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Improvement in reactivity, reproducibility and stability of Fe–Mo catalysts by wet mixing

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Abstract

Two series of Fe–Mo catalysts were prepared using conventional mixing and wet mixing, respectively. Their catalyst behaviors in the oxidation reaction of methanol to formaldehyde were determined. The reaction result shows that wet mixing provided catalysts with higher reactivity and better reproducibility. Comparative FT-IR spectra of the two series catalysts treated at various temperatures indicated that the thermal stability of the catalyst prepared by wet mixing was also better. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Fe–Mo catalyst; Formaldehyde; Methanol oxidation; Wet mixing

1. Introduction

Fe–Mo catalysts are widely used industrially for the selective oxidation of methanol to formaldehyde. The catalysts always contain an excess of molybdenum in respect to that necessary stoichiometrically for the molybdate. They are believed to be composed of $Fe_2(MoO_4)_3$, MoO_3 and a molybdenum-rich phase [1]. A great amount of literature disclosed the preparation methods of this kind of catalysts. Among them, coprecipitation is the most common one [2–6]. But this method involves too long a procedure and too many factors affecting the composition, structure, and properties of the final catalyst. Therefore, the reproducibility of the catalyst performance is poor and the manufacturing cost is high. Another method is mechanic dry mixing [7], which has advantages of simple procedures and possibility to maintain the designed Mo/Fe ratio because there is no loss of both molybdenum and iron in the preparation process. But the reproducibility of the catalyst performance is also poor because a thorough mixing between the starting materials cannot be achieved.

In order to overcome the drawbacks of the above-mentioned methods, an improved mixing method was developed to prepare Fe/Mo catalysts-wet mixing. This method is similar to the conventional mixing except that an adequate amount of water was added to the mixture before grinding. The catalyst prepared in this way was proved to have not only high reactivity and good reproducibility, but also a good stability towards thermal treatment.

This paper will report this method and the property and performance of the catalyst prepared by this method.

2. Experimental

Industrial grade $Fe(NO)_3\cdot 9H_2O$ and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ were used to prepare all the catalysts in this study. Two series of catalysts were prepared, one

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of them (series I) used conventional (dry) mixing similar to the method disclosed in reference [6]: 5 g $Fe(NO)_3 \cdot 9H_2O$ and 5 g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ were crushed in a mortar and the mixture was ground until a rubbery and transparent green gel was formed. This took about 10 min and had to stop because the gel was too sticky. Then the gel was dehydrated for 6 h at 110°C in an oven to produce a transparent brownish gel, which was heated for 4 h in an oven at 420°C in an air atmosphere to produce a yellowish green product with a Mo/Fe molar ratio of 2.23. Then the product was ground, tableted into a plate and crushed to 20–40 mesh particles for use.

Another series of the catalysts (series II) were prepared by wet mixing in the similar way as used in the conventional mixing except that before grinding, an adequate amount of deionized water was added to the mixture. The grinding duration could be much longer than in the conventional mixing before the rubbery gel was formed.

The thermal treatment of the catalysts was conducted at different temperatures by heating them in an oven at 650°C, 700°C, 750°C, and 800°C in an atmosphere of air.

Two pure compounds were prepared for the purpose of better assignment of IR bands. The calcination of AR grade of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ at 420°C resulted in yellow powders of pure MoO_3. Pure $Fe_2(MoO_4)_3$ was prepared in the same way as in the preparation of catalysts series II except that Mo/Fe molar ratio was 1.5 and that AR grade of starting materials were used.

The reactivity measurement was conducted in a fixed-bed tubular reactor with an inner diameter of 6 mm. Catalyst loading was 1 ml. Before the reaction, the catalyst bed was subjected to a flow of dry air at the reaction temperature for 1 h. An over-heated gaseous mixture of air and methanol containing 6.5% by volume of methanol passed through the catalyst bed at 280°C, atmospheric pressure, and a space velocity of 9500 h^{-1} (based on STP). The inlet and outlet gases were analyzed on-line using a chromatograph with a TCD detector and a GDX-403 column for CH_2O, CH_3OH, DME (dimethyl ether), and H_2O. The analysis of CO was conducted using another chromatograph with a TCD detector and a TDX-01 column. According to our observation, a steady state of the reaction system was established in 45 min after a run started. Therefore, the reaction data were taken at least 1 h after each run had started.

The IR spectra of the samples were recorded with a PE-2000 IR Spectrometer having a resolution of 4 cm^{-1}.

The BET surface of the catalyst was determined with nitrogen adsorption on a CHEMBET-3000 type instrument under liquid-nitrogen temperature.

A duration test was conducted for catalyst II-b using the same reactor system and the same conditions as in the reactivity measurement.

3. Results and discussion

3.1. Reactivity and its reproducibility of the catalyst

Five catalysts repeatedly prepared using conventional dry mixing (series I) with exactly the same procedure as described previously, were measured for activity and selectivity under exactly the same conditions as given in Section 2. The results are given in Table 1.

The same data for five catalysts repeatedly prepared using wet mixing (series II) are shown in Table 2.

It is clearly seen from Tables 1 and 2 that the CH_2O yield and its reproducibility over the catalysts of series II was much better than those over the catalysts of series I.

The difference in CH_2O yield over the catalysts of series I was mainly caused by the difference in the activity of the catalysts, while the selectivity to CH_2O only changed slightly. This indicates that the ratio of the active sites for CH_2O to those for the by-products was roughly the same in the five catalysts of series I. It was the number of the active sites for CH_2O that was responsible for the diversified yield of CH_2O over the five catalysts of series I. This was initiated from the incomplete mixing during the grinding step and the incomplete reaction between Fe- and Mo-containing compounds in the calcination step. As for the catalysts of series II, this drawback was avoided and therefore the activity and selectivity to CH_2O were high and reproducible.

3.2. IR spectra of the catalysts

The IR spectra of two representative catalysts of the two series, I-b and II-b, are comparatively shown in

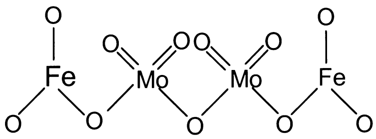
Table 1
Reaction results of the catalysts prepared by dry mixing (series I)

Catalyst	Methanol conversion (mol%)	Selectivity (carbon mol%)			CH_2O yield (mol%)
		CH_2O	DME	CO	
I-a	96.3	95.8	2.0	2.1	92.3
I-b	85.0	96.2	2.6	1.3	81.8
I-c	89.4	94.6	2.9	2.5	84.6
I-d	94.4	95.9	2.3	1.8	90.5
I-e	88.8	95.1	2.5	2.4	84.4

Table 2
Reaction results of the catalysts prepared by wet mixing (series II)

Catalyst no.	Methanol conversion (mol%)	Selectivity (carbon mol%)			CH_2O yield (mol%)
		CH_2O	DME	CO	
II-a	99.7	94.5	0.8	4.8	94.2
II-b	100.0	94.6	1.1	4.3	94.6
II-c	99.5	95.0	1.0	4.1	94.5
II-d	99.4	95.3	1.2	3.5	94.7
II-e	99.5	95.0	0.9	4.1	94.6

Fig. 1. This kind of spectrum is typical of a mixture of $Fe_2(MoO_4)_3$ and MoO_3 [1,8]. It contains all the bands appearing in the spectra of MoO_3 and $Fe_2(MoO_4)_3$ as shown in Figs. 2 and 3, respectively. The strong asymmetrical band at around 848 cm^{-1} is composed of the bands ascribed to Mo–O (tetrahedral) in $Fe_2(MoO_4)_3$ and MoO_3 and Mo=O (wherein Mo is connected with Fe through a –O– bridge) in $Fe_2(MoO_4)_3$. The weak bands at around 961 and 996 cm^{-1} are ascribed to Fe–O–Mo vibrations in $Fe_2(MoO_4)_3$ and to terminal Mo=O vibration of MoO_3, respectively. The band at about 605 cm^{-1} is attributed to Mo–O (octahedral) vibrations of MoO_3. The bands of MoO_3 in the more active catalyst II-b is weaker than in I-b. Now that the Mo/Fe ratios are the same in both the catalysts, it is reasonable to suppose that in catalyst II-b, more MoO_3 incorporates into the frame of $Fe_2(MoO_4)_3$ to form a structure as follows:



This structure is more active because more active sites (Mo^{6+} in connection with Fe^{3+} through a –O– bridge) exist.

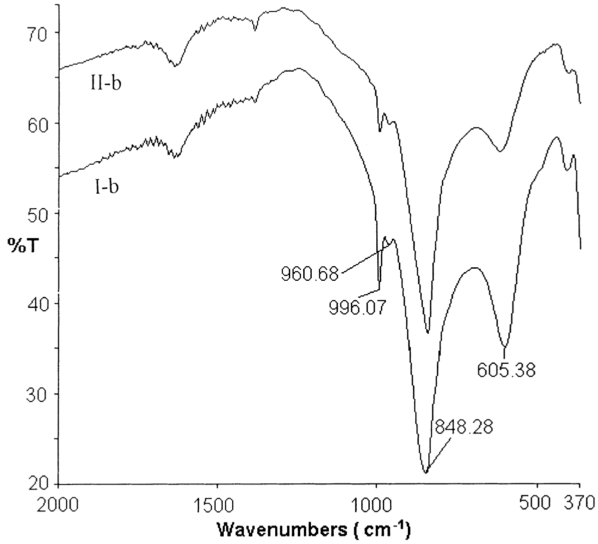


Fig. 1. IR spectra of catalysts I-b and II-b.

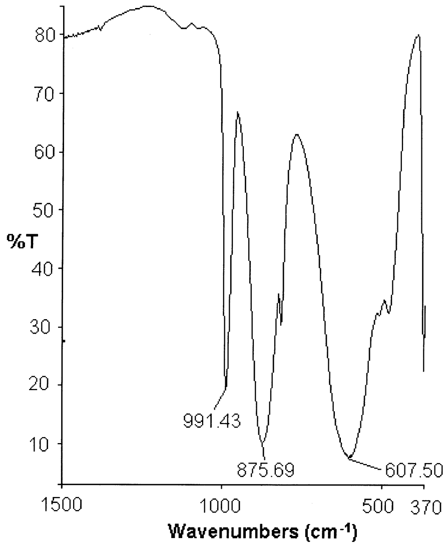


Fig. 2. IR spectra of pure MoO_3

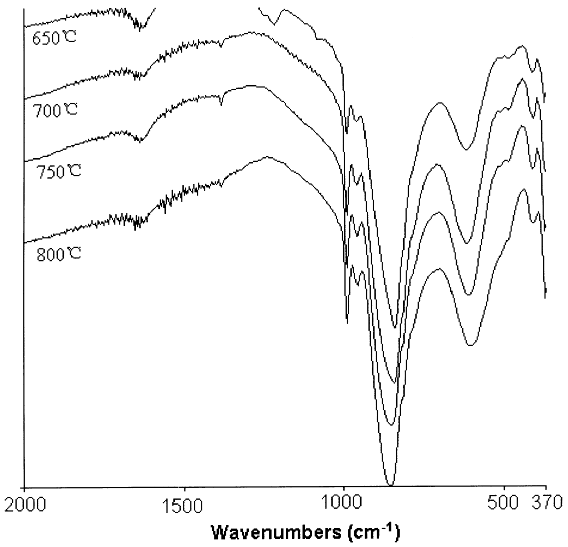


Fig. 4. IR spectra of catalysts I-b treated at various temperatures.

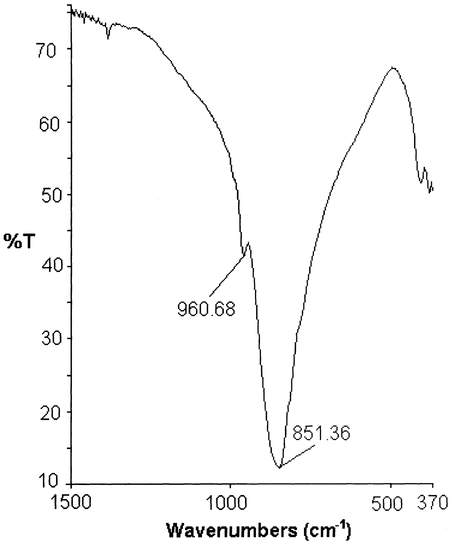


Fig. 3. IR spectra of pure $Fe_2(MoO_4)_3$.

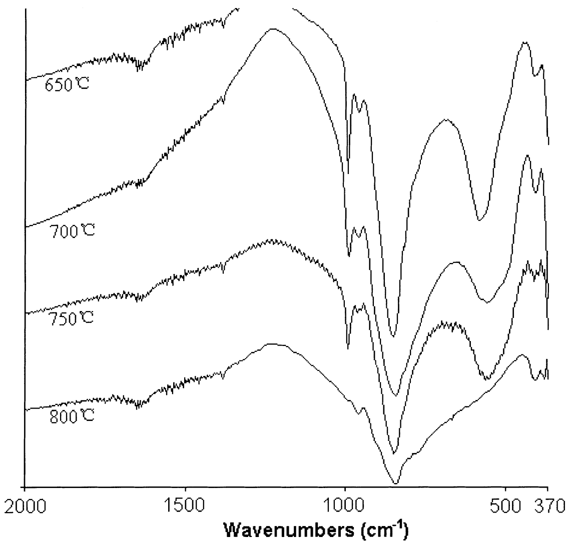


Fig. 5. IR spectra of catalysts II-b treated at various temperatures.

Table 3
Comparison between catalysts I-b and II-b for reactivity and BET surface after thermal treatment at 600°C for 2 h

Catalyst no.	Methanol conversion (mol%)	Selectivity (carbon mol%)		CH_2O yield (mol%)	BET surface (m^2/g)
		CH_2O	DME		
I-b	8.0	0	100	0	2.1 (7.1)[a]
II-b	30.0	92.7	7.3	7.4	0.2 (6.2)

[a] Figures in the brackets indicate the BET surface before thermal treatment.

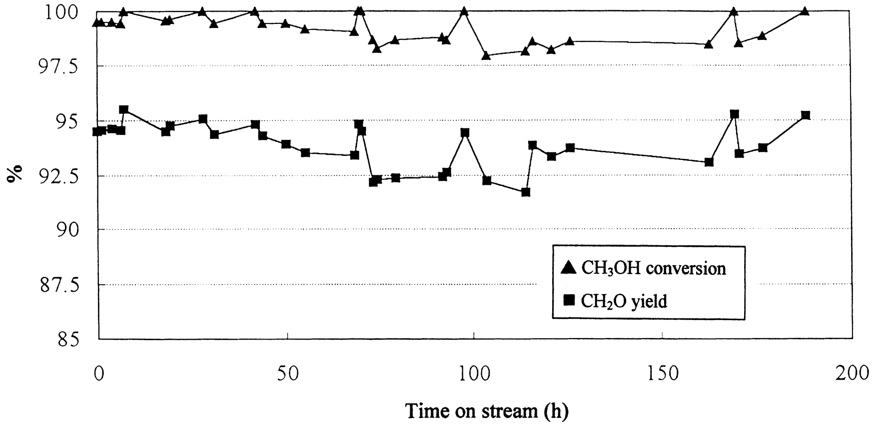


Fig. 6. Duration test of catalyst II-b.

3.3. *Thermal stability of the catalysts*

The IR spectra of catalysts I-b and II-b after thermal treatment at various temperatures are shown in Figs. 4 and 5, respectively. Along with the rising temperature, the normal structure of catalyst I-b was destroyed gradually and totally broken down at 800°C. At this temperature, $Fe_2(MoO_4)_3$ decomposed into Fe_2O_3 and MoO_3 and all MoO_3 sublimated with Fe_2O_3 remained [9]. The IR spectra of catalyst II-b had little change after thermal treatment at a temperature as high as 800°C. This convincingly indicates that the thermal stability of the catalyst prepared by wet mixing was much better. It is believed that deactivation of a Fe–Mo catalyst is mainly caused by thermal decomposition of the catalyst. Therefore, catalysts with better thermal stability are expected to possess a longer life.

The reactivity and BET surface of catalysts I-b and II-b after thermal treatment at 600°C for 2 h were also determined comparatively. The data are shown in Table 3. The BET surfaces of the two catalysts before thermal treatment are also given in the brackets. These data also indicate the improved thermal stability of II-b prepared by wet mixing.

3.4. *Duration test*

Fig. 6 shows the result of the duration test for catalyst II-b, which indicates that the improved reactivity may be kept rather long. The fluctuation of CH_2O yield of about $\pm 1.5\%$ was mainly due to the inaccuracy of the flow rate and the chromatographic analysis. The accuracy of the data in Tables 1 and 2 is much better because each datum is an average of three repeatedly measured data.

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