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A Study on Bi–Fe–Mo Oxide Catalysts by Means of ^{57}Fe Mössbauer Spectroscopy and Electron Microscopy

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Bi–Fe–Mo oxide catalysts of various compositions have been investigated using X-ray diffraction, ^{57}Fe Mössbauer measurements, and analytical electron microscopy. When a Bi–Fe–Mo oxide catalyst with a composition of Bi/Fe/Mo = 3/1/2 is calcined at 523–773 K, two kinds of tetragonal $Bi_3FeMo_2O_{12}$ particles are generated, their average diameters being different from each other. Paramagnetic doublets in the Mössbauer spectra of these tetragonal particles are identical to those in an earlier report analyzed as monoclinic $Bi_3FeMo_2O_{12}$. In the case of a Bi–Fe–Mo oxide catalyst of a composition, Bi/Fe/Mo = 1/1/1, calcined at 523–773 K, fine particles 15 nm in diameter are produced along with tetragonal $Bi_3FeMo_2O_{12}$ particles. The fine particles are found to be superparamagnetic α-Fe_2O_3 and/or small crystallites of tetragonal $Bi_3FeMo_2O_{12}$. During calcination at 823 K, the tetragonal $Bi_3FeMo_2O_{12}$ phase decomposed to a mixture of monoclinic $Bi_3FeMo_2O_{12}$, Bi_2O_3 MoO_3, $Fe_2(MoO_4)_3$, and ferromagnetic α-Fe_2O_3. Their particle sizes were from 15 to 50 nm in diameter. The Mössbauer spectrum of the $BiFeMoO_6$ phase reported by T. Notermann, G. W. Keulks, A. Skliarov, Yu. Maximov, L. Ya. Margolis and O. V. Krylov (*J. Catal.* **39,** 286 (1975)) was not observed but the pattern detected was interpreted to be the superposition of the spectra of the $Bi_3FeMO_2O_{12}$ and α-Fe_2O_3 phases. This was also confirmed by analytical electron microscopy.

INTRODUCTION

Multicomponent molybdate catalysts of a Mo–Bi–Fe–Me(II)–alkali or –Tl system partially oxidize propylene, isobutene, and *n*-butenes with high activity and selectivity (*1–3*). Especially, the Bi–Fe–Mo oxide components are known to play an important role in catalysts employed in industry.

A number of investigations have been performed on the structure of the above catalysts and the role of each component in catalytic reactions (*4–10*). However, no consistent conclusions have been achieved, since the compositions and preparation methods of the catalysts were not always the same.

In this report, Mössbauer spectroscopy (*4*) and analytical electron microscopy were applied to the study of Bi–Fe–Mo oxides in order to clarify the structures and the reaction mechanisms of multicomponent molybdate catalysts.

In Bi–Fe–Mo oxides, Sleight and Jeitschko (*5*) reported the existence of a $Bi_3FeMo_2O_{12}$ phase of scheelite structure. Notermann *et al.* (*6*) and LoJacono *et al.* (*7*) suggested the existence of a $BiFeMoO_6$ phase and showed an X-ray diffraction pattern for the phase quite similar to that of $Bi_3FeMo_2O_{12}$ but a Mössbauer spectrum that is different. They concluded that $BiFeMoO_6$ has the same crystal structure as $Bi_3FeMo_2O_{12}$ but that the crystal position of Fe in $BiFeMoO_6$ is not the same as that in $Bi_3FeMo_2O_{12}$. The ^{57}Fe Mössbauer spectrum obtained from $BiFeMoO_6$ shows a superposition of magnetically split 6 lines and a doublet absorption. The Mössbauer parameters of the doublet are as follows: The isomer shift (IS) relative to α-Fe is 0.35 mm/sec at room temperature (RT), and the quadrupole splitting (ΔEq) is 1.00 mm/sec. On the other hand, Linn and Sleight (*8*) pointed out that $BiFeMoO_6$ does not exist and that the supposed substance is actually

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a mixture of $Bi_3FeMo_2O_{12}$ crystallites and fine particles of α-Fe_2O_3.

METHODS

Powder specimens of Bi–Fe–Mo oxides and a typical Fe–Mo oxide, $Fe_2(MoO_4)_3$, were prepared as follows: First, three kinds of aqueous solution were prepared, which will be called solutions A, B, and C, respectively. Solution A was a 1-liter aqueous solution of $Bi(NO_3)_3 \cdot 5H_2O$ (485 g) and 63% nitric acid (134 g). The Bi concentration in A was 1 mole Bi/liter. Solution B was a 1-liter aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$ (404 g). The Fe concentration in B was 1 mole Fe/liter. Solution C was a 1-liter aqueous solution of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (176.6 g). The Mo concentration in C was 1 mole Mo/liter.

Appropriate amounts of A and/or B were poured into solution C to induce precipitation. After precipitation, the pH of the slurry was adjusted to 7.5 by adding aqueous ammonium hydroxide or nitric acid and the solutions were dried at 373 K. The dried precipitates were crushed, heated at a rate of 200 K/hr to a desired temperature, and calcined for 1 hr at that temperature.

Samples prepared by the above method are shown below.

$Fe_2(MoO_4)_3$	calcined at 773 K
Bi/Fe/Mo = 3/1/2	calcined at 773 K
Bi/Fe/Mo = 3/1/2	calcined at 823 K
Bi/Fe/Mo = 1/1/1	calcined at 773 K
Bi/Fe/Mo = 1/1/1	calcined at 823 K

In this investigation, the samples are labeled according to the Bi/Fe/Mo concentration ratio and calcination temperatures.

X-ray powder patterns were taken by a Rigaku Denki Rotaflex instrument using an acceleration voltage of 40 kV and a filament current of 100 mA.

^{57}Fe Mössbauer spectra were measured at room temperature using an Elron commercial set which consisted of an MFG-2 signal generator, an MVT-2 velocity transducer, and an MD-2 amplifier. Spectra were stored using a Tracor-Northern NS-600 multichannel analyzer. Every spectrum was analyzed using a thin foil approximation in which least-squares fitting assuming Lorentzian absorption lines was carried out.

The values of isomer shift are relative to the center position of α-Fe at room temperature.

For electron microscopy, the catalyst powder specimen was embedded in epoxy resin. After hardening, it was sliced by an ultramicrotome with a diamond knife into thin films less than 100 nm thick. Transmission electron micrographs were taken with a Hitachi-H800 electron microscope operated at an acceleration voltage of 200 kV. Constitutional elements in the specimen were analyzed with an energy dispersive X-ray analyzer, Kevex-7000, attached to a Hitachi H-500 electron microscope operated at 75 kV. Contents of Bi, Fe, and Mo were determined by the peak heights of the Bi$L\text{III}\alpha_2$ (10.73 keV), Fe$K\alpha$ (6.39 KeV), and Mo$K\alpha_2$ (17.36 keV) lines, respectively.

RESULTS AND DISCUSSION

X-ray Diffraction Spectra

Figure 1 shows the X-ray diffraction spectra of Bi/Fe/Mo = 3/1/2 and 1/1/1 specimens calcined for 1 hr at 773 K (500°C) and 823 K (550°C). Specimens 3/1/2 and 1/1/1 calcined at 773 K are composed of tetragonal $Bi_3FeMo_2O_{12}$ which is a precursor of monoclinic $Bi_3FeMo_2O_{12}$ obtained by the calcination for long times at temperatures between 523 and 773 K. Peaks were rather diffuse, indicating that the specimens were weakly crystallized. Very weak peaks of $Bi_2O_3 \cdot MoO_3$ (koechlinite) were also observed.

By the calcination at 823 K, the tetragonal $Bi_3FeMo_2O_{12}$ transformed to the monoclinic $Bi_3FeMo_2O_{12}$. In this reaction $Fe_2(MoO_4)_3$ is also generated together with a trace of $Bi_2O_3 \cdot MoO_3$. Monoclinic $Bi_3FeMo_2O_{12}$ appeared with a weaker intensity in the 1/1/1 specimen than in the 3/1/2 specimen.

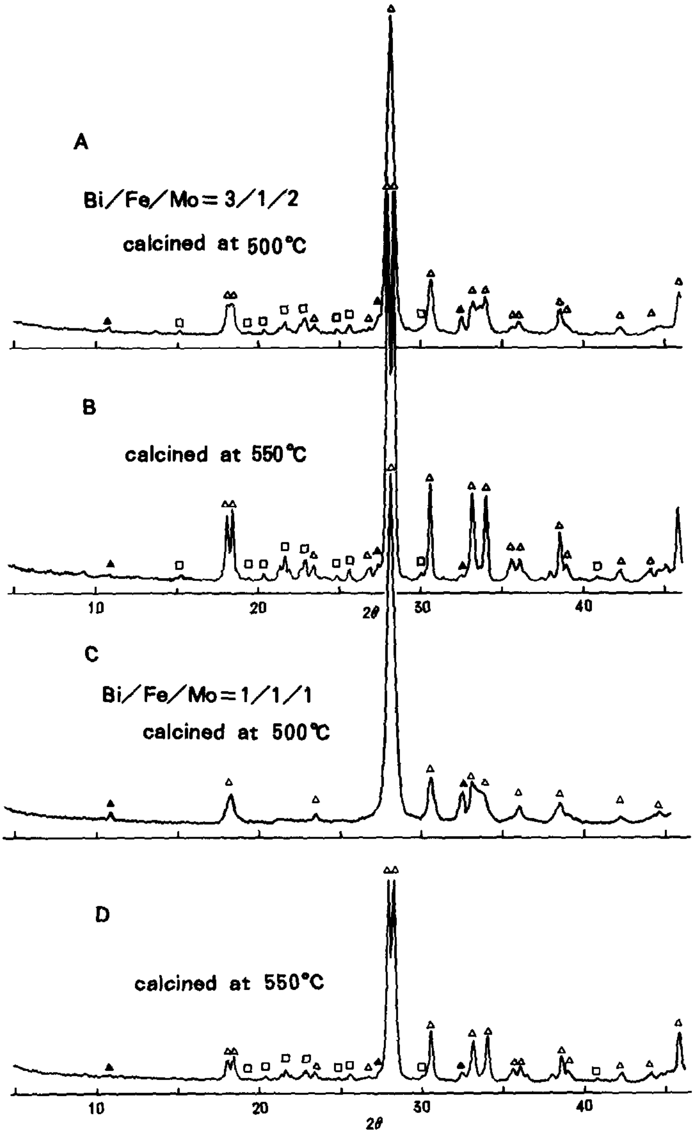


FIG. 1. X-ray diffraction spectra of the Bi–Fe–Mo oxide systems □, $Fe_2(MoO_4)_3$; △, $Bi_3FeMo_2O_{12}$; ▲, $Bi_2O_3 \cdot MoO_3$.

^{57}*Fe Mössbauer Spectra*

Figure 2 shows the Mössbauer spectrum of $Fe_2(MoO_4)_3$. The IS value of the singlet was 0.40 ± 0.01 mm/sec (Table 1) relative to α-Fe at room temperature and close to the values of 0.50 mm/sec reported earlier by Carbucicchio and Trifiro (9) and 0.43 mm/sec by Prasada Rao and Menon (*10*).

Figure 3 shows the Mössbauer spectra of Bi/Fe/Mo = 3/1/2 and 1/1/1 calcined at 773 and 823 K. The spectrum of the 3/1/2 specimen calcined at 773 K showed a symmetrical doublet (IS was 0.30 ± 0.02 mm/sec; ΔEq was 0.96 ± 0.01 mm/sec) in contrast to an asymmetrical doublet of the 1/1/1 specimen. Assuming that the doublet of the 1/1/1 specimen contains another doublet component, a least-squares fitting was performed

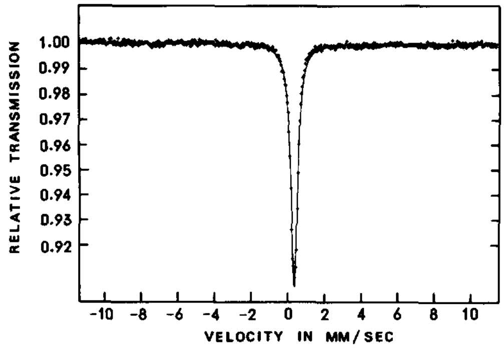


FIG. 2. Mössbauer spectrum of $Fe_2(MoO_4)_3$.

and it was found that 40% of the area of the 1/1/1 spectrum arose from a new doublet component, in which the IS was 0.37 ± 0.02 mm/sec and ΔEq was 0.44 ± 0.11 mm/sec.

The spectrum of the 3/1/2 specimen calcined at 823 K showed a superposition of a single line (IS = 0.41 ± 0.01 mm/sec), magnetically split 6 lines and a doublet (IS = 0.28 ± 0.01 mm/sec, ΔEq = 1.03 ± 0.01 mm/sec). The single line was identified to be of $Fe_2(MoO_4)_3$. The doublet was similar to that of the 773 K calcined sample. X-ray diffraction data confirmed that the doublet is due to a monoclinic $Bi_3FeMo_2O_{12}$ phase.

The spectrum of the 1/1/1 specimen calcined at 823 K was quite similar to that of the 3/1/2 specimen calcined at 823 K except that the singlet absorption due to $Fe_2(MoO_4)_3$ and magnetically split 6 line component were more prominent.

Notermann *et al.* (*6*) have not discussed the difference in Mössbauer spectra of monoclinic and tetragonal $Bi_3FeMo_2O_{12}$. The 3/1/2 specimen calcined at 773 K is composed of the almost pure tetragonal $Bi_3FeMo_2O_{12}$ phase, its spectrum being composed of only one doublet absorption. It was suggested that the spectrum of the

TABLE 1

Summary of Mössbauer Parameters

		Composition: Bi/Fe/Mo ratio				
Calcination temperature:	$Fe_2(MoO)_3$ 773 K	3/1/2 773 K	3/1/2 823 K	1/1/1 773 K		1/1/1 823 K
Singlet						
IS (mm/sec)[a]	0.40 ± 0.01		0.41 ± 0.01			0.41 ± 0.01
Γ (mm/sec)[b]	0.43 ± 0.01		0.32 ± 0.01			0.40 ± 0.04
I (%)[c]	100		19			19
Doublet						
IS (mm/sec)		0.30 ± 0.02	0.28 ± 0.01	0.30 ± 0.02	0.37 ± 0.02	0.28 ± 0.03
ΔEq (mm/sec)[d]		0.96 ± 0.01	1.03 ± 0.01	0.96 ± 0.01	0.44 ± 0.01	1.00 ± 0.02
Γ (mm/sec)		0.60 ± 0.02	0.33 ± 0.01	0.37 ± 0.02	0.40 ± 0.03	0.33 ± 0.03
I (%)		100	41	60	40	20
6 lines						
IS (mm/sec)			0.25 ± 0.03			0.25 ± 0.03
ΔE'q (mm/sec)[e]			0.23 ± 0.01			0.22 ± 0.02
Γ (mm/sec)			0.33 ± 0.01			0.46 ± 0.03
IF (*T*)[f]			50.6 ± 0.5			50.6 ± 0.5
I (%)			40			61

[a] 1 mm/sec = 1×10^{-3} m/sec.

[b] Full-width at half-maximum of absorption line.

[c] Area percentage of the component.

[d] $\Delta Eq = e^2qQ\,(1 + \eta^2/3)^{1/2}/2$.

[e] $\Delta E'q = e^2qQ\,(1 - 3\cos^2\theta)/8$.

[f] Internal magnetic field.

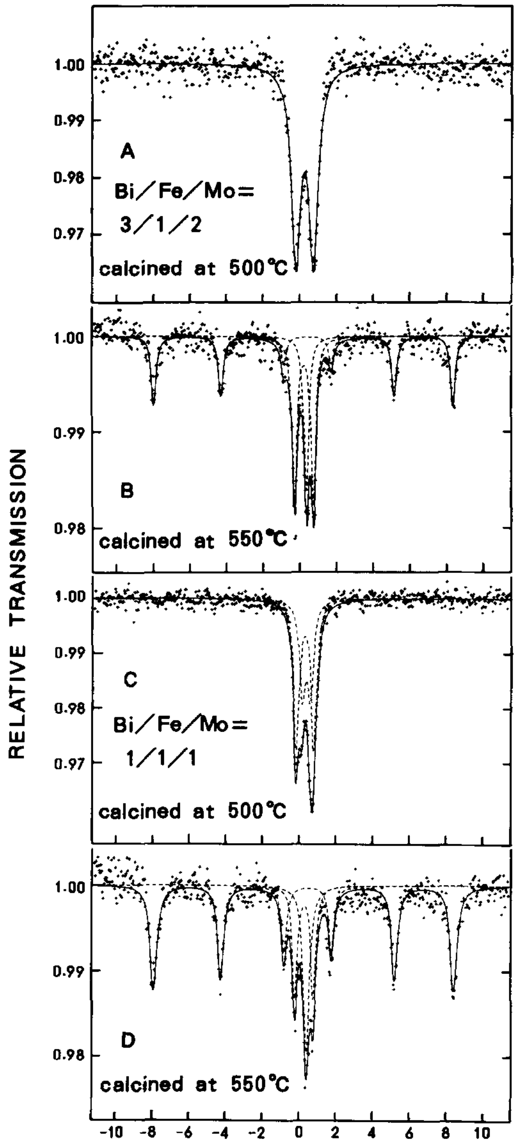


FIG. 3. Mössbauer spectra of Bi–Fe–Mo oxide systems.

tetragonal $Bi_3FeMo_2O_{12}$ phase is the same as that of the monoclinic phase. The doublet absorption due to monoclinic $Bi_3FeMo_2O_{12}$ phase was observed also in the 3/1/2 and the 1/1/1 specimens calcined at 823 K. Notermann *et al.* (*6*) suggested that $BiFeMoO_6$ shows 6 lines or more complex absorption lines in the 1/1/1 form. From the Mössbauer line shape they discussed the lattice distortion of the Fe ion sites in the $BiFeMoO_6$ phase.

The spectra obtained by the present investigation can be considered as the superposition of doublets arising from $Bi_3FeMo_2O_{12}$ and 6 lines from a certain magnetically ordered iron compound which was not detected by X-ray diffraction measurements because of its small particle size. From comparison with the Mössbauer parameters of hematite, it is concluded that the 6 line component is due to small particles of α-Fe_2O_3 (*11*). Observations by analytical electron microscopy confirmed the above conclusions.

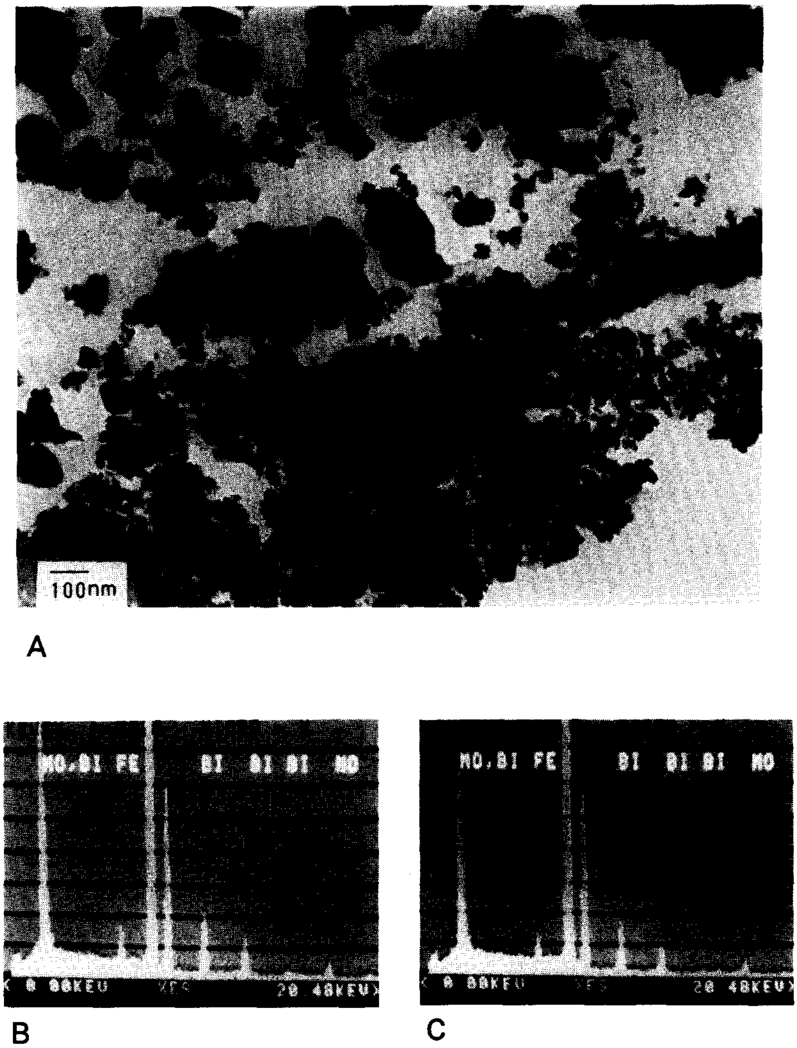
Observation by Analytical Electron Microscopy

Figures 4 and 5 show the transmission electron micrographs and the X-ray spectra from different particles of the 3/1/2 specimen calcined at 773 and 823 K, respectively. The two lines at 8.03 and 8.97 keV in the X-ray spectra were from the copper grid of the specimen mounting holder.

Large particles (150–400 nm in diameter) and small particles (15–40 nm) were observed in the sample calcined at 773 K. Both of them contained the same Bi/Fe/Mo ratio and both showed the electron diffraction pattern characteristic of $Bi_3FeMo_2O_{12}$.

Figure 6 shows a composition diagram obtained by the X-ray analysis of the 3/1/2 specimen calcined at 773 and 823 K. The plotted data were obtained from different particles. The data for 773 K calcination are indicated with black circles. Three of them are from small particles and the other two are from large particles. The five particles have almost the same Bi/Fe/Mo ratio. From the X-ray diffraction spectra, it is concluded that the large and the small particles are composed of tetragonal $Bi_3FeMo_2O_{12}$.

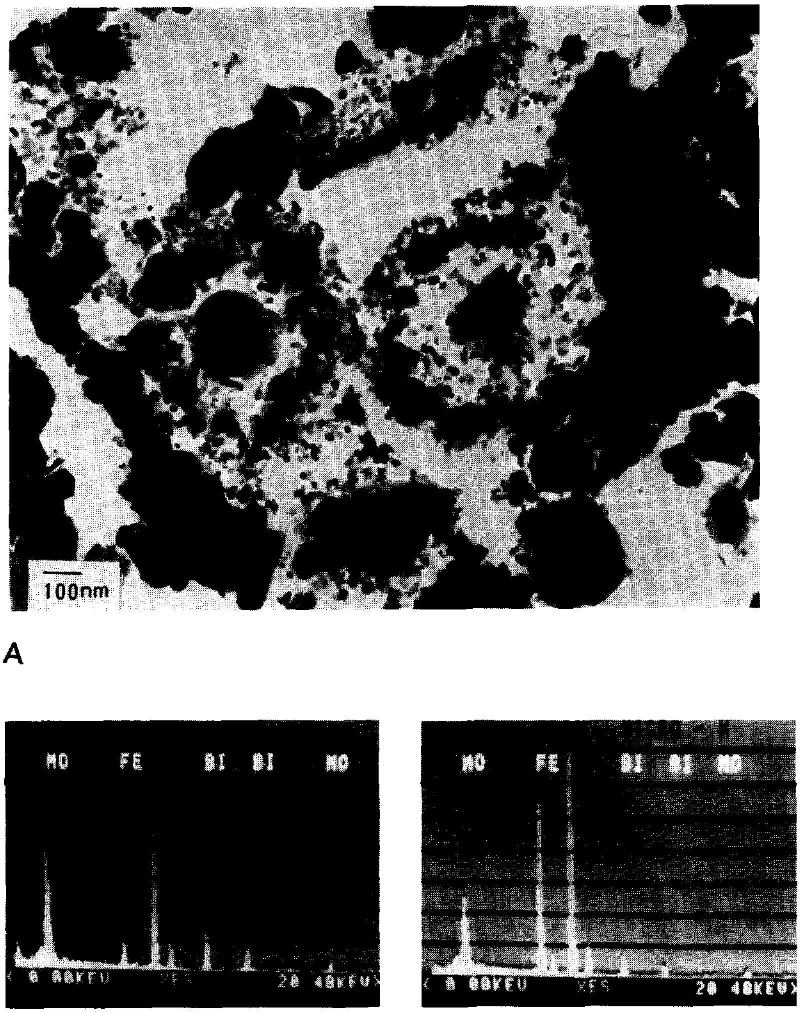
The transmission electron micrograph of the 3/1/2 specimen calcined at 823 K showed the existence of three different kinds of particles. Large particles of the first type, which had diameters of 100–400 nm, were identified to be of $Bi_3FeMo_2O_{12}$



large particles ($Bi_3FeMo_2O_{12}$) small particles ($Bi_3FeMo_2O_{12}$)

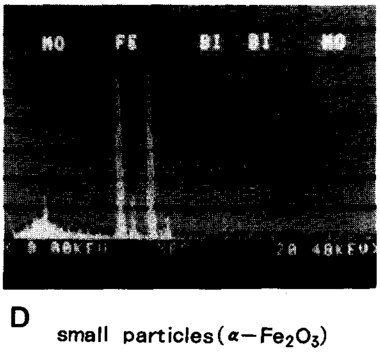
FIG. 4. Electron microscope image and X-ray spectra of Bi/Fe/Mo = 3/1/2 calcined at 773 K.

and large particles of the second type were of $Fe_2(MoO_4)_3$. Figures 5B and C show their X-ray energy spectra. A third type of particle had very small diameter (15–20 nm) and did not show any clear electron diffraction pattern. Figure 5D shows their X-ray spectrum, which consists of only iron peaks. The above electron microscopy and X-ray energy dispersion analysis results are in good agreement with the Mössbauer spectroscopy results. The existence of α-Fe_2O_3, which was observed in the Mössbauer spectra, was not confirmed by the electron microscopy most probably because of its extremely small particle size. It is therefore concluded that the sample is a mixture of four compounds, i.e., monoclinic $Bi_3FeMo_2O_{12}$ (100–400 nm), $Fe_2(MoO_4)_3$ (100–400 nm), α-Fe_2O_3 (15–20 nm), and $Bi_2O_3 \cdot MoO_3$ (koechlinite). The last compound was observed in X-ray diffraction patterns, as shown in Fig. 1. Analytical results from the 3/1/2 specimen are plotted in the compositional diagram in Fig. 6. In this figure, the



B large particles ($Bi_3FeMo_2O_{12}$)

C large particles ($Fe_2(MoO_4)_3$)



D small particles ($\alpha-Fe_2O_3$)

FIG. 5. Electron microscope image and X-ray spectra of Bi/Fe/Mo = 3/1/2 calcined at 823 K.

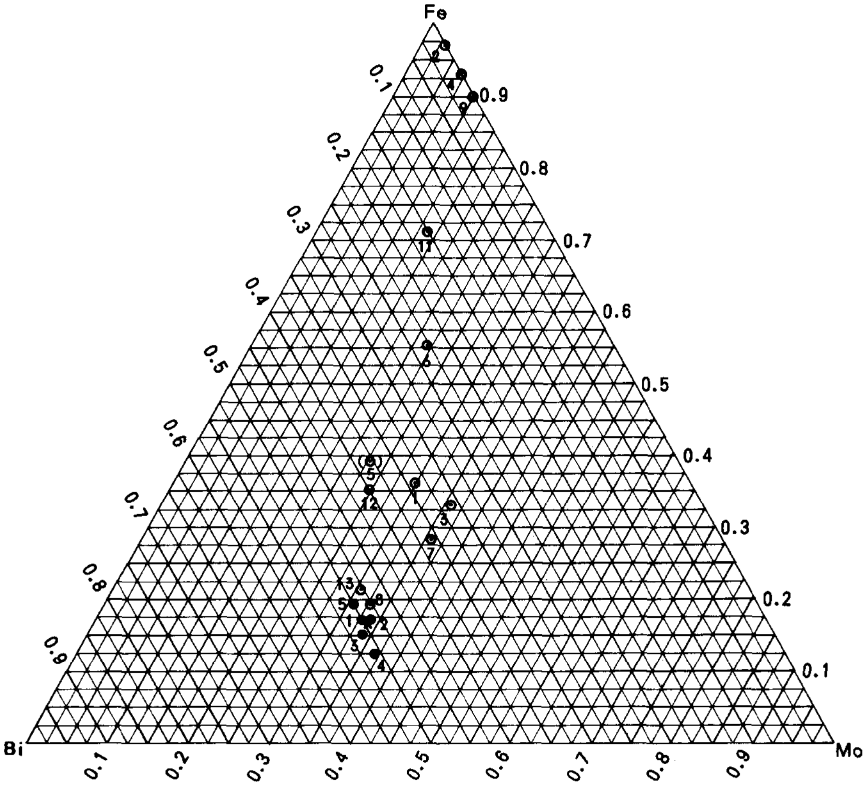
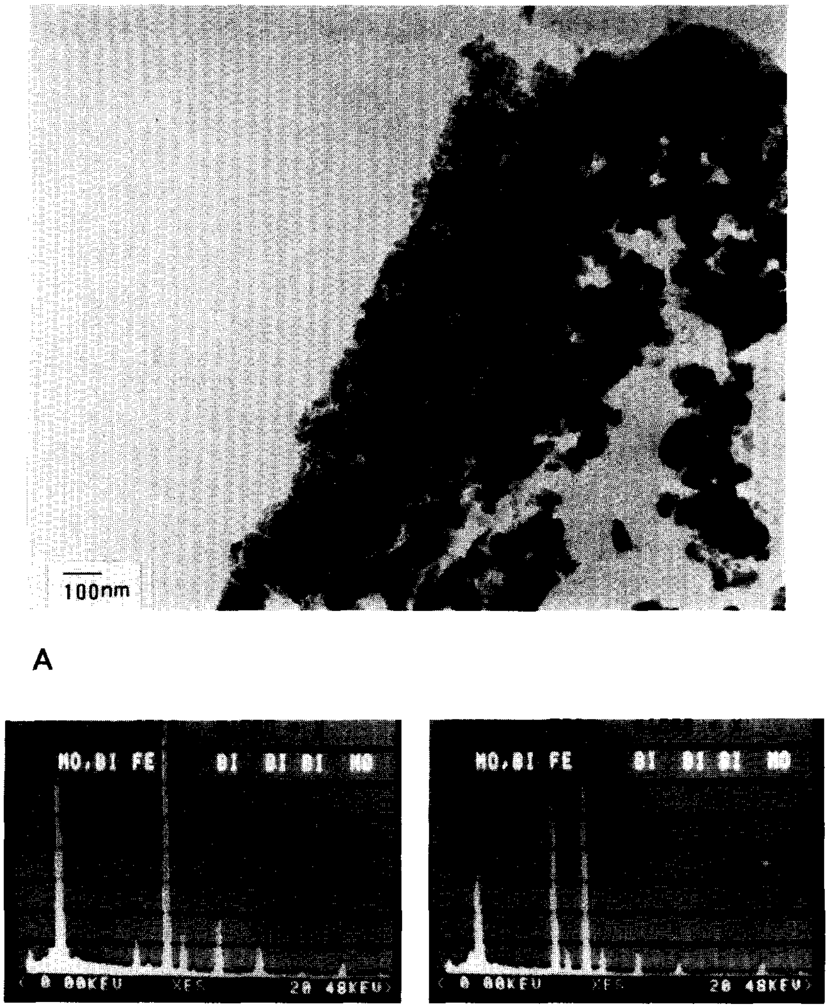


FIG. 6. Analytical results of Bi/Fe/Mo = 3/1/2 by analytical electron microscopy. ●, calcined at 773 K (point analysis); ○, calcined at 823 K (point analysis); (○), calcined at 823 K (area analysis); ×, preparative composition and $Bi_3FeMo_2O_{12}$ (between points 1 and 2).

concentrations, especially of iron, widely spreads, indicating that the specimen is a mixture of four different phases. Since monoclinic $Bi_3FeMo_2O_{12}$ is stable even above 1073 K, a part of tetragonal $Bi_3FeMo_2O_{12}$ may decompose into $Bi_2O_3 \cdot MoO_3$, $Fe_2(MoO_4)_3$, and α-Fe_2O_3 during the transformation to the monoclinic phase.

Figures 7 and 8 show transmission electron micrographs of the 1/1/1 specimen calcined at 773 and 823 K, respectively. Large (100–200 nm) and small particles (<15 nm) have been observed after calcination at 773 K. The large particles are determined to be tetragonal $Bi_3FeMo_2O_{12}$ by the electron and X-ray diffraction patterns. The small particles were distributed among large particles, and the electron diffraction pattern from these small particles could not be taken separately. The electron diffraction pattern from the area which included above two kinds of particles showed tetragonal $Bi_3FeMo_2O_{12}$. Therefore, small particles can be thought of as the tetragonal $Bi_3FeMo_2O_{12}$ or amorphous oxides from which the clear diffraction pattern could not be obtained.

X-ray energy analysis showed that more Fe and Bi are contained in the small particles than in large particles of $Bi_3FeMo_2O_{12}$. Mössbauer spectra showed a doublet which might be from these small particles in addition to that of tetragonal $Bi_3FeMo_2O_{12}$. It is known that fine particles of α-Fe_2O_3, having a diameter smaller than about 10 nm, show a doublet due to their superparamagnetism at room temperature (*12*). The isomer shift value of the paramagnetic doublet coincided with that of superparamagnetic α-Fe_2O_3.



large particles ($Bi_3FeMo_2O_{12}$)

small particles ($\alpha-Fe_2O_3$ and /or $Bi_3FeMo_2O_{12}$)

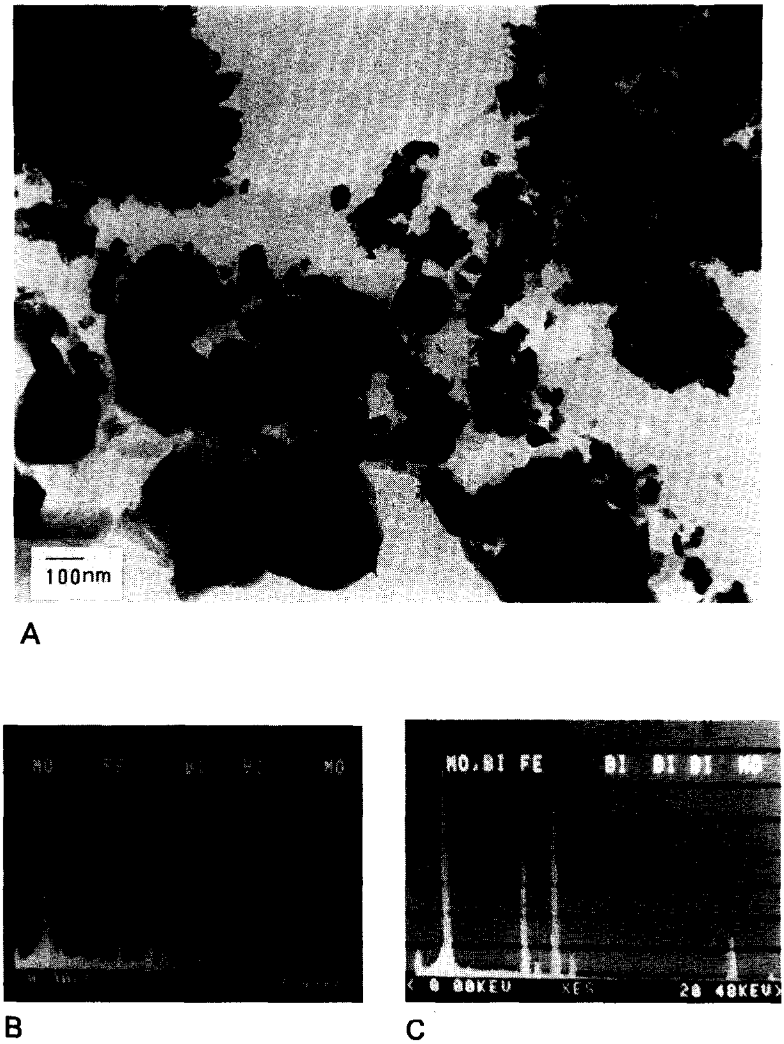
FIG. 7. Electron microscope image and X-ray spectra of Bi/Fe/Mo = 1/1/1 calcined at 773 K.

Three different particles, monoclinic $Bi_3FeMo_2O_{12}$ (100–400 nm), $Fe_2(MoO_4)_3$ (100–600 nm), and α-Fe_2O_3 (20–50 nm), are observed in the 1/1/1 specimen calcined at 823 K. The particle size of α-Fe_2O_3 was larger than that of the 3/1/2 specimen. The X-ray diffraction pattern implies that the $Bi_2O_3 \cdot MoO_3$ compound also exists in the 1/1/1 specimen calcined at 773 K. The results obtained from the 1/1/1 specimen calcined at 823 K were same as those obtained from the 3/1/2 specimen calcined at 823 K.

Figure 9 shows a composition diagram obtained by X-ray analysis of the 1/1/1 specimen. The plotted data were obtained from different particles. It suggested that the compositions of particles are quite different from each other as expected.

SUMMARY

Phase analysis of Bi–Fe–Mo oxide catalysts was performed using X-ray diffraction



large particles ($Bi_3FeMo_2O_{12}$)

large particles ($Fe_2(MoO_4)_3$)

FIG. 8. Electron microscope image and spectra of X-ray Bi/Fe/Mo = 1/1/1 calcined at 823 K.

pattern, ^{57}Fe Mössbauer measurements, and analytical electron microscopy. The obtained results are summarized in Table 2.

After calcination at 523–773 K, the 3/1/2 specimen has two kinds of tetragonal $Bi_3FeMo_2O_{12}$ particles with different diameters. Mössbauer spectra of these tetragonal $Bi_3FeMo_2O_{12}$ showed paramagnetic doublets similar to those of monoclinic $Bi_3FeMo_2O_{12}$, having slightly different Mössbauer parameters.

After calcination at 823 K, the tetragonal $Bi_3FeMo_2O_{12}$ transformed to monoclinic $Bi_3FeMo_2O_{12}$ phase. At the same time it happened to decompose partially into Bi_2O_3 MoO_3, $Fe_2(MoO_4)_3$, and fine particles (15–20 nm in diameter) of α-Fe_2O_3.

Tetragonal $Bi_3FeMo_2O_{12}$ particles (100–200 nm) and fine particles (<15 nm) are observed in the 1/1/1 specimen calcined at 773 K. Fine particles in this specimen contain more Fe than the 3/1/2 specimen. The particles showed Mössbauer spectra and electron diffraction pattern quite similar

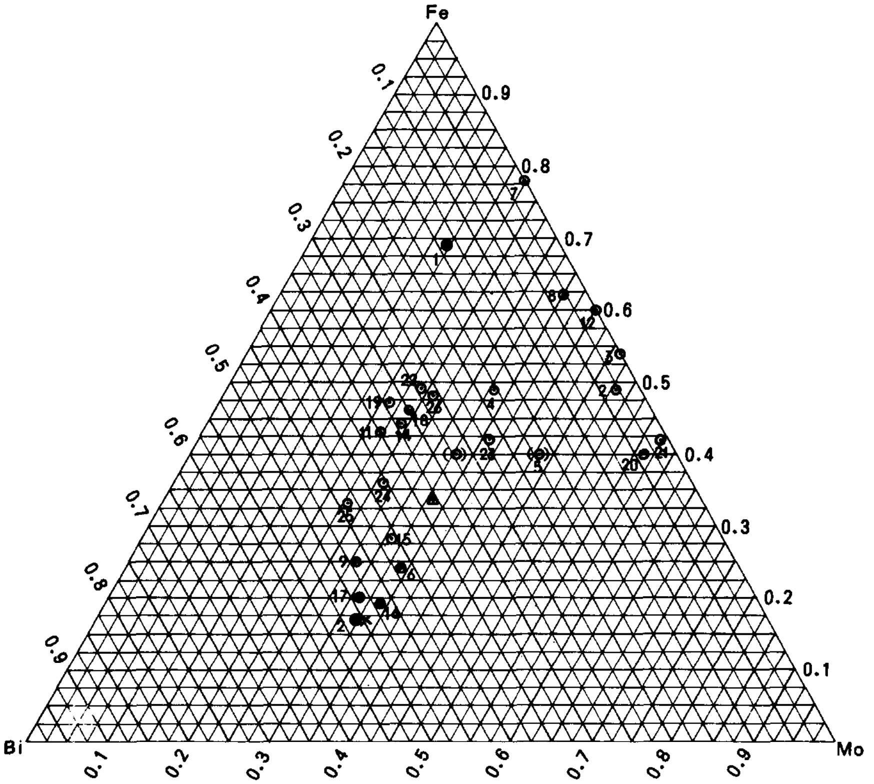


FIG. 9. Analytical results of Bi/Fe/Mo = 1/1/1 by analytical electron microscopy. ●, calcined at 773 K (point analysis); ⊙, calcined at 823 K (point analysis); (⊙), calcined at 823 K (area analysis); △, preparative composition; ×, $Bi_3FeMo_2O_{12}$.

to tetragonal $Bi_3FeMo_2O_{12}$. These results suggested that they are mixtures of tetragonal $Bi_3FeMo_2O_{12}$ and superparamagnetic α-Fe_2O_3 particles.

TABLE 2

Summary of Bi–Fe–Mo Oxide Systems

	Composition: Bi/Fe/Mo	
	3/1/2	1/1/1
Calcined at 773 K	$Bi_3FeMo_2O_{12}$ (tetragonal) 150–400 nm	$Bi_3FeMo_2O_{12}$ (tetragonal) 100–200 nm
	$Bi_3FeMo_2O_{12}$ (tetragonal) 15–40 nm	α-Fe_2O_3 (superparamagnetic) 15 nm
	$Bi_2O_3 \cdot MoO_3$	$Bi_2O_3 \cdot MoO_3$
Calcined at 823 K	$Bi_3FeMo_2O_{12}$ (monoclinic) 100–400 nm	$Bi_3FeMo_2O_{12}$ (monoclinic) 100–400 nm
	$Bi_2O_3 \cdot MoO_3$	$Bi_2O_3 \cdot MoO_3$
	$Fe_2(MoO_4)_3$ 100–400 nm	$Fe_2(MoO_4)_3$ 100–600 nm
	α-Fe_2O_3 15–20 nm	α-Fe_2O_3 20–50 nm

After calcination at 823K, the 1/1/1 specimen showed almost same results as the 3/1/2 specimen. Particle size of α-Fe_2O_3 was slightly larger than that of the 3/1/2 (20–50 nm) and showed the magnetic 6 line splitting in the Mössbauer spectrum, since the large size of α-Fe_2O_3 induced a static magnetic hyperfine field at Fe nucleus.

The above results lead to the conclusion that the $BiFeMoO_6$ phase suggested by Notermann *et al.* (*6*) was interpreted in this investigation as a mixture of $Bi_3FeMo_{12}O_{12}$ and α-Fe_2O_3.

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