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Structure of Co–K–Mo/γ-Al_2O_3 catalysts and their catalytic activity for mixed alcohols synthesis

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Abstract

A series of oxidized Co–K–Mo/γ-Al_2O_3 catalyst samples, prepared by impregnating oxidized K–Mo/γ-Al_2O_3 samples with an aqueous solution of calculated $Co(NO_3)_2$ and then calcining in air at temperatures of 350°C, 500°C, 650°C and 800°C, respectively, were sulfided and then investigated for the activity in the synthesis of mixed alcohols from CO hydrogenation under conditions of P=5.0 MPa, T=350°C and GHSV=4800 h^{-1}. The results demonstrate that the addition of cobalt promoter is favorable to the formation of higher alcohols and the optimum calcination temperatures after impregnating with Co^{2+} are about 500–650°C.

The structure of Co and Mo species on the oxidized and sulfided samples was determined by X-ray diffraction (XRD), laser Raman spectrum (LRS) and extended X-ray absorption fine structure (EXAFS). For oxidized sample calcined at 350°C, cobalt exists as Co_3O_4 species and covers the surface of K–Mo–O species, the structure of K–Mo–O species is the same as that in K–Mo/Al_2O_3 sample. The interaction between cobalt and K–Mo–O species is relatively weak. After sulfidation, cobalt exists as sulfide crystallites with an octahedral coordinated structure, and molybdenum as MoS_2 crystallites. For oxidized samples calcined at 500–650°C, Co component interacts with the K–Mo–O species and destroys the long-range order of the K–Mo–O species gradually. After sulfidation, Co tends to exist as a sulfide with tetrahedral coordinated structure and Mo still as MoS_2 crystallites. For oxidized sample calcined at 800°C, Co component exists mainly as $CoAl_2O_4$ species, most of which cannot be sulfided during sulfidation.

Keywords: Co–K–Mo/γ-Al_2O_3 catalyst; Calcination temperature; Mixed alcohols synthesis; Structure

1. Introduction

Mixed alcohols synthesis from syngas is an important reaction in C_1 chemistry, to which increasing attention has been paid because it offers a possibility for producing renewal clean fuel from coal, natural gas or some hydrocarbon waste via gasification. The mixed alcohols can also be used as an additive to increase the octane number of gasoline. Sulfided molybdenum based catalysts have drawn a special attention because of their high activity for mixed alcohols synthesis and superior sulfur-resistant property [1–7].

By several years of research work, our lab succeeded in preparing a new kind of sulfided K–Mo/Al_2O_3 catalyst, which showed relatively high activity and selectivity for mixed alcohols synthesis. Under the reaction conditions of 385°C, 14.0 MPa and 11 000 h^{-1}, the alcohols space–time–yield (STY) was up to 416.7 ml/l cat h and alcohols selectivity was 82%, but methanol content in the alcohols product was relatively high [4–6]. Increasing the content

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of C_2^+ alcohols is desirable from the practical point of view.

Santiesteban et al. [7] has reported that the addition of cobalt to the alkali/MoS_2 catalyst was in favor of the synthesis of C_2^+ alcohols. Storm [8] and Fujimoto and Oba [9] have also reported that cobalt is a necessary promoter for high STY of higher alcohols on reduced K–Mo/Al_2O_3 and K–Mo/SiO_2 catalysts, respectively.

Cobalt-promoted Mo based catalyst has been extensively used in hydrotreating process, which leads to a continuous drive to clarify the structure and the related catalytic activity of the catalyst system. Many aspects of the preparation–structure–activity relationship have been and are being studied [10–12]. Adding Co^{2+} promoter to the sulfided K–Mo/Al_2O_3 catalyst has been studied in our lab with the aim of increasing the content of C_2^+ alcohols in mixed alcohols. In the present work, we report the influence of calcination temperature of the K–MoO_3/Al_2O_3 sample after impregnating with a Co^{2+} compound on the catalytic properties for the synthesis of mixed alcohols, and the structural changes characterized by XRD, LRS, and EXAFS.

2. Experimental

2.1. Sample preparation and activity measurement

The oxidized K–Mo/Al_2O_3 sample was prepared by impregnating γ-Al_2O_3 support (BET surface area was 270 m^2/g) with an aqueous KCl solution, followed by drying and calcination in air at 300°C for 1 h, and then impregnating this sample with a $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ solution, followed by drying and calcination in a flow of O_2 at 500°C for 24 h, and calcination in air at 800°C for 12 h. The oxidized Co–K–Mo/Al_2O_3 samples were prepared by impregnating the obtained K–Mo/Al_2O_3 samples with an aqueous $Co(NO_3)_2$ solution followed by drying and calcination in air at temperatures of 350°C, 500°C, 650°C and 800°C, respectively (denoted as A, B, C, D). The oxidized samples were sulfided in the stream of 8.7%CS_2/H_2 (30 ml/min) at 400°C for 6 h. The molybdenum content in the samples, expressed as weight ratio of MoO_3/Al_2O_3, is 0.24, potassium content, as K/Mo atomic ratio, is 0.8, and cobalt content, as Co/Mo atomic ratio, is 0.5.

The activity of the sulfided catalyst samples for the alcohols synthesis from syngas was measured by using a fixed bed reactor equipped with an on-line gas chromatography. The synthesis gas was composed of CO 33 vol%, H_2 55 vol% and N_2 12 vol%. The alcohol products were collected in a collector cooled with ice-water at high pressure. The effluent gas from the reactor was leaded on to a sample valve for analysis by gas chromatography. The analysis conditions were described in detail elsewhere [5].

2.2. Structure characterization

XRD patterns were obtained using a D/MAX-γA rotatory target diffractometer with Cu K_α radiation (the wavelength was 0.15418 nm) with a conventional powder method.

Raman spectra of the oxidized and sulfided K–MoO_3/Al_2O_3 samples were recorded with thin wafer on a Spex-1403 spectrometer with the 488.0 nm line from a Spectra-Physics-2020 argon laser. The spectrum slit width was 3.5 cm and the spectrometer resolution was 2 cm^{-1}.

X-ray absorption data around the Co K-absorption edge were collected at EXAFS station of the Beijing Synchrotron Radiation Facility (BSRF). The EXAFS data analysis used here involved a background subtraction by means of cubic spline functions, normalization by the jump height and multiplication of the EXAFS in k space by a factor k^3. Fourier transform ranges for all samples were 30.0–130.0 nm^{-1}.

3. Results and discussion

3.1. Activity for CO hydrogenation

The data in Table 1 show the influence of adding Co promoter to the sulfided K–Mo/Al_2O_3 sample on the catalytic features for the synthesis of mixed alcohols from syngas. Reaction conditions are P=5.0 MPa, GHSV=4800 h^{-1}, T=350°C for the Co– promoted K–Mo/Al_2O_3 samples and P=5.0 MPa, GHSV= 4800 h^{-1}, T=310°C for the unpromoted K–Mo/Al_2O_3 sample. Although the reaction temperature is 40°C higher for the Co promoted samples compared to the unpromoted sample, the selectivity to alcohols does not decrease notably. This exhibits that the

Table 1
Performance of sulfided Co–K–Mo/Al_2O_3 catalysts for mixed alcohols synthesis

Sample	CO conversion (%)	Alcohol selectivity (C%)	CnOH selectivity (CO%)				C_1OH ($C_{2+}OH$)	Alcohol STY[a] (g/l h)
			MeOH	EtOH	PrOH	BuOH		
K–Mo/Al_2O_3[b]	2.75	36.40	21.03	10.70	3.39	1.34	1.37	16.80
A	3.13	22.35	11.50	6.42	3.33	1.10	1.06	11.42
B	6.83	26.19	13.39	6.65	4.48	1.68	1.05	29.07
C	5.58	30.59	15.75	9.09	4.28	1.46	1.07	27.83
D	5.84	26.96	13.34	7.88	4.40	1.35	0.97	25.49

[a] Space–time yield, which was determined from liquid products analysis.
[b] Reaction temperature for this sample is 310°C.

optimum reaction temperature is raised significantly for the Co promoted samples. Another obvious change is that the alcohol ratios of C_2^+/C_1 in the products for Co promoted samples increase notably relative to that for the unpromoted sample. Murchison et al. [1] have reported that CoMo sulfide catalysts can be operated over higher temperature and still give high total alcohol selectivities. They also reported that over CoMo sulfide catalyst, a mixed alcohol product with lower methanol level could be obtained. These are in agreement with our results. From Table 1 it is also shown that for the samples calcined at 350°C or 800°C after impregnating Co promoter, the space–time–yield (STY) of mixed alcohols is lower than that for the samples calcined at 500°C and 650°C. The calcination temperature of the sample after impregnating Co promoter is important for preparing good catalyst for mixed alcohols synthesis.

3.2. *XRD*

The oxidized Co promoted samples were examined by XRD, and the K–Mo/Al_2O_3 sample was also measured as a comparison. Some XRD patterns are shown in Fig. 1. For the oxidized sample calcined at 350°C, XRD pattern includes all the diffraction peaks that exist on the pattern of the unpromoted K–Mo/Al_2O_3 sample. These peaks are assigned to the γ-Al_2O_3 support (d=0.280, 0.239, 0.228, 0.198, 0.152, 0.139 nm), $Al_2(MoO_4)_3$ (d=0.391, 0.276, 0.195 nm) and some K–Mo–O species such as $K_2Mo_4O_{13}$ (d=0.354, 0.311, 0.690), $K_{0.85}Mo_6O_{24}$ (d=0.391, 0.276, 0.195 nm), $K_6Mo_7O_{24}$ (d=0.397, 0.285, 0.276 nm), $K_2Mo_3O_{10}$ (d=0.328, 0.688, 0.351 nm) [4]. This result indicates that the interaction between the Co promoter and the K–Mo species is weak. Besides these peaks that exist on the unpromoted K–Mo/Al_2O_3 sample there exist some new peaks (d=0.244, 0.286, 0.143 nm), which can be assigned to Co_3O_4 and/or $CoAl_2O_4$ compounds. These two compounds give similar diffraction profiles in XRD pattern, but the color of Co_3O_4 is dark and that of $CoAl_2O_4$ is blue, so they can be distinguished easily. The color of the sample calcined at 350°C is dark, Co promoter on this sample should be presented as Co_3O_4. For the samples calcined at 650°C and 800°C, the peaks assigned to K–Mo–O species become weaker, which suggests the structure of the K–Mo–O species is changed by the addition of Co promoter. The diffraction peaks assigned to Co_3O_4 or $CoAl_2O_4$ compound are still sharp for the samples calcined at 500°C and 650°C. The color of the sample calcined at 650°C is still dark but the color of the sample calcined at 800°C is changed to blue, which suggests that Co promoter still exists in Co_3O_4 form on the sample calcined at 650°C, but changes to $CoAl_2O_4$ on the sample calcined at 800°C. Some researcher found that $CoAl_2O_4$ could form on the oxidized Co/Al_2O_3 sample easily while the sample was calcined at a temperature higher than 750°C. This is consistent with our results. For these Co promoted K–Mo/Al_2O_3 samples, small diffraction peaks (d=0.336, 0.381, 0.465 nm) assigned to $CoMoO_4$ compound are also detected.

Fig. 2 presents the XRD pattern for sulfided Co-promoted K–Mo/Al_2O_3 samples. For the sample calcined at 350°C, besides the diffraction peaks assigned to γ-Al_2O_3 support, only a small peak (d=0.615 nm) is

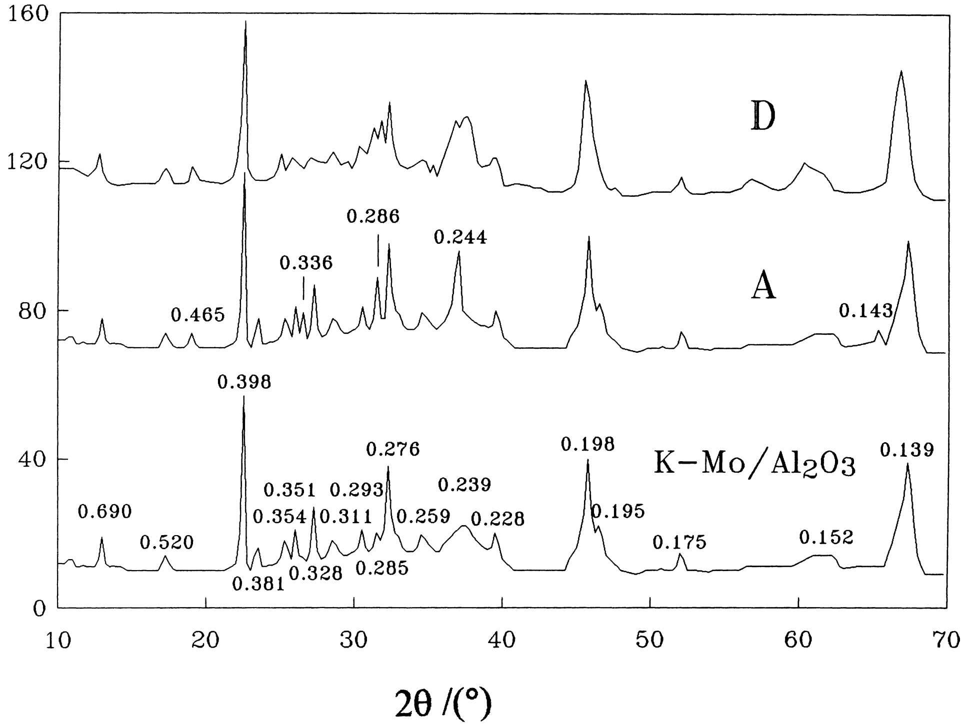

Fig. 1. XRD pattern of oxidized Co–K–Mo/Al_2O_3 sample.

detected, this peak is also detected for sulfided K–Mo/Al_2O_3 sample, which is assigned to MoS_2 crystallites. For the samples calcined at 500°C and higher temperatures, new XRD peaks are detected. They are assigned to compounds of $CoMoS_{3.13}$ (d=0.615, 0.194, 0.272 nm), $CoMoS_{2.17}O_{1.12}$ (d=0.615, 0.339, 0.194 nm) and Co_9S_8 (d=0.176, 0.298, 0.191 nm). With increasing calcination temperature, these diffraction peaks grow stronger.

3.3. LRS

Fig. 3 presents the LRS spectra of oxidized Co promoted samples. For the sample calcined at 350°C, an obvious signal at about 690 cm^{-1} is detected. According to the literature [13], this signal may be assigned to Co_3O_4 or $CoMoO_4$ species. But for $CoMoO_4$ species, the main LRS vibration is at about 950 cm^{-1} and which is much stronger than that at 690 cm^{-1}. The vibration at 950 cm^{-1} for the sample calcined at 350°C is not stronger than that at 690 cm^{-1}, and it also includes the contribution from octahedral Mo^{6+} species. So, the signal at about 690 cm^{-1} is mainly contributed from Co_3O_4 species. The vibrations at 950, 932, 374, 214 cm^{-1} correspond to some Mo–O bond in K–Mo–O species, but these vibrations are obviously weak compared to those for unpromoted K–Mo/Al_2O_3. This suggests that the K–Mo–O species on the Co promoted sample are partly covered by the Co species, because LRS can only detect species on the sample surface with a thickness of about 2 nm. For the samples calcined at 500°C and 650°C, the LRS band at about 690 cm^{-1} grows up in intensity but for 800°C calcined sample, this band vanishes, which indicates the disappearance of the Co_3O_4 species. The results obtained from LRS are in good agreement with those from XRD. $CoAl_2O_4$ species cannot be detected by LRS, because it does not show Raman activity.

The LRS measurement for sulfided Co promoted samples exhibited that only two bands (404 and 376 cm^{-1}) were detected for all the four samples (the figures are not shown here). They were assigned to the characteristic vibrations of MoS_2 species. The

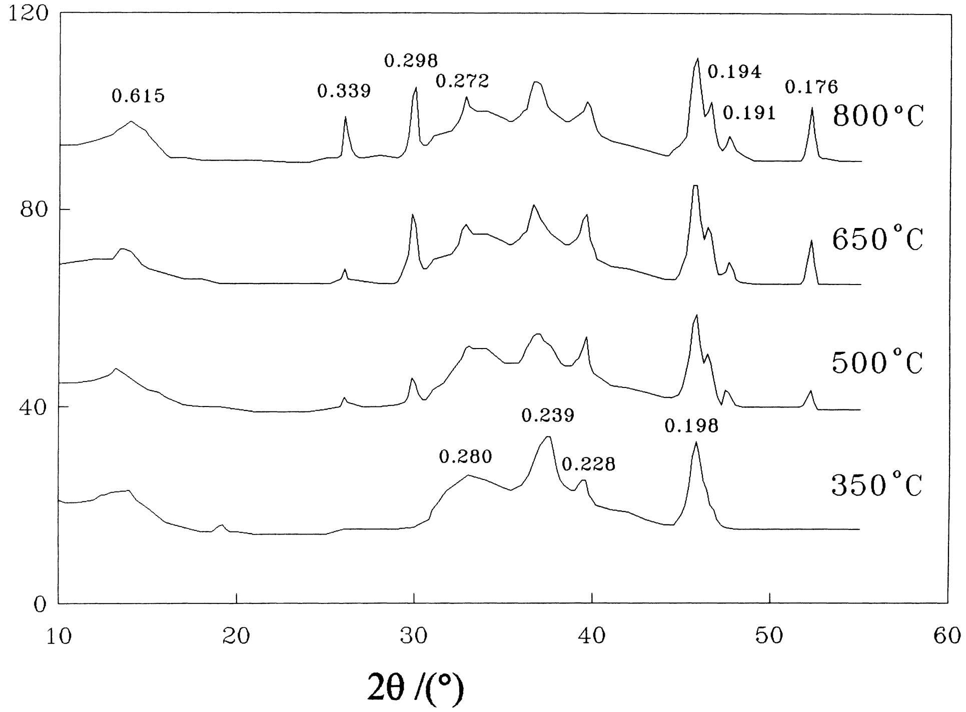

Fig. 2. XRD pattern of sulfided Co–K–Mo/Al_2O_3 samples.

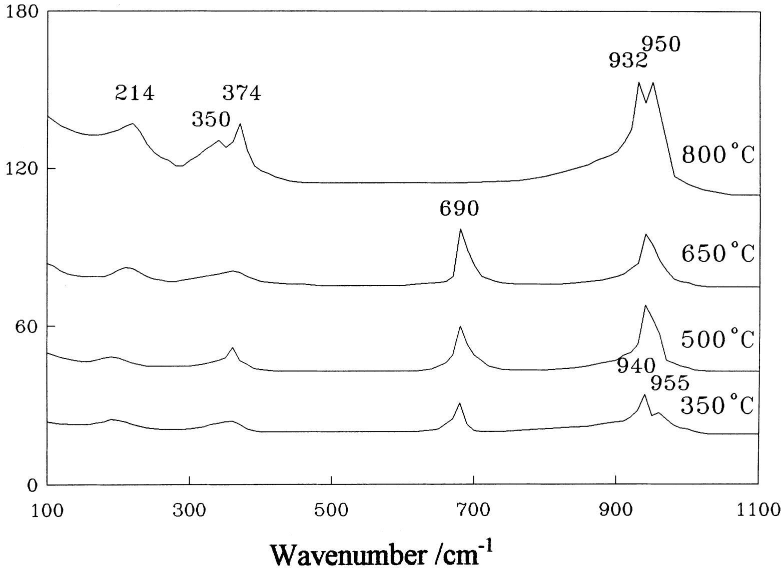

Fig. 3. Raman spectra of oxidized Co–K–Mo/Al_2O_3 samples.

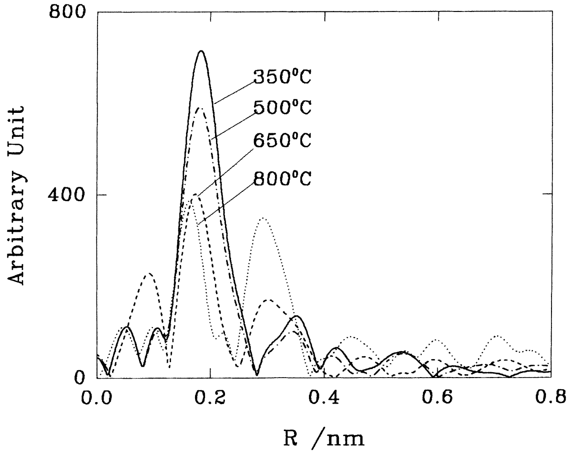

Fig. 4. RDF of Co for sulfided Co–K–Mo/Al_2O_3 samples.

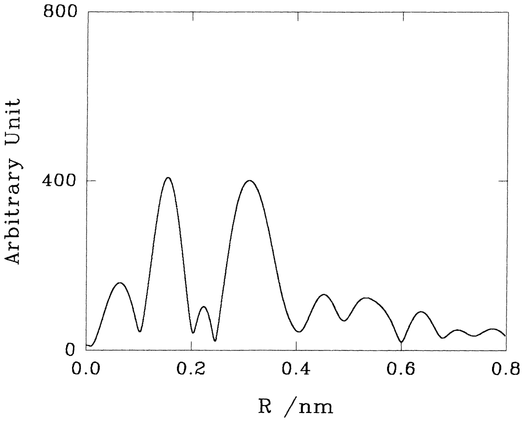

Fig. 5. RDF of Co for $CoAl_2O_4$ compound.

bands for the sample calcined at 350°C were weaker than those of other three samples. The others had no remarkable difference from each other.

3.4. EXAFS

Fig. 4 shows the radial distribution functions (RDF) around the central Co atoms for sulfided Co–K–Mo/Al_2O_3 samples, where R is the uncorrected distance from the Co atom. It is observed that for the sample calcined at 350°C, a strong peak due to the first coordination shell is located at 0.19 nm, with a small peak due to the second coordination shell at about 0.35 nm. For the sample calcined at higher temperature, the peak due to the first coordination shell becomes weaker and shifts to lower R side. The peak corresponding to the second coordination shell becomes stronger and also shifts to lower R side. For the sample calcined at 800°C, the peak corresponding to the first coordination shell shifts to 0.16 nm, and the second coordination peak shifts to 0.30 nm with a similar intensity to the first peak.

The Co K-edge of $CoAl_2O_4$ was also measured by EXAFS, and the obtained RDF is shown in Fig. 5. According to the position of Co–O coordination peak in the RDF and the shift from its interatomic distance, the interatomic distances between the central Co atom and the nearest coordination atoms in the sulfided Co–K–Mo/Al_2O_3 samples were determined. The results are shown in Table 2. According to the literature [14–16], the nearest Co–S distance in octahedral Co–S structure is about 0.23–0.24 nm, and the nearest Co–S distances in the tetrahedral Co–S structure is about 0.21–0.22 nm. In oxygen- containing cobalt compounds such as $CoAl_2O_4$ and Co_3O_4, the Co–O coordination distances are about 0.195 nm. So, the Co atoms in the sulfided sample calcined at 350°C are coordinated with S atoms in an octahedral structure, and Co atoms in the samples calcined at 500°C and 650°C are coordinated with S atoms in a tetrahedral structure, for the sample calcined at 800°C Co atoms are still coordinated with O atoms after the sulfidation. Therefore, for the samples calcined at 650°C and lower temperature, the oxygen atoms round central Co atoms are mostly exchanged by sulfur atoms during sulfidation, but for the sample calcined at 800°C, most of the oxygen atoms around Co atoms are not exchanged at same sulfidation conditions. These results demonstrate that cobalt oxide in the

Table 2
Structure parameters of several Co compounds

Sample	Shell	R (nm)	Shell	R (nm)	Reference
CoS_2	Co–S(o)	0.232	Co–Co	0.390	[16]
Co_9S_8	Co–S(o+t)	0.221	Co–Co	0.350	[16]
$CoAl_2O_4$	Co–O(t)	0.195			[14]
A	Co–S	0.230	Co–Co	0.390	
B	Co–S	0.221	Co–Co	0.375	
C	Co–x	0.216	Co–Co	0.350	
D	Co–x	0.201	Co–Co	0.350	

Note: 1. o denotes octahedral shell; t denotes tetrahedral shell.
2. x means that both O and S atoms are included in the shell.

samples can be sulfided but $CoAl_2O_4$ species are difficult to be sulfided.

EXAFS results show that the coordination situation of Co component on the sulfided sample calcined at 800°C is similar to that in $CoAl_2O_4$, but no peaks belonging to $CoAl_2O_4$ is detected by XRD for this sample. EXAFS can detect the coordination structure in the nearest shell even for amorphous phase with short-range order, whereas XRD can only detect the species with obvious long-range order. So, most of Co species on the sulfided sample should exist as amorphous $CoAl_2O_4$ species and a small amount of Co component exists as Co–S or Co–Mo–S species which are in long-range order and can be detected by XRD.

According to the literature [16], Co species show a relatively strong interaction with Mo component and form Co–Mo–S structure in Co–Mo catalysts, which exist in the form of tetrahedral structure, and the Co–S interatomic distance is about 0.22 nm. The sample calcined at 500–650°C shows a relatively high activity for the synthesis of mixed alcohols from CO hydrogenation, which may be, to some extent, connected with the fact that Co atoms in the sample show a stronger interaction with Mo species. The lower activity of the sample calcined at 800°C for the synthesis of mixed alcohols should be attributed to that most of Co species are not sulfided. The lower activity of the sample calcined at 350°C may be caused by the coverage of Co species over Mo species.

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