$.

Effect of space velocity Figure 7 shows the effect of the space velocity on the selective oxidation of propane. The conversion of propane decreased gradually with the increase of the space velocity, while the yields of liquid products, especially the AA had a maximum value at the space velocity 960 h^{-1}. It illustrated that the lower space velocity benefited sufficient contact between the catalyst and the reactant gases, but it also resulted in over oxidation since the delayed desorption of the products.

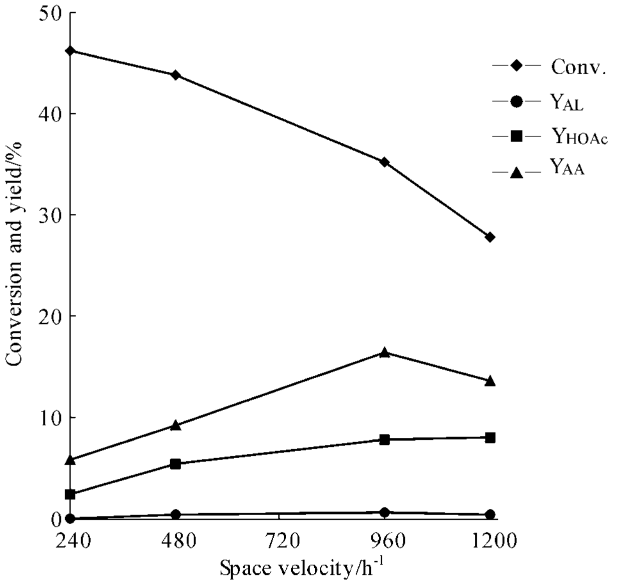

Figure 7 Effect of the space velocity for the selective oxidation of propane catalyzed by (2$^{\#}$) $Cs_{1.8}Fe_{0.16}H_xPVAs_{0.4}Mo_{11}O_{40}$. Reaction conditions: C_3H_8 : O_2 : N_2 =1 : 3 : 6.4 (mol/mol), T=420 ℃.

Effect of O_2/C_3H_8 ratio Effect of the O_2/C_3H_8 ratio on the selective oxidation of propane is shown in Figure 8.

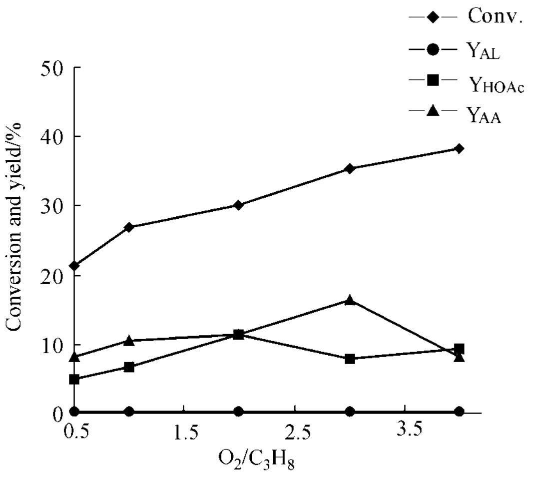

Figure 8 Effect of the O_2 /C_3H_8 ratio on the selective oxidation of propane catalyzed by $Cs_{1.8}Fe_{0.16}H_xPVAs_{0.4}$ (2$^{\#}$). Reaction conditions: O_2 : N_2=3 : 6.4 (mol/mol), space velocity=960 h^{-1}, T =420 ℃.

It was reported that the concentration of oxygen in the feed gases influences the distribution of surface active sites of the catalysts.[24] With the increase of the concentration of oxygen, the conversion of propane increased gradually. The results show that the oxygen-rich conditions are of benefit to the reaction. It may suggest that under oxygen-rich conditions the enhancement of reaction is due to the promotion of the production of catalyst. But the excessive oxygen will also lead to the over oxidation of AA, so decreasing the selectivity of AA. Therefore, maintaining the optimum O_2/C_3H_8 ratio is very important for the selective oxidation of propane. In our experiments, the optimum ratio was $C_3H_8 : O_2 : N_2 = 1 : 3 : 6.4$ (mol/mol).

The stability test of the catalyst Figure 9 shows the relationship between reaction time and catalytic performance of $2^{\#}$ catalyst at 420 ℃. The conversion and yields of liquid products increased gradually during the first 4 h. The conversion of propane was 35.27%. The yields of AA and HOAc were 7.77% and 16.42%, respectively. Then, with prolongation of reaction time, the activity of catalyst decreased fast. The conversion of propane was only 12.83%, the yields of AA and HAc were only 1.43% and 0.98%, respectively, after 12 h. Here a question is raised: why did the best catalytic performance of the catalyst only last so short duration? Through the analysis of SEM above, the decrease of activity may mainly be caused by the sintering phenomenon or surface coking. Specific surface of catalyst area of $2^{\#}$ catalyst became smaller, so the catalytic activity of the catalyst decreased violently. The utilization of the catalyst carrier may improve the poor stability of the catalysts and decrease the sintering phenomenon, so prolonging the lifetime of the catalysts. This will be our next research task.

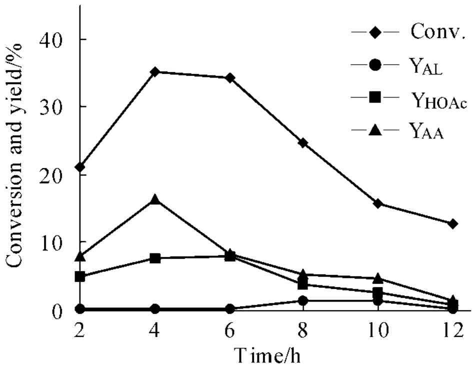

Figure 9 Time course of the selective oxidation of propane catalyzed by ($2^{\#}$) $Cs_{1.8}Fe_{0.16}H_xPVAs_{0.4}Mo_{11}O_{40}$. Reaction conditions: $C_3H_8 : O_2 : N_2 = 1 : 3 : 6.4$ (mol/mol), space velocity = 960 h^{-1}, $T = 420$ ℃.

Conclusions

The addition of As increased the catalyst oxidative ability and the addition of Cs^+ mainly increased the selectivity to AA and HOAc. The no-partially reduced catalyst exhibits the best catalytic performance. Results show that the optimum reaction conditions for the selective oxidation of propane were $T = 420$ ℃, $C_3H_8 : O_2 : N_2 = 1 : 3 : 6.4$ (mol/mol) and space velocity = 960 h^{-1}. Under such conditions, the conversion of propane and yield of acrylic acid reached 35.27% and 16.42%, respectively. The yield of acrylic acid has surpassed the present record of the highest yield of acrylic acid.[15]

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