# Influence of Water on the Methanation Performance of Mo-Based Sulfur-Resistant Catalysts with and without Cobalt Additive

Haiyang Wang, Can Lin, Zhenhua Li,\* Baowei Wang, and Xinbin Ma\*

Key Lab for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Collaborative Innovation Center of Chemical Science and Engineering, Tianjin University, Tianjin 300072, China. \*E-mail: zhenhua@tju.edu.cn; xbma@tju.edu.cn Received June 9, 2014, Accepted September 15, 2014, Published online January 5, 2015

The activities of Mo-based and Co-containing Mo-based catalysts for sulfur-resistant methanation in the presence and the absence of water are compared. When water was added to the Mo-based catalyst, its methanation activity decreased and the activity could not be recovered even after the water was removed from the system. However, for the Co-containing Mo-based catalysts, the formation of  $Co_9S_8$  improved not only the methanation activity of the catalyst as active sites but also the stability of the catalyst especially in water-containing hydrogenation. The deactivation of the Mo-based catalyst in the presence of water is mainly due to reduction of the external acid sites and fewer molybdenum sulfide (MoS<sub>2</sub>) stacks. The addition of Co protects the active MoS<sub>2</sub> phase, thereby preventing the deactivation of the catalyst in the presence of water.

Keywords: Sulfur-resistant, Methanation, Deactivation, Water

#### Introduction

Today, the global need for vast amounts of energy is a pressing concern. In addition, methods to utilize coal in an environmentally friendly manner are also greatly desired. With both goals in mind, methanation is considered an important means of producing substitute natural gas from biomass or coal.<sup>1</sup> Often the catalysts for the methanation of syngas contain nickel or cobalt as the active ingredient. These metallic catalysts are relatively cheap and very active for the reaction. However, they are extremely sensitive to poisoning by sulfur compounds.<sup>2</sup> Thus attention has turned to Mo-based methanation catalysts which are sulfur-resistant and can tolerate the gases of low H<sub>2</sub>/CO ratios that come from gasifiers. It is possible for a Mo-based catalyst to cover the shortage of their relatively low activity by using simplified production technology without enhancing the H<sub>2</sub>/CO mole ratio or removing sulfur species.

Mo-based sulfides are used widely in hydrotreating processes to produce clean fuels and aromatic compounds.<sup>3</sup> These catalysts are also used extensively in commercial catalytic hydrogenations<sup>4,5</sup> (e.g., hydrodesulfurization (HDS), hydrodenitrogenation, and hydrotreating). It has been well established that their active sites are located on the edges of the molybdenum sulfide (MoS<sub>2</sub>) nanocrystallites, which correspond to the (100) edge planes of their layered structures.<sup>6</sup>

Water can deactivate sulfided hydrotreating catalysts by changing their structure or chemical composition. The presence of water can modify the structure of the active edges of the sulfide phase and can influence the stability of the catalysts.<sup>7</sup> During the hydrotreating of low-sulfur content feeds, sulfided catalysts usually undergo a continuous deactivation as a result of the partial reoxidation of the sulfide phase.<sup>8</sup> In

addition, water may cause sulfate species to form; these then cover the active phase and reduce the catalytic activity.<sup>9</sup>

Cobalt molydates are important components of catalysts used for the partial oxidation of hydrocarbons<sup>10</sup> and for the synthesis of HDS catalysts.<sup>11</sup> The desulfurization and denitrogenation performance of MoS<sub>2</sub> catalysts can be substantially improved by the addition of a cobalt promoter. It is believed that the Co atoms are mostly localized on the S-edges, although in the case of a high Co/Mo ratio, some Co atoms are also located on the Mo-edges.<sup>12</sup> Co atoms can substitute for Mo atoms at these edges, which results in S-vacancies since the Co ions have a lower valency than the Mo ions.<sup>13</sup> This generates new active sites. It is generally accepted that this so-called Co–Mo–S phase (structure), in which the Co atoms are located on the edges of the MoS<sub>2</sub> particles, is the active phase.<sup>14</sup>

Feed stock gases from a coal gasifier contain a certain amount of water. And the sulfur-resistant methanation  $(2CO + 2H_2 \rightarrow CH_4 + CO_2)$  that occurs on Mo-based catalyst is actually a sum of the methanation  $(3H_2 + CO \rightarrow CH_4 +$ H<sub>2</sub>O) and water gas shift reaction (CO + H<sub>2</sub>O  $\leftrightarrow$  CO<sub>2</sub> + H<sub>2</sub>). This means that the catalysts should be active in a watercontaining environment. Therefore, it is necessary to investigate the effect of water on the methanation performance of Mo-based sulfide catalysts and to elucidate the change of active sites on the catalysts in the presence of sulfur. In addition, the effect of adding Co to the Mo-based catalyst on the stability of the catalyst in the presence of water vapor is also investigated in this work. The catalysts are characterized for their surface area, crystallinity, cluster dimension, and surface chemical composition. This study provides information for the design of catalysts with better activities and stabilities for sulfur-resistant methanation of gas feedstocks containing water.

## Experimental

Catalyst Preparation. A commercially available  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support (Yixing, China) was used to prepare the catalysts. Catalysts with 25 wt% MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> (283 m<sup>2</sup>/g) and 5 wt% CoO-25 wt% MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> were prepared via a conventional incipient wetness impregnation method by impregnating the support with an aqueous solution of ammonium heptamolybdate or an aqueous solution of ammonium heptamolybdate and cobalt nitrate, respectively. The impregnated samples were dried at 30 °C for 24 h in air, and then at 120 °C for 6 h, and finally calcined at 600 °C for 4 h with a heating rate of 3 °C/min. These catalysts are denoted as Mo/Al and Co-Mo/Al. Catalyst Characterization. Nitrogen physisorption analysis of the prepared catalysts was performed at -196 °C on a Tristar-3000 apparatus (Micromeritics, Atlanta, Georgia, USA) to obtain the textural properties of the catalysts (specific surface area and pore volume). Prior to measurement, the sample was degassed at 300 °C for 3 h under vacuum. The surface areas were determined by physical adsorption of N<sub>2</sub> at liquid nitrogen temperature, using the Brunauer-Emmett-Teller (BET) equation. The pore volumes and pore size distributions were obtained from the desorption curves of the isotherms using the Barrett-Joyner-Halanda (BJH) model.

The temperature-programmed reduction (TPR) and temperature-programmed desorption (TPD) profiles of the catalysts were obtained using an AutoChem 2910 analyzer (Micromeritics) equipped with a thermal conductivity detector (TCD) for measuring the hydrogen consumption. In the TPR experiments, a stream of gas with the composition  $H_2/Ar = 1:9$ at a flow rate of 30 mL/min was introduced into the catalyst sample (0.20 g). The catalyst was then heated from 60 to 1000 °C at a heating rate of 10 °C/min.

For each of the TPD runs, 0.20 g of sample was first treated at 200 °C for 1 h and then cooled to 50 °C under an argon flow. Ammonia (1 mL) was injected into the Ar at 50 °C, and the injection was repeated for 3–5 times in order to fill the adsorption sites. TPD was then performed by heating the samples at the rate of 10 °C/min under 30 mL/min Ar flow.

X-ray diffraction (XRD) measurements were performed on a D/max-2500 X-ray diffractometer (Rigaku, Japan) with a Cu K $\alpha$  radiation source ( $\lambda = 1.54056$  Å). The scan speed was 8°/min, with a scanning angle range of 5–85°. The phase identifications were determined by comparison with the Joint Committee on Powder Diffraction Standards (JCPDS).

Before transmission electron microscopy (TEM) analysis, the catalysts were kept under dry vacuum conditions. The TEM specimens were prepared by ultrasonically dispersing the catalysts in ethanol, and then placing drops of the suspensions onto a micro-mesh copper grid. The morphology and structure of the catalysts were characterized by a Tecnai  $G^2$ F20 (200 kV) transmission electron microscope (FEI, Eindhoven, Noord-Brabant, Netherlands), with a high resolution of 0.15 nm/200 kV.

Prior to X-ray photoelectron spectroscopy (XPS) analysis, the samples were pretreated under dry vacuum conditions. The

samples were outgassed in the pretreatment chamber for 1 h under ultrahigh vacuum and then transferred into the analysis chamber. The XPS analysis for the catalyst was performed using a PHI-1600 ESCA spectrometer equipped with monochromic Mg K $\alpha$  X-ray radiation. The pressure of the analysis chamber was maintained at 2 × 10<sup>-10</sup> Torr. The binding energies (BEs) were calibrated using the C 1s line at 284.6 eV. The error in the BEs with this reference was estimated to be ±0.1 eV. The peak area intensities were measured by planimetry of the graphic displays of the spectra assuming Shirley baselines.

**Catalytic Activity Evaluation.** Catalytic performance evaluations were carried out in a continuous-flow, fixed-bed reactor. The stainless steel reactor (70 cm in length and 12 mm in internal diameter) was heated by an enclosed electric furnace. The temperature was controlled by using three K-type thermocouples placed in the furnace, and the reaction temperature was monitored using a K-type thermocouple placed in the middle of the 3 mL catalyst bed (0.43–0.85 mm particle size). The catalysts were sulfurized using a 3 vol%  $H_2S/H_2$  gas mixture at 400 °C for 4 h before activity testing.

The catalytic reaction was conducted under the following conditions: A mixed gas (CO/H<sub>2</sub>/N<sub>2</sub> = 2:2:1 in volume ratio) with 1.2 vol% H<sub>2</sub>S was used as the feed gas. The space velocity was 5000 h<sup>-1</sup>, the reaction temperature was 560 °C, and the reaction pressure was 3 MPa. Water was injected into the vaporizer by a micro piston pump and mixed with the feed gas. Then a mixture containing 10 vol% water vapor was supplied to the reactor to investigate the effect of water.

The outlet gases were analyzed online using an Agilent 7890A gas chromatograph equipped with six columns (three Porapak-Q and two Carboxen (Restek, Bellefonte, Pennsylvania, USA) and one capillary column (Agilent Technologies Inc., Santa Clara, California, USA)) and three detectors (two thermal conductivity detectors and one flame ionization detector), using N<sub>2</sub> or H<sub>2</sub> as the carrier gas. The compositions of CO, CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>, and N<sub>2</sub> were measured and then used to calculate the H<sub>2</sub> conversion, CO conversion, CH<sub>4</sub> selectivity, and CO<sub>2</sub> selectivity according to the following formulas:

$$XH_2 = \frac{n(H_{2in}) - n(H_{2out})}{n(H_{2in})} \times 100\%$$
(1)

$$X_{\rm co} = \frac{n(\rm CO_{in}) - n(\rm CO_{out})}{n(\rm CO_{in})} \times 100\%$$
(2)

$$S_{\rm CH_4} = \frac{n(\rm CH_{4out}) - n(\rm CH_{4in})}{n(\rm CO_{in}) - n(\rm CO_{out})} \times 100\%$$
(3)

$$S_{\rm CO_2} = \frac{n(\rm CO_{2out}) - n(\rm CO_{2in})}{n(\rm CO_{in}) - n(\rm CO_{out})} \times 100\%$$
(4)

$$S_{C_{2}H_{6}} = 2 * \frac{n(C_{2}H_{6out}) - n(C_{2}H_{6in})}{n(CO_{in}) - n(CO_{out})} \times 100\%$$
(5)

where  $X_{H_2}$  and  $X_{CO}$  refer to the H<sub>2</sub> and CO conversions, respectively, and  $S_{CH_4}$ ,  $S_{CO_2}$ , and  $S_{C_2H_6}$  refer to the CH<sub>4</sub>, CO<sub>2</sub>, and C<sub>2</sub>H<sub>6</sub> selectivities, respectively.

## **Results and Discussion**

**Catalyst Activity Evaluation.** The sulfided catalysts were exposed to two different conditions for studying the effect of water: one is methantion without water added (Blank test), and the other is water addition to the feed gas during reaction (with water). The methanation activities in the presence and the absence of water were tested for about 40 h, and the results are shown in Figure 1 (Mo/Al) and Figure 2 (Co–Mo/Al). For both catalysts, the effect of water was tested by adding 10% water to the reaction after 5 h of methanation with no water present. The water was continually added from 5 to 25 h, and then it was removed after 25 h to test the recovery of the methanation activity.

Comparing Figures 1 and 2, a clear differentiation between two catalysts can be found. The Mo/Al catalyst showed around 50% CO conversion, but CoMo/Al showed 60% CO conversion with almost same selectivities.

In the absence of water, the activity of the Co–Mo/Al catalyst had the same regularity as that of the Mo/Al catalyst. The conversion of H<sub>2</sub> was ~10% higher than the conversion of CO. The CO and H<sub>2</sub> conversions decreased with time for both catalysts, but the decline on the Co–Mo/Al catalyst was less. In addition, the CO and H<sub>2</sub> conversions on the Co–Mo/Al catalyst were higher than those on the Mo/Al catalyst, indicating that the Co has a promoting effect on the Mo-based catalyst. The CO<sub>2</sub> and CH<sub>4</sub> selectivities on the Mo-based catalysts were both ~50%.

When water was added, for both catalysts the CO conversion did not decline much, but the H<sub>2</sub> conversion decreased greatly. This is due to the water gas shift reaction, as indicated by the increase in the CO<sub>2</sub> selectivity. After the water was stopped, most of the methanation activity of the Co–Mo/Al catalyst was recovered but the methanation activity of the Mo/Al catalyst was not. Previously, it had been reported that the CO uptake by the sulfide sites on both the Mo and Co–Mo catalysts strongly decreased after water addition.<sup>13,15</sup> As shown in Figure 3, the Co–Mo/Al catalyst showed less deactivation (about 2%) than the Mo/Al catalyst (about 6%). This implies that the addition of Co inhibits the deactivation caused





**Figure 1.** Effect of water on the methanation activity and selectivity of the Mo/Al catalyst: with water (solid smbols) and blank test (empty symbols).

**Figure 2.** Effect of water on the methanation activity and selectivity of the Co–Mo/Al catalyst: with water (solid symbols) and blank test (empty symbols).

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by water, and the Co atoms may help in protecting the  $MoS_2$  active sites.

**Characterization of Mo-Based Catalysts.** The textural properties of the Mo/Al and Co–Mo/Al catalysts were determined using  $N_2$  adsorption–desorption isotherms, and the results are listed in Table 1. Compared with the fresh catalyst, the surface areas of both catalysts decreased greatly after sulfidation. However, the surfaces areas changed little after the activity tests with and without water. The difference in the textural properties between the two catalysts can be attributed to the addition of Co. The Co promoter may block the micropores of the catalysts and make the average pore diameter larger and the surface area smaller. When the surface area and pore volume of the catalyst supports are compared to the activity results, it appears that they are not critical factors that affect the methanation activity.



Figure 5. Influence of H<sub>2</sub>O of the catalyst deactivation

Table 1. Textural properties of the catalysts.

Catalyst		BET surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Average pore diameter (nm)
Mo/Al	Fresh <sup>a</sup>	223	0.33	5.8
	Sulfided <sup>b</sup>	165	0.25	6
	Spent blank test <sup>c</sup>	154	0.26	6
	Spend with $H_2O^d$	153	0.14	4.2
Co-Mo/Al	Fresh <sup>a</sup>	204	0.27	5
	Sulfided <sup>b</sup>	154	0.21	5.1
	Spent blank test <sup>c</sup>	133	0.2	6
	Spent with $H_2O^d$	141	0.22	5.8

<sup>&</sup>lt;sup>*a*</sup> As-prepared catalyst.

<sup>b</sup> After sulfided at 560 °C.

<sup>c</sup> After the blank test.

<sup>d</sup> After the test with water.

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The Mo/Al catalyst used in the presence of water had a smaller pore volume and average pore diameter than the catalyst used with no water. This could be related to the deactivation effect of the water vapor. This effect is probably due to the formation of a sulfate layer that covers the active phase and/or to structural changes in the alumina support. In contrast, the Co–Mo/Al catalyst used with water showed no distinctive textural changes. This suggests that the Co additive effectively modified the interactions between the active phase and the support in such a way that the original textural properties of catalyst were maintained when water was added to the system. So the methanation activity of the Co–Mo/Al catalyst changed little between reacting with and without water.

The TPR patterns of fresh Mo/Al and the Co–Mo/Al catalysts are presented in Figure 4. Both samples have two reduction peaks. The first peak corresponds to the partial reduction of  $Mo^{6+}$  to  $Mo^{4+}$ , and the second peak to the reduction of  $Mo^{4+}$  to  $Mo^{0.16}$  The reduction peaks for the Co–Mo/Al catalyst are at slightly lower temperatures than those for Mo/Al, which indicates that the species are easier to reduce. This is due to the polarization effects of Co<sup>2+</sup> on the Mo<sup>6+</sup> terminal oxygen atoms.<sup>17</sup> The degree of reduction was evaluated by the integration of the TPR curves between 60 and 600 °C (the reaction temperature was 560 °C) and found to be 65.1 for the Co–Mo/Al catalyst and 60.3 for the Mo/Al catalyst. This result is in good agreement with the methanation activities, and it presents a promotion of Co on the active sites.

The XRD spectra of the different Mo/Al and Co–Mo/Al catalysts are shown in Figure 5. The sulfided catalysts were obtained by sulfurizing the oxide catalysts with 3% H<sub>2</sub>S/H<sub>2</sub> (100 mL/min) at 560 °C for 4 h. The XRD spectra of the Mo/Al catalysts in Figure 5 shows several broad diffraction peaks corresponding to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> ( $2\theta = 33.4^{\circ}$ , 37.5°, 45.7°, 59.1°, and 66.8°).<sup>18</sup> No obvious XRD peaks specific to Mo sulfides were detected, suggesting that the Mo species may be present as small nano-sized particles that are well dispersed on the support  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.<sup>19</sup> Figure 5 confirms the presence of



Figure 4. TPR profiles of the fresh catalysts.

 $MoS_2 peak (2\theta = 14.1^{\circ})$  appearing in the sulfurized Co–Mo/Al catalysts, so the crystalline  $MoS_2$  phases were detected by XRD. There were no changes in the structure of the aluminum support when cobalt was added.

When water vapor was added to the reaction feed,  $H_2$  was produced inside the reactor, which transformed the crystalline  $MoS_2$  phases to well-dispersed amorphous  $MoS_2$  nanocrystallites.<sup>20</sup> Consequently, the  $MoS_2$  peak disappeared after the methanation test with water.

Diffraction peaks for  $\text{Co}_9\text{S}_8$  ( $2\theta = 29.9^\circ$  and  $52.0^\circ$ ) are observed in all the sulfided Co–Mo/Al samples. And the  $\text{Co}_9\text{S}_8$  crystals are decorated with MoS<sub>2</sub> stacks, which makes them longer.<sup>21</sup> This, combined with the catalytic activity results, suggests that the Co<sub>9</sub>S<sub>8</sub> structures are beneficial for the methanation activity. Moreover, it had previously been reported that Co<sub>9</sub>S<sub>8</sub> can enhance the stability of catalysts in hydrotreating reactions.<sup>22,23</sup> The disappearance of the sulfide species such as MoS<sub>2</sub> and Co<sub>9</sub>S<sub>8</sub> could be attributed to oxidation when water is present during the reaction. The welldispersed Co–Mo sulfides, including Co<sub>9</sub>S<sub>8</sub>, exhibited excellent catalytic performance and good stability as active sites for the reaction, as shown in Figure 2.

Previously, TEM had been used to show that sulfided Mo/ Al and Co–Mo/Al catalysts contain black, thread-like fringes that correspond to the  $MoS_2$  slabs.<sup>24</sup> To compare the distribution of the slabs lengths and stacking after the sulfidation treatment, and the methanation reactions with and without water, about 15 images and 200 slabs for each sample were statistically analyzed. The distributions of the slab lengths in the Mo/ Al and Co–Mo/Al catalysts are presented in Figure 6. The average size and the number of slabs in a stack (*n*) of  $MoS_2$ particles are summarized in Table 2. Representative TEM images of Mo/Al and Co–Mo/Al catalysts are presented in Figures 7 and 8.

As shown in Table 2, the  $MoS_2$  slabs became longer for both the Mo-based catalysts after 40 h of methanation reaction. This is because some of the amorphous  $MoS_2$  particles grew into well-crystallized stacks at high-temperature calcination.<sup>25</sup>



**Figure 5.** XRD patterns of the catalysts: (a) After sulfided at 560 °C, (b) after the blank test, and (c) after the test with water.



**Figure 6.** Effect of water on the slab lengths of the catalyst obtained from TEM analysis.

**Table 2.** The average slab length (*L*) and number of slabs (*n*) in a stack of the  $MoS_2$  particles for the Mo/Al and Co–Mo/Al catalysts determined from TEM micrographs.

	Mo/A	41	Co-Mo/Al		
Catalyst	L (nm)	п	L (nm)	n	
Sulfided at 560 °C	3.1	2.2	4.5	2.5	
After the blank test	4.1	1.6	4.5	2	
After the test with water	3.2	1	4	1.8	



Figure 7. Representative TEM images of different Mo/Al catalysts: (a) After sulfided at 560 °C, (b) after the blank test, and (c) after the test with water.



Figure 8. Representative TEM images of different Co–Mo/Al catalysts: (a) After sulfided at 560  $^{\circ}$ C, (b) after the blank test, and (c) after the test with water.

When water was added during the reactions, the slabs became shorter under the severe reaction conditions. So, longer slabs and more stacking are not responsible for the higher activity.

When water is added during the methanation reaction, the  $MoS_2$  surface is alternately oxidized by water and then reduced by CO.<sup>26</sup> For the Mo/Al catalyst, after the methanation reaction with water, the number of stacks in the  $MoS_2$  slabs decreased from 2.2 to 1.0 and the slab length became smaller. This decrease may be due to the exchange of oxygen for sulfur at the outer layer of the sulfide slabs in the presence of water.<sup>27</sup> The formation of an oxy-sulfide outer layer led to a loss of the crystallinity in the external sulfide slab layer. This is accompanied by a decrease in the  $MoS_2$  particle size, which is responsible for the absence of diffraction fringes at the outer layer. The decrease in the number of sulfide edge sites resulted in the decrease in the CO uptake on the catalyst, as well as the decrease in the methanation activity when water was added.

As shown in Figure 8, clear  $MoS_2$  crystallites can be seen on the sulfided Co–Mo/Al sample, which is in agreement with the XRD results. In this catalyst,  $MoS_2$  acts as a frame and the Co atoms decorate the  $MoS_2$  edge sites to form the active phase, which is a highly dispersed cobalt sulfide  $(Co_9S_8)$ .<sup>28</sup> After the methanation reactions in both the absence and the presence of water, the average lengths of the  $MoS_2$  slabs and the average number of layers in the stacks are fairly close to those in the sulfided sample (Table 2). These results show that Co stabilized the sulfide phase and thus the methanation activity also improved.

The presence of strong Lewis (coordinatively unsaturated metal atoms) and Brönsted (proton donor groups) acid sites on a catalyst surface is important for their adsorptive and catalytic applications. The TPD profiles of the catalyst that reacted in the absence and the presence of water are presented in Figure 9. The profiles for the Mo/Al catalyst show that, in the presence of water, the intensity of the profile decreased greatly, which means that the number of acid sites decreased as well. This corresponds with the decreased activity of the catalyst in the presence of water. For the Co–Mo/Al catalyst, the decrease in the number acid sites in the presence of water is less significant.

During the impregnation and calcination processes, molybdenum is anchored to the Brönsted acid sites (aluminum) and Mo–O–Al groups are formed.<sup>29,30</sup> Water can absorb on the unsaturated surface molybdenum sites, which can lead to S–O exchanges. This strongly changes the surface. From the changes in MoS<sub>2</sub> stacking (TEM results), it is proposed that some of the molybdenum species are bonded to the catalyst surface by alumina hydroxyl groups, forming Mo–O– Al bonds.

XPS analysis was used to further study the effect of water on the surface compositions of the two catalysts (Mo/Al and Co– Mo/Al). The ratio of  $A_{Mo3d}/A_{Al2p}$  is an indication of the dispersion of Mo. The Mo/Al ratio was 0.11 for Mo/Al and 0.18 for



Figure 9. TPD profiles of the catalysts reacted in the absence and the presence of water.

Co-Mo/Al, and these ratios did not change after water was added. This indicated that no loss of molybdenum occurred.

The spectra shown in Figures 10 and 11 show the Mo and S states that are present on the surfaces of the used catalysts. These are useful to determine the extent of sulfidation and the distribution of the active species on the support. The molybdenum exists mainly as disulfide (MoS<sub>2</sub>, Mo<sup>4+</sup>), as indicated by the peaks at 229.0 ± 0.1 and 232.2 ± 0.1 eV. The peaks at 232.7 ± 0.1 and 235.8 ± 0.2 eV are due to the presence of a Mo oxide phase (MoO<sub>x</sub>, Mo<sup>6+</sup>). The other phase is an intermediate Mo oxysulfide (MoO<sub>x</sub>S<sub>y</sub>, Mo<sup>5+</sup>),<sup>31</sup> as indicated by the doublet at 230.2 ± 0.1 and 233.4 ± 0.1 eV. The BEs of Mo 3d and S 2s partly overlapped each other. In this case, we attributed the overall contribution of S 2s to the peak located at 226.1 ± 0.1 eV (MoS<sub>2</sub>) and 227.2 ± 0.2 eV (MoO<sub>x</sub>S<sub>y</sub>).

The results in Figure 11 indicate that the sulfur existed as  $S^{2-}$  in MoS<sub>2</sub>, CoMoS, or Co<sub>9</sub>S<sub>8</sub> as indicated by the peaks at 161.8  $\pm 0.1$  and 162.7  $\pm 0.1$  eV. These are close to the values reported in the literature.<sup>32</sup> The doublet at 163.2  $\pm 0.1$  and

163.9 ± 0.1 eV indicates the presence of a MoO<sub>x</sub>S<sub>y</sub> phase (S<sub>2</sub><sup>2–</sup>). All samples contain a large amount (82–87%) of S<sup>2–</sup>. A sulfate species at 169.2 ± 0.2 eV is also observed, and this could be attributed to the reoxidation of sulfide ions when the sample is exposed to air or water during storage and transfer.<sup>33</sup>

The relative intensities of the XPS peaks were used to estimate the fractional distribution of different Mo species on the catalyst surfaces.<sup>34,35</sup> Table 3 lists the percentages of the different atom states present in the catalysts. The Mo<sup>4+</sup> species accounted for about 80% of the Mo species in the Co–Mo/Al catalyst, whereas for the Mo/Al catalyst it was below 75%. The Mo/Al catalyst had a lower percentage of the sulfide phase (Mo<sup>4+</sup>), which is in agreement with other observations. The contents of both Mo<sup>4+</sup> and Mo<sup>5+</sup> decreased in the sample that reacted in the presence of water. So the formation of the inactive species occurred in both disulfide and oxysulfide intermediates, while these species were not promoted with Co atoms. And molybdenum phases with lower valence states were slightly oxidized.

For the Co–Mo/Al catalyst, the Mo distribution on the used catalysts was not greatly affected by the presence of water, indicating that no significant changes in the Mo valence states occurred during the methanation process with water. The phase changes of the Mo species were not so severe, which means the Co–Mo–S phase and  $Co_9S_8$  species may enhance the activity of Mo-based catalyst for the hydrogenation reaction as active sites in the presence of sulfur. Furthermore, the stable distribution of Mo shows that the formation of inactive species was inhibited by the Co-promoted catalyst.

### Conclusion

Adding water to a Mo–Al catalyst decreased the methanation activity, and the activity could not be recovered after the water was removed from the system. In contrast, for a Co– Mo/Al catalyst, the methanation activity that was lost upon the addition of water was mostly recovered. The Co improved not only the methanation activity of the catalyst but also the catalytic stability of the catalyst especially in a watercontaining atmosphere. The Co additive inhibited the sulfur–oxygen exchanges that occur in the presence of water. In addition, cobalt sulfide species (Co<sub>9</sub>S<sub>8</sub>) and Co-decorated MoS<sub>2</sub> stacks protect the active MoS<sub>2</sub> stacks. The formation of these structures protects the surface acid sites and the MoS<sub>2</sub> stacks. These results give a better understanding of the methanation performance of sulfur-resistant catalysts in watercontaining environments.

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Figure 10. High-resolution XPS Mo 3d spectra: (a) Mo/Al catalyst after the blank test, (b) Mo/Al catalyst after the test with water, (c) Co–Mo/Al catalyst after the blank test, (d) Co–Mo/Al catalyst after the test with water.



Figure 11. High-resolution S 2p spectra by XPS: (a) Mo/Al catalyst after the blank test, (b) Mo/Al catalyst after the test with water, (c) Co–Mo/Al catalyst after the blank test, and (d) Co–Mo/Al catalyst after the test with water.

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Catalyst	Mo <sup>4+</sup>		Mo <sup>5+</sup>		Mo <sup>6+</sup>		$S^{2-}$		$S_2^{2-}$	
	BE (eV)	%atom	BE (eV)	%atom	BE (eV)	%atom	BE (eV)	%atom	BE (eV)	%atom
Mo/Al	229.0	74.36	230.2	6.50	232.6	19.15	161.8	80.87	163.1	19.13
Mo/Al <sup>a</sup>	229.0	65.70	230.2	10.34	232.8	23.96	161.8	85.02	163.2	14.98
Co-Mo/Al	229.0	77.15	230.2	6.50	232.6	16.35	161.9	33.33	163.3	66.67
Co-Mo/Al <sup>a</sup>	229.1	80.62	230.2	3.30	232.6	16.08	161.8	33.33	163.2	66.67

<sup>a</sup> Methanation reaction with water added.

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