



Cu or Fe Modified $\text{Cs}_2\text{HPMo}_{12}\text{O}_{40}$ as Catalysts for Selective Oxidation of Methacrolein

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Abstract

The Cu^{2+} or Fe^{3+} substituted $\text{Cs}_2\text{HPMo}_{12}\text{O}_{40}$ was synthesized to study the effect of transitional metal cations on selective catalytic oxidation of methacrolein by polyoxometalates. Adding of Cu^{2+} could reduce acidity and enhance oxidizing ability of the catalyst. The catalytic experiments showed that the addition small amount of Cu^{2+} to the catalyst could increase the conversion of methacrolein from 65% to 96% and the selectivity to methacrylic acid to 55%, at 300-340°C. It is found adding of Cu^{2+} could promote the reduction process of catalysts should be the main reason of the performance enhancement. Adding of Fe^{3+} to the catalyst could induce some new weak acidic sites due to the formation of iron aqua complexes. Whereas, Fe^{3+} had no significant effect on redox ability of the catalyst. The conversion of methacrolein could reach 96% with the existence of Fe^{3+} . However, the addition of Fe^{3+} had no significant effect on selectivity to methacrylic acid.

Keywords: Methacrolein (MAL); Polyoxometalates (POMs); Copper; Iron; Catalysis

Introduction

Methacrylic acid (MAA) is an important mediate chemical for producing methyl methacrylate, which can be used to synthesize polymethylmethacrylate, other derivatives for coatings, PVC modifier and so on. To date, POMs with the so-called Keggin structure, especially the cesium salts of 12-molybdophosphoric acid, have been proved to be a good catalyst for selective oxidation of MAL to MAA [1-10]. Cesium salts of 12-molybdophosphoric acid present an organized three-level structure. The primary structure is also known as Keggin structure consists of $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ heteropolyanion, a central atom P bonding with four O atoms forming a PO_4 tetrahedron, which is surrounded with twelve MoO_6 octahedra. The secondary structure is composed of the heteropolyanion, counterions, crystalline water, and other additional molecules. The tertiary structure relates to the particle size, pore structure, the distribution of protons in the particles. Former researches indicate that POMs can be applied in both acidic and redox-catalyzed reactions, and their acidic and redox properties can be finely tuned by choosing constituent elements or counter cations [11,12]. The effect of counter cations on performance of POM catalyst had been extensively studied. Stytsenko et al. [1] found that cesium defines the acidity and specific area, vanadium controls the selectivity, and the transition metals define the mobility of oxygen in the bulk and the catalytic activity. Some other studies have pointed that the addition of copper and iron as counter cations into the POMs-catalysts can improve catalytic performance, as copper and iron play an important role in the redox processes [13,14]. Langpape et al. [15] found that the Cu^{2+}/Cu redox couple could enhance the redox of the solids when protons were substituted by copper cations. The same effect of Fe was also confirmed [3]. In our former works, we found Cu and Fe co-doped acidic cesium salts of molybdovanadophosphoric acids could improve the redox properties and thereby enhance the catalytic behavior during the vapor-phase selective oxidation of MAL to MAA [7]. As a most simple and effective catalyst for selective oxidation of MAL to MAA, $\text{Cs}_2\text{HPMo}_{12}\text{O}_{40}$, the effect of Cu and Fe doping on this catalyst is still parse and ambiguous. In order to clarify the effects of Cu and Fe modification on $\text{Cs}_2\text{HPMo}_{12}\text{O}_{40}$ for selective oxidation of MAL, two series of catalysts with general formula $\text{Cs}_2\text{Cu}_x\text{H}_{1-2x}\text{PMo}_{12}\text{O}_{40}$ and $\text{Cs}_2\text{Fe}_x\text{H}_{1-3x}\text{PMo}_{12}\text{O}_{40}$ ($x=0.0-0.3$) have been prepared

and characterized. The catalytic performances of these two series catalysts were investigated at different reaction temperature. It is found that doping of both Cu and Fe can increase the catalytic performance of $\text{Cs}_2\text{HPMo}_{12}\text{O}_{40}$, but with different mechanism.

Experiment

Preparation of the samples

A conventional method was utilized to prepare the $\text{Cs}_2\text{HPMo}_{12}\text{O}_{40}$ (Cs_2H). 1.62 g Cs_2CO_3 (TP, 99%, Hubei, Baijierui Advanced Materials Co. Ltd.) and 11.36 g $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (AR, Shanghai, Huayi (Group) Company) were dissolved in deionized water to form an aqueous solution, respectively. Then the Cs_2CO_3 aqueous solution was dropped into $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ aqueous solution at 50°C. The precipitate rapidly generated and aged for 5 h. The precipitate was separated by centrifugation, washed with deionized water and dried in vacuum oven at 50°C. The iron- and copper-containing cesium salts of 12-phosphomolybdic acid, simplified as Cs_2Cu_x catalysts and Cs_2Fe_x catalysts ($x=0.05-0.3$), were prepared by the same procedure. Certain amount of $\text{Cu}(\text{OH})_2$ or $\text{Fe}(\text{OH})_3$ was added into the aqueous solution of 12-molybdophosphoric acid to get clear solution before the addition of Cs_2CO_3 aqueous solution. Then the precipitate was collected by filtration, washed with water and dried in an oven. The calcination was carried out at 350°C under synthetic air atmosphere for 12 h. The obtained samples were crushed and sieved as 0.38-0.55 mm to be tested as catalysts for selective oxidation of MAL to MAA.

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Characterization techniques

Elemental composition of catalysts was confirmed by atomic emission for Mo, Cu, Fe, Cs, and P using the Shimadzu Multitype ICP Emission Spectrometer (ICPE-9000). FT-IR spectra of the samples were recorded by a Thermo Nicolet FT-IR 380 with anhydrous KBr as standard to confirm the primary Keggin structure of these samples. Raman spectra of the samples obtained by using a laser Raman (HR800 UV, Horiba Scientific Co., Ltd.) with a 100 mV laser, equipped with a wavelength of 514 nm and CCD detector. X-ray diffraction (XRD) data were recorded on a Rigaku Smart Lab X-ray powder diffractometer operated at an accelerating voltage of 45 kV and an emission current of 200 mA with Cu K α radiation. The surface structure of samples was studied by SEM on a SU8020 SEM instrument (Hitachi High-Technologies Corporation). The NH₃-TPD and the H₂-TPR measurements were carried out on a Micromeritics Autochem II 2920 apparatus. In the NH₃-TPD experiment, 50 mg of the sample was pre-treated under helium flow (20 mL·min⁻¹) at 150°C for 1 h. Then, samples cooling to 50°C were treated under an atmosphere of 10% NH₃-He flow, and the desorption profile was recorded in flowing helium at a heating rate of 10°C·min⁻¹ to 650°C. The TPR analysis was carried out in a 10% H₂-Ar flow at a heating rate of 10°C·min⁻¹ to 650°C until the baseline was stable.

Selective catalytic oxidation of MAL to MAA

Catalytic experiments were performed in a fixed-bed reactor under atmospheric pressure. 0.8 g of catalyst was loaded into the constant temperature zone of a stainless steel tubular reactor, and quartz sand (0.38-0.55 mm) was used to fill the leaving space of the reactor. The composition of reaction gas at a flow rate of 150 mL·min⁻¹ was a mole ratio of MAL: O₂: N₂: H₂O=1: 2.5: 15: 8. Before reaction, the temperature was raised to reaction temperature and the gaseous reactants were delivered into the reactor. The inside temperature of the reactor was showed by a temperature indicator. The reaction products were gathered and analyzed using the internal standard method and ethanol as the internal standard. Analytical equipment we used by an Agilent 6820 gas chromatograph equipped with an FID detector using a DB-624 capillary column.

Results and Discussion

FT-IR analysis

Figure 1 showed the FT-IR of the prepared catalysts recorded between 1200 and 700 cm⁻¹. Four strong characteristic peaks were found in the spectra of all samples which are attributed to the vibration bands of Keggin structure. The Keggin ion bands were observed at 1066 cm⁻¹ for $\nu_{as}(\text{PO}_4)$ vibration, 962 cm⁻¹ for terminal $\nu_{as}(\text{Mo}=\text{O}_d)$ vibration, 870 and 801 cm⁻¹ for $\nu_{as}(\text{Mo}-\text{O}_b-\text{Mo})$ and $\nu_{as}(\text{Mo}-\text{O}_c-\text{Mo})$, respectively [16,17]. Comparison of the FT-IR of the catalyst before and after calcination, little difference was observed, indicating the prepared catalyst reserved the Keggin structure after reaction with Cu or Fe cations.

Raman analysis

Raman spectra further confirmed the structure of the catalysts. As shown in Figures 2a and 2c, before calcination, the catalysts exhibited main bands that attributed to Keggin structure. The split bands in the region 220-270 cm⁻¹ were caused by the deformation vibrations of the terminal M=O groups and the entire framework [18,19]. Bands at 605 and 890 cm⁻¹ were assigned to Mo-O_c-Mo and Mo-O_b-Mo vibration bands, respectively. Bands at 984 cm⁻¹ (shoulder) and 999 cm⁻¹ were

assigned to Mo=O_d stretching bands [20,21]. After calcination, the main bands of Keggin structure were still reserved (Figures 2b and 2d). According to Raman spectra and FT-IR, the Keggin structure kept integral after calcination. In addition, it is also observed that the Raman spectra showed little difference for different composition of cations. For Cs₂Cu_x, only a small band appeared at 940 cm⁻¹ after calcination, which can be assigned to copper oxide [CuO_x]^{(2-2x)+} [22]. In comparison, Cs₂Fe_x had almost the same bands indicating Cs₂Fe_x was more stable at high temperature. Additionally, no characteristic peak assigned to MoO₃ was observed in all the samples, suggesting the prepared catalyst was not decomposed during preparation process.

XRD analysis

XRD patterns of the samples were given in Figure 3. The XRD patterns of Cs₂Cu_x and Cs₂Fe_x catalysts exhibited a single cubic structure of Keggin-type HPCs (PDF No.46-0481). According to previous studies, the cubic phase only formed for salts with more than two cesium atoms [4]. In addition, the addition of Cu and Fe cations did not affect the fundamental crystal structure of the heteropoly compounds as previously reported by Deng et al. [23]. Comparison between Figures 3a and 3b, there is little difference in XRD for all the prepared catalyst before and after calcination indicating the crystal structure of the catalyst does not vary significantly after calcination. Additionally, no peak from orthorhombic MoO₃ (PDF No. 35076) was observed in all the samples. Hence, the results further confirmed the prepared catalyst kept stable and did not decompose.

The crystalline sizes of the prepared catalyst were calculated by Scherrer equation. Figure 4 depicted the crystalline sizes of catalysts before and after calcination. Before calcination, crystalline sizes of Cs₂Cu_x and Cs₂Fe_x keep constant at about 16-19 nm. After calcination, both the crystalline sizes of Cs₂Cu_x and Cs₂Fe_x increased significantly. Doping small amount of Cu or Fe can further increase the crystalline size of the catalyst. However, the crystalline size decreased when more content of Cu or Fe was added in the catalyst. SEM of the catalyst with different compositions confirmed such decrease trend. As shown in Figures 5a and 5b, for Cs₂Cu_x, when x value increased from 0.1 to 0.3, the mean particle size decreased from 31 nm to 28 nm. This trend is more obviously for Cs₂Fe_x, as shown in Figures 5c and 5d. The mean particle size of Cs₂Fe_x decreased from 30 nm to 24 nm when x increased from 0.1 to 0.3. This observation illustrated that the high content of Cu and Fe can restrain the growth of crystal grain size.

NH₃-TPD analysis

It can be expected that the replacement of protons by Cu or Fe will lead to changes in acidic properties. NH₃-TPD results were presented in Figure 6, all samples were calcinated under air atmosphere at 350°C for 12 h. The acid amount calculated from integration of peak area was exhibited in Tables 1 and 2. For Cs₂Cu_x catalysts, NH₃ may react with the Cu species in the catalyst resulting in the formation of Cu ammonia complex. Thus, it was necessary and reasonable to adjust the acid. The T_{max} of desorption and the adjusted acid amounts were listed in Table 1. As described in Figure 6, all samples had a main desorption peak in the temperature range of 370-500°C, representing the main acidity sites of the catalysts. Compared with Cs₂H, the T_{max} of both Cs₂Cu_x and Cs₂Fe_x decreased. Moreover, for Cs₂Fe_x (0.15≤x≤0.3) a small peak around 100°C and a big broad peak at temperatures between 250°C and 330°C were observed, indicating the presence of more weak acid sites in these catalysts. The formation of iron aqua complexes may result in such observation [3].

The acid amounts calculated from integration of peak area (Table

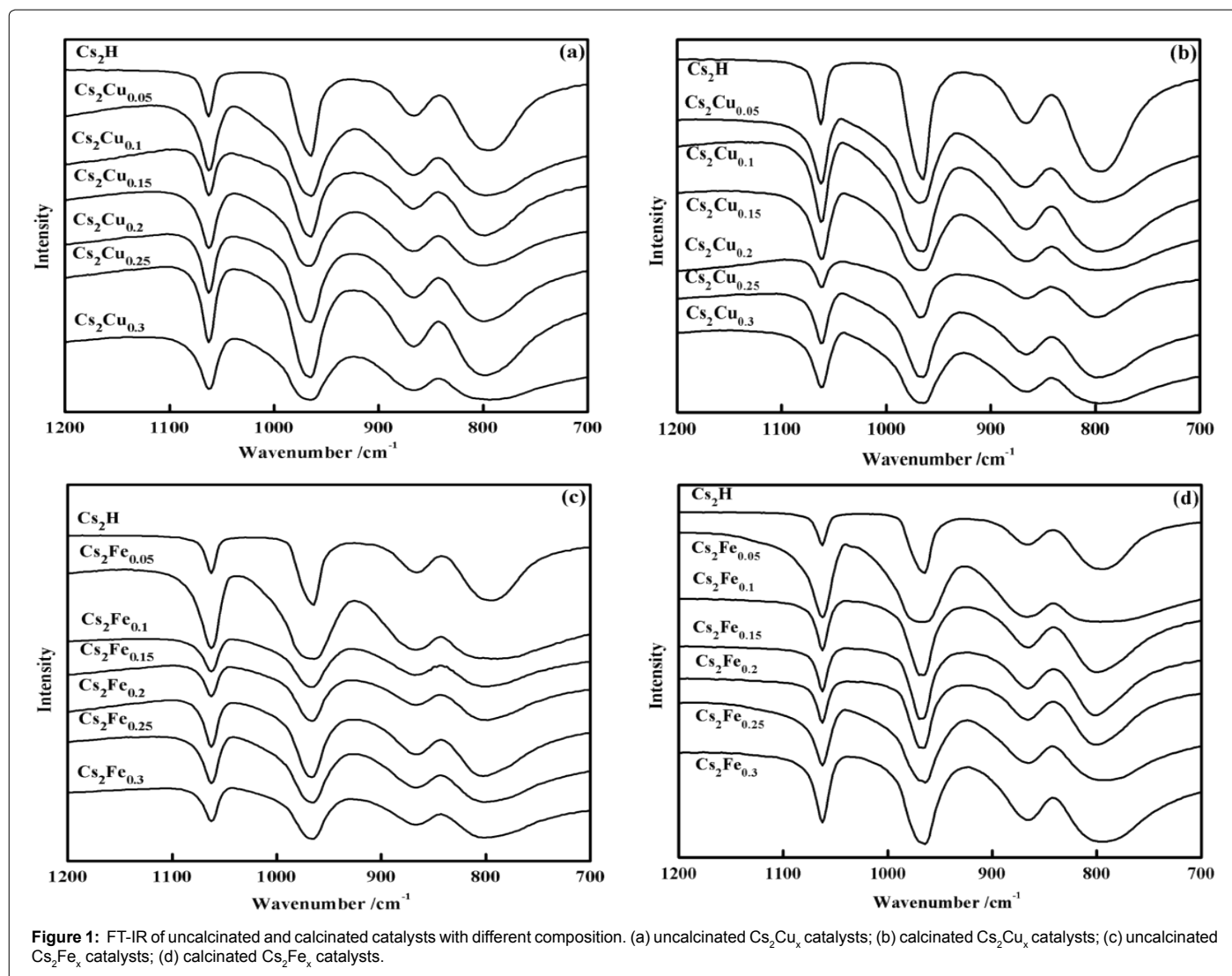


Figure 1: FT-IR of uncalcinated and calcinated catalysts with different composition. (a) uncalcinated Cs₂Cu_x catalysts; (b) calcinated Cs₂Cu_x catalysts; (c) uncalcinated Cs₂Fe_x catalysts; (d) calcinated Cs₂Fe_x catalysts.

Sample	T _{max} of desorption /°C	Acid amount /(mmol·g ⁻¹)
Cs ₂ H	436	0.57
Cs ₂ Cu _{0.05}	418	0.43
Cs ₂ Cu _{0.1}	414	0.42
Cs ₂ Cu _{0.15}	415	0.38
Cs ₂ Cu _{0.2}	420	0.31
Cs ₂ Cu _{0.25}	414	0.29
Cs ₂ Cu _{0.3}	411	0.20

Table 1: The acid amounts of the calcinated Cs₂Cu_x catalysts.

Sample	Desorption T _{max} /°C	Acid amount /(mmol·g ⁻¹)		
		Weak	Strong	Total
Cs ₂ Fe _{0.05}	431	0.16	0.56	0.72
Cs ₂ Fe _{0.1}	429	0.22	0.55	0.77
Cs ₂ Fe _{0.15}	425	0.25	0.57	0.82
Cs ₂ Fe _{0.2}	425	0.40	0.54	0.94
Cs ₂ Fe _{0.25}	422	0.47	0.52	0.99
Cs ₂ Fe _{0.3}	413	0.43	0.48	0.91

Table 2: The acid amounts of the calcinated Cs₂Fe_x catalysts.

1) showed that the acid amounts of Cs₂Cu_x catalysts decreased from 0.57 to 0.20 mmol·g⁻¹ when x value increased from 0.0 to 0.3. As for Cs₂Fe_x, there are both weak and strong acid sites existed in the catalysts, and the total amount of surface acid increased from 0.57 to 0.91 (Table 2) with the increase of Fe content from x=0.0 to 0.3. As Fe can react with water to form iron aqua complexes which showed weak acidity [24], the total amount of acid in Cs₂Fe_x catalysts increased with the increasing of Fe content.

H₂-TPR analysis

Figure 7 showed the H₂-TPR profiles of the calcinated catalysts. The temperature range of the main reduction peaks of all samples was between 450-600°C. According to the TG-DSC analysis, Cs₂Cu_x and Cs₂Fe_x catalysts completely decomposed when temperature was above 430°C. Hence, the reduction peaks between 450 and 600°C can be assigned to the reduction of the MoO₃ formed from the decomposition of the Keggin anions during the H₂-TPR experiment [19]. As shown in Figure 7a, with increasing Cu content, the main peak shifted from 582°C to 493°C suggesting that the replacement of protons by Cu would enhance the oxidizing ability of catalysts. In addition, a small reduction peak emerged around 200-250°C in H₂-TPR profiles of Cs₂Cu_(0.1-0.3) which was associated with the reduction of copper

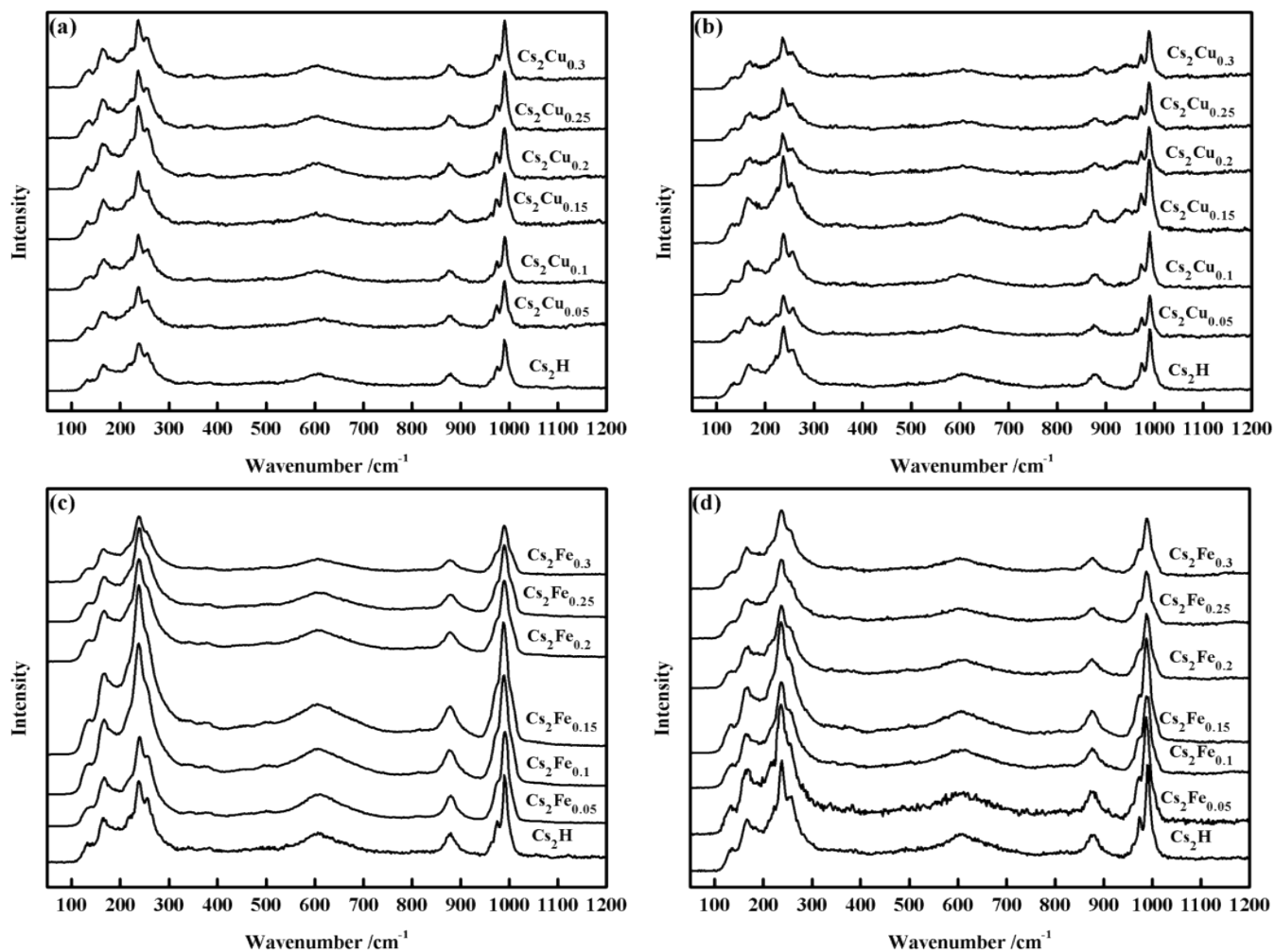


Figure 2: Raman spectra of (a) uncalcinated Cs₂Cu_x catalysts; (b) calcinated Cs₂Cu_x catalysts; (c) uncalcinated Cs₂Fe_x catalysts; (d) calcinated Cs₂Fe_x catalysts.

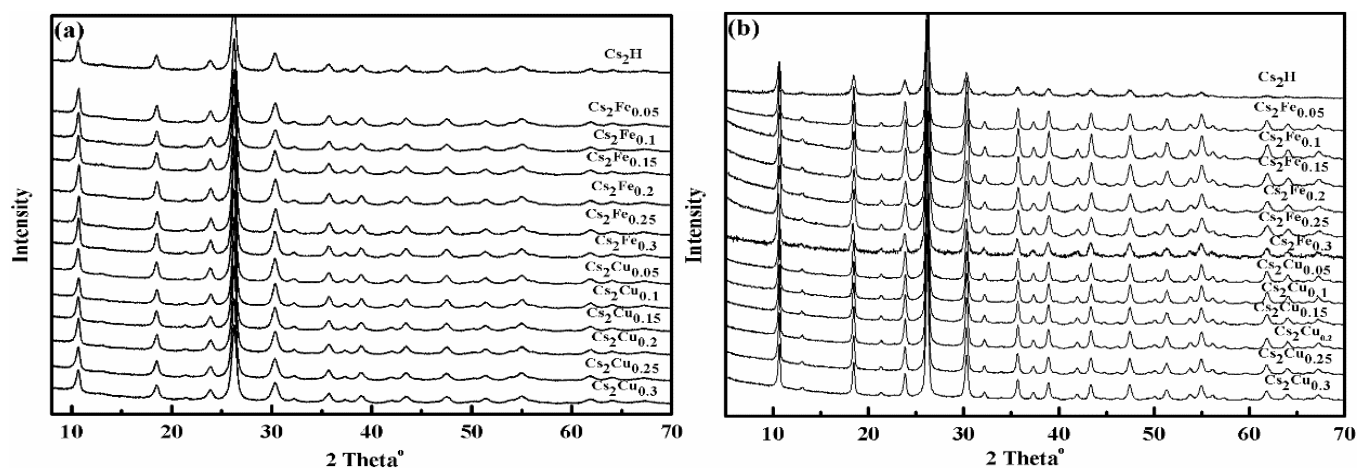


Figure 3: XRD patterns of (a) before calcination; (b) after calcination.

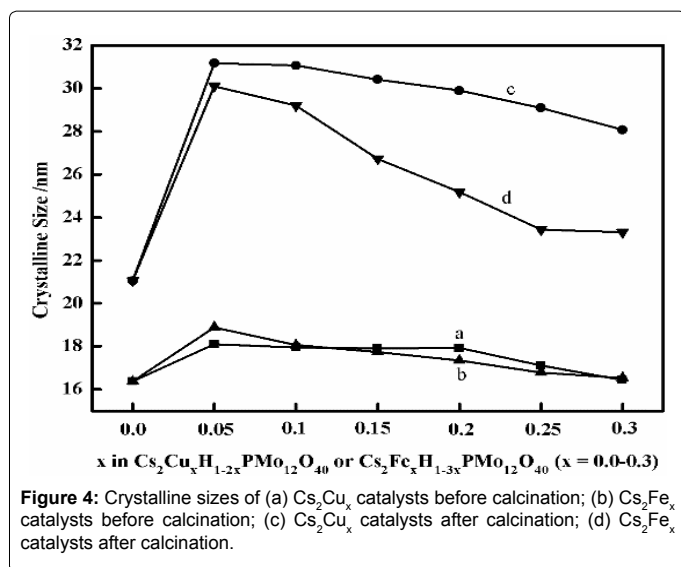


Figure 4: Crystalline sizes of (a) Cs_2Cu_x catalysts before calcination; (b) Cs_2Fe_x catalysts before calcination; (c) Cs_2Cu_x catalysts after calcination; (d) Cs_2Fe_x catalysts after calcination.

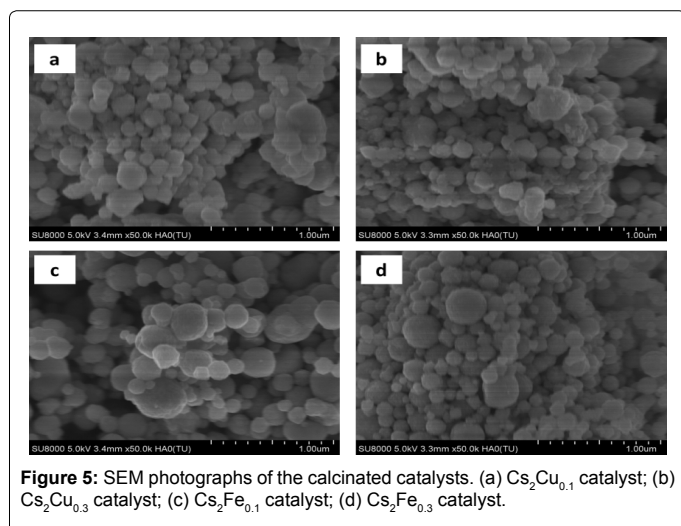


Figure 5: SEM photographs of the calcinated catalysts. (a) $\text{Cs}_2\text{Cu}_{0.1}$ catalyst; (b) $\text{Cs}_2\text{Cu}_{0.3}$ catalyst; (c) $\text{Cs}_2\text{Fe}_{0.1}$ catalyst; (d) $\text{Cs}_2\text{Fe}_{0.3}$ catalyst.

oxide that produced during the decomposition of catalyst at high temperature. Compared with the Cs_2H , the main reduction peak of Cs_2Fe_x showed little difference, indicated that the Fe modification has no obvious effect on the oxidizing ability of the catalyst. Additionally, there is no characteristic peak of Fe_2O_3 was found in Cs_2Fe_x catalysts.

Catalytic tests

The surface area of prepared Cs_2Cu_x and Cs_2Fe_x catalysts were characterized by BET measurements. It is found that all the prepared catalyst have close surface area to be about $10 \text{ m}^2\text{g}^{-1}$. The results of MAL conversion over Cs_2Cu_x catalysts with different Cu content at varied reaction temperatures were shown in Figure 8. When the reaction temperature was below 300°C , the addition of Cu just had small positive effect on the conversion of MAL. When the temperature raised to 300°C , MAL conversion of Cs_2Cu_x can be improve significantly from 65% to 96% when small quantity of Cu was contained in the catalyst ($x=0.05$). However, further increase of Cu content in the catalyst induce decrease of conversion. Such phenomena can also be observed at higher reaction temperature like 320 and 340°C . The great improvement of MAL conversion indicated that small amount of Cu can enhance the

oxidizing ability of catalysts when it reached a certain temperature. According to the former analysis, further increase of Cu content in the catalyst will decrease the acidity of the catalysts and thus weaken the adsorption of MAL on the catalyst and lower the catalytic activity. Therefore, the balance between Cu and proton content were important for promoting the catalytic activity [25]. It is also reported that in the presence of copper, the formation of oxygen vacancies turned to be easier [26], as a consequence of proton elimination associated with oxygen of the heteropolyanion [27]. This is consistent with our results. When the reaction temperature reached 320°C and 340°C , the MAL conversions on the $\text{Cs}_2\text{Cu}_{0.05}$ catalyst kept unchanged as 96%. But the conversion on the catalyst $\text{Cs}_2\text{Cu}_{0.25}$ and $\text{Cs}_2\text{Cu}_{0.3}$ fell to 89% and 83%, respectively, even lower than that of Cs_2H .

Figure 9 depicted the selectivity of the prepared Cs_2H and Cs_2Cu_x catalyst at different temperature. The results are complicated due to the complex reaction mechanism. First of all, the selectivity to MAA did not improved significantly when Cu was induced in to catalyst. For Cs_2H , the selectivity to MAA was about 47% at three temperatures. For Cs_2Cu_x ($x=0.05-0.10$), the selectivity to MAA even decreased at all the tested temperatures. When x value reached 0.15-0.20, the selectivity to MAA improved to 55%. Further increase of Cu content ($x>0.20$) result in the decline of MAA selectivity. Thus optimal x value in Cs_2Cu_x catalyst was between 0.15-0.20. The result indicated the balance between the oxidation ability and acidity of the catalyst played a key role in determination the activity of the catalyst (Figure 10). Too low or too high loading of Cu would not good for the catalytic performance.

The MAL conversions of Cs_2Fe_x catalysts were shown in Figure 11. At relative low reaction temperatures (260°C and 280°C), when x value in Cs_2Fe_x catalyst is larger than 0.15, the conversion showed strong dependence on the content of Fe in the catalyst. At 300°C , the conversion showed almost linear relationship with the content of Fe in the catalyst. However, at higher temperatures (320 and 340°C), the conversion could reach 96%, but kept stable and showed little dependence on x value. This phenomenon was quite different from that of Cs_2Cu_x catalyst, indicating different enhancement mechanism with these two kinds of catalysts. As we illustrated before, addition of Fe could only induce some weak acid sites in the catalyst and did not have any effect on oxidizing ability. Thus, the increase of MAL conversion may due to the enhanced water transfer by introduction of Fe in the catalyst, which can promote the reoxidation of the catalysts [28]. Additionally, the hydrated and dehydrated iron species should be in equilibrium in the secondary structure of Cs_2Fe_x catalysts.

The selectivity of Cs_2Fe_x catalysts was shown in Figure 12. Compared with Cs_2H and Cs_2Cu_x catalysts, the selectivity to MAA over Cs_2Fe_x catalysts were about 52% and showed little dependence on the Fe content. This is in agreement with that only reoxidation process of catalysts is speeded up by Fe modification (Figure 13).

Conclusions

In summary, the influence of Cu and Fe doping on $\text{Cs}_2\text{HPMo}_{12}\text{O}_{40}$ catalyst for selective oxidation of methacrolein to methacrylic acid has been investigated. The introduction of Cu or Fe into catalyst did not modify the Keggin structure of the catalyst. Introduction of certain amount of Cu and Fe can improve the conversion of methacrolein from 65% to 96%. It is found that addition of Cu can enhance the oxidizing ability of the catalyst, whereas addition of Fe can enhance the reoxidation process of the catalyst.

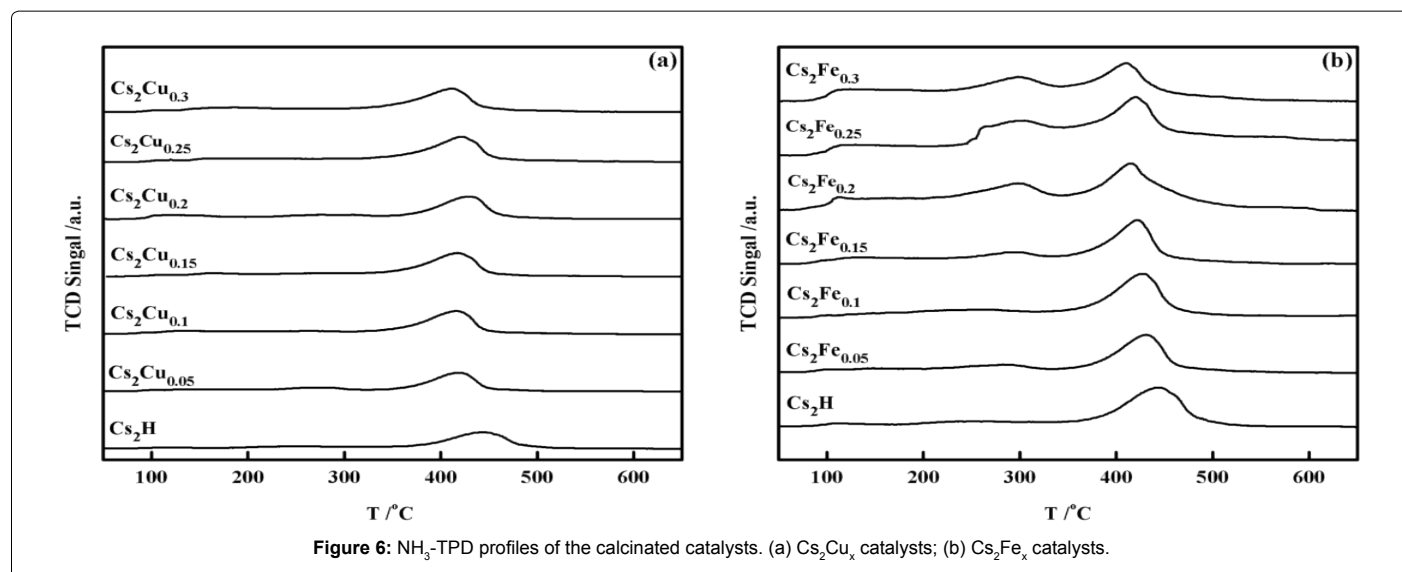


Figure 6: NH₃-TPD profiles of the calcinated catalysts. (a) Cs₂Cu_x catalysts; (b) Cs₂Fe_x catalysts.

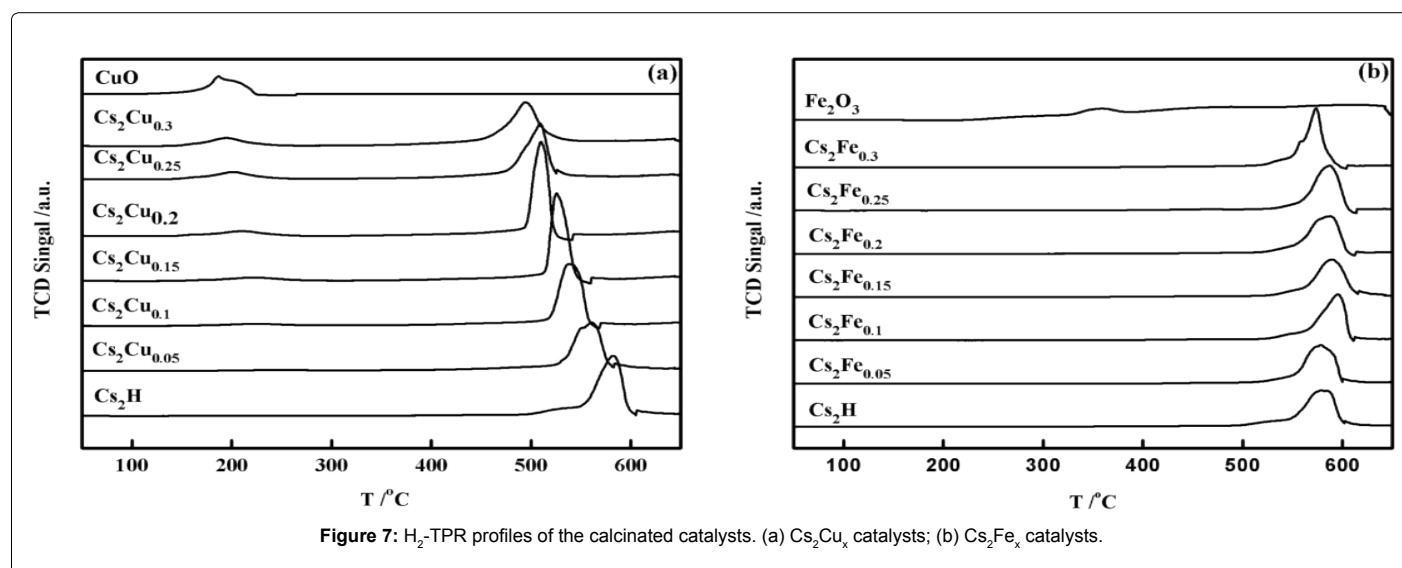


Figure 7: H₂-TPR profiles of the calcinated catalysts. (a) Cs₂Cu_x catalysts; (b) Cs₂Fe_x catalysts.

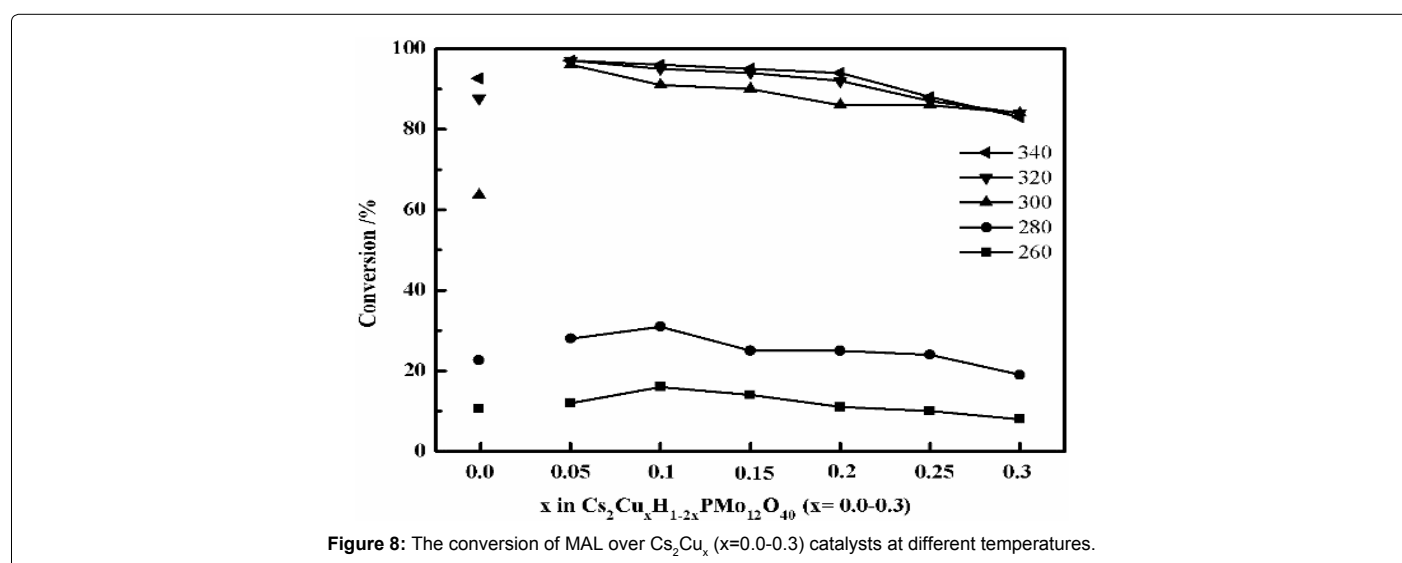


Figure 8: The conversion of MAL over Cs₂Cu_x (x=0.0-0.3) catalysts at different temperatures.

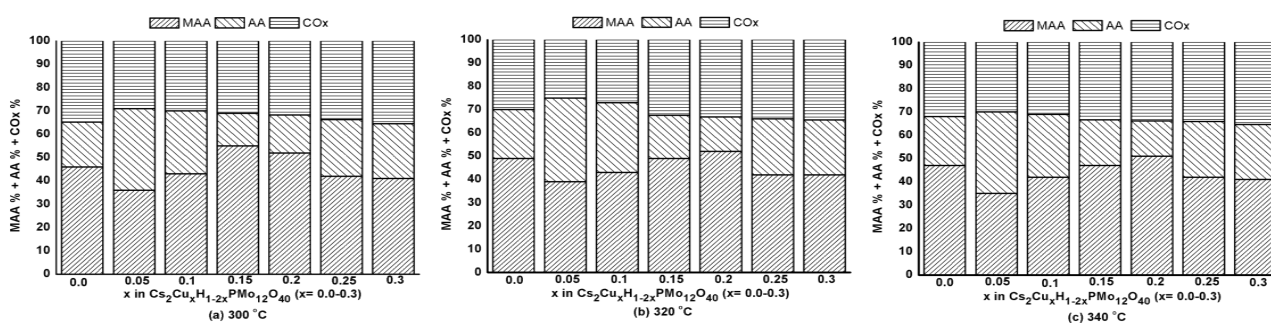


Figure 9: The selectivity to MAA, acetic acid (AA) and CO_x (oxocarbon) over Cs_2Cu_x ($x=0.0-0.3$) catalysts (a) 300°C; (b) 320°C; (c) 340°C.

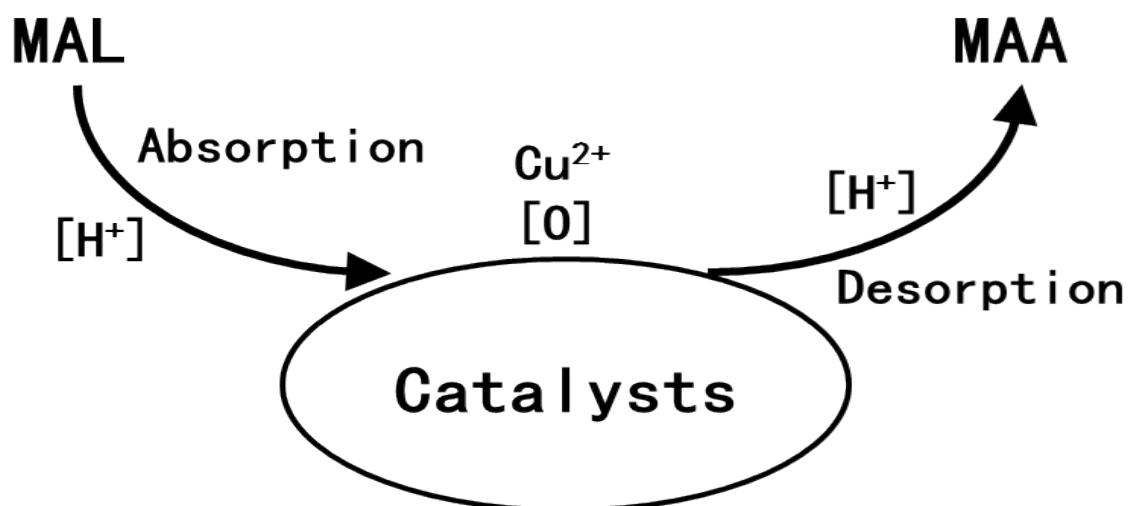


Figure 10: Cu promoted the reduction process of catalysts by increasing oxidizing ability.

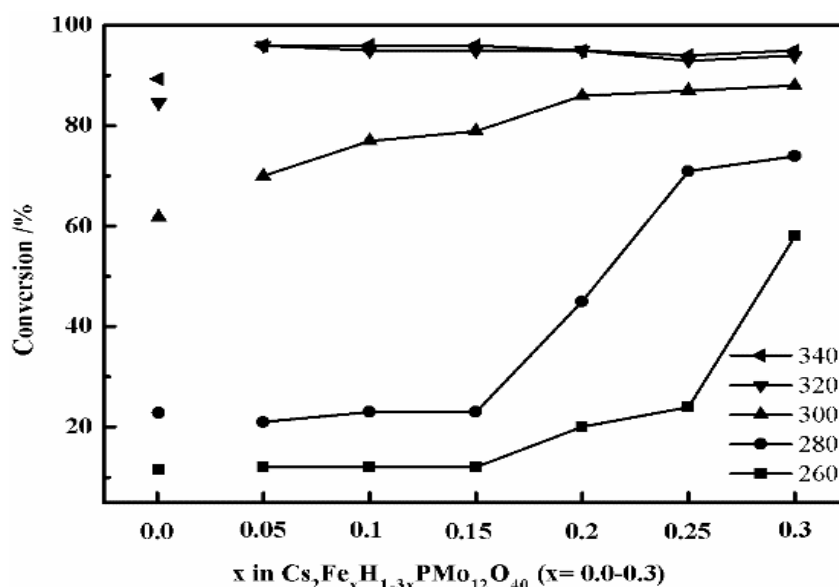


Figure 11: The conversion of MAL for Cs_2Fe_x ($x=0.0-0.3$) catalysts at different temperatures.

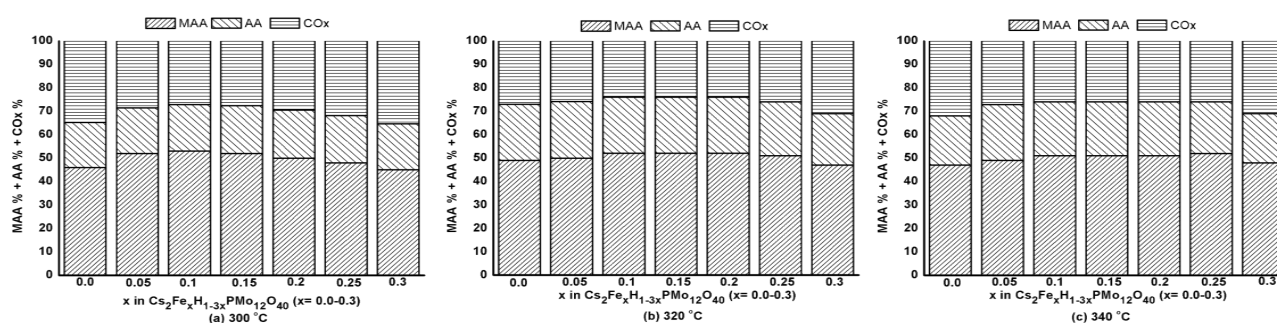


Figure 12: The selectivity of MAA, AA and oxocarbon for Cs₂Fe_x (x=0.0-0.3) catalysts (a) 300°C; (b) 320°C; (c) 340°C.

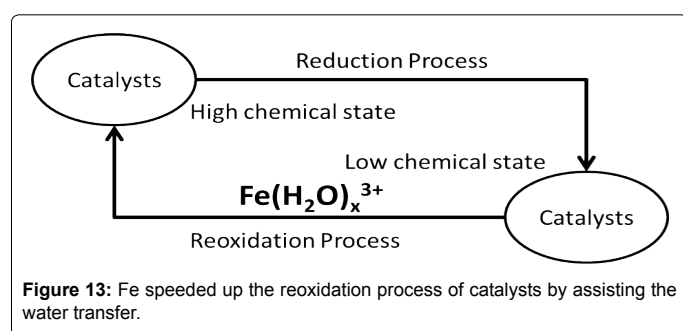


Figure 13: Fe speeded up the reoxidation process of catalysts by assisting the water transfer.

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