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Effect of Titania Addition on the Performance of CoMo/Al₂O₃ Sour Water Gas Shift Catalysts under Lean Steam to Gas Ratio Conditions

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ABSTRACT: CoMo/Al₂O₃ sour water gas shift catalysts with and without TiO₂ modification have been tested in parallel industrial reactors under lean steam/gas conditions for two years, and part of catalyst samples was taken out each year during the maintenance period. The catalyst samples have been characterized using temperature programmed sulfurization (TPS), X-ray diffraction (XRD), and laser Raman and BET surface area measurements. The results have shown that adding TiO₂ to the catalyst makes the active components, e.g., Mo and Co, easier to be sulfurized with higher sulfur capacity in the catalyst itself. This may be the main reason why the TiO₂ modified CoMo catalyst to be active even at low H₂S gas stream. The results from industrial operation showed that adding TiO₂ to the shift catalyst increases the catalyst activity and stability, presents the higher shift activity in a broader range of H₂S content, depresses the aggregating of the molybdenum oxide, and reduces carbon deposition. In addition, the TiO₂ additive in the catalyst also helps to maintain the physical properties of the shift catalysts. In the freshly prepared catalyst, the active components e.g., MoO₃ is mainly present in the internal surface or sublayer of the catalyst, but it gradually migrates to the catalyst surface with the time on stream. In summary, the CoMo/Al₂O₃ based sour water gas shift catalyst showed stable shift performance under the lean steam/gas conditions, adding TiO₂ to the catalyst significant improves the catalyst activity and resulting into stable operation in the industrial reactor operation in a wide range of H₂S concentrations.

1. INTRODUCTION

Gasification processes have the potential to be more efficient than conventional combustion processes in coal utilization and are also an effective way to convert carbon containing compounds into desirable chemicals. In addition, there are other possible benefits of gasification, e.g., more stable solid waste residues; ability to safely destroy hazardous wastes; lower visual impact; and greater public acceptance.[1−5] However, there have been always impurities left in the gasified products. Of these impurities, H₂S tends to be present at the highest concentration in raw coal-derived syngas, but can vary significantly (1000−13 000 ppmv) depending on the sulfur level in the feed coal.[6−12] This major impurity can have deleterious impacts on the downstream processing of syngas, and it is important to understand its effect on the performance of the conventional water−gas shift catalyst, which has been widely used in natural gas and oil conversion for decades. In this regard, the conventional water−gas shift catalyst based on Fe or Cu are easily deactivated by the H₂S.[13,14]

To overcome the deactivation of the conventional shift catalyst by H₂S, a highly active sulfur-tolerant (referred to as sour water−gas shift catalyst) catalyst has shown advantages, especially when it is used to adjust the syngas composition. To date, most sour water gas shift catalysts have been developed for conventional water coal slurry gasification processes, where the steam to carbon ratio in the gasified products is approximately 2 or greater[5,15−21] However, the latest developments of coal gasification technologies give rise to the gasified products with low steam to carbon ratio, in most cases less than 2, which reduces the number of the recycles needed.[22−24] These new gasification technologies introduce challenges to the sour water−gas shift catalyst to operate in the lean steam to carbon ratio feeding gas.

Recently we have developed a series of CoMo catalysts with various supports for use with lean steam to carbon ratio gases in sour water−gas shift reaction. The catalysts have been used in more than 30 coal to chemical plants with very broad range of steam to carbon ratios and various H₂S contents.[24−27] It is found that modification of the alumina support with TiO₂ can significantly improve the catalyst shift activity and give high activity even with low H₂S content. The catalyst can start up the reaction at much lower temperature than the benchmark catalyst and is resistant to carbon deposition. So far, little research has been done to correlate the catalyst performance with TiO₂ loading and there have been no industrial performance comparison between the catalyst with and without TiO₂.[28−34] In this work, the effect of TiO₂ addition on the sour water gas shift CoMo catalyst has been studied in parallel industrial reactor systems in the same plant, and the TiO₂ promoting mechanism has been explored.

2. EXPERIMENTAL SECTION

2.1. Catalyst Preparation. The industrial catalyst has been prepared using incipient wetness impregnation method, which has been reported in the patents.[32,33] Here it is briefly described as follows. The alumina support (supplied by Zibo Alumina Corporation) was made by calcinating beomite and some binders and pore formation materials at 500 °C for 5 h. For the TiO$_2$ modified support manufacture, the TiO$_2$ powder (industrial grade from Jinan Yuxing Chemical plant) was mixed with the beomite (Zibo Alumina Corporation, China) and the binder (<3 wt %) and 3 wt % ethylene glycol as pore formation materials (as used in the alumina support), then extrudated into trilobe, and calcined at 500 °C for 5 h to get the shaped supports. The TiO$_2$ content in the resultant support is 10 wt %. Before impregnating with the CoMo mixed solution, the supports were first dried to remove the moistures and absorbed impurities. The dried supports were then mixed with a specific amount of solution containing the desired amount of Co(NO$_3$)$_2$ and (NH$_4$)$_6$Mo$_7$O$_{24}$ ammonia solution according to the pickup volume of the supports, dried at 100 °C for 4 h, calcined at 450 °C in static air for 5 h, to obtain a catalyst oxide form containing 3.5 wt % CoO and 8.0 wt % MoO$_3$.

2.2. Industrial Side Stream Test, Catalyst Loading, Sulfurization and Unloading. As the sour shift catalyst is normally supplied in oxide form, it needs activation through sulfurizing. Approximately 2 kg of the catalyst samples were packed in a side-stream of the main reactors and sulfurized using industrial activation conditions. The sulfurizing agent is a mixture of H$_2$/N$_2$ with pumping CS$_2$. The catalyst bed is initially heated in 28 vol % H$_2$/N$_2$ stream at the heating rate of 1 °C/min to 200 °C, then CS$_2$ is pumped into the reactor, the pumping rate of CS$_2$ is controlled by the outlet H$_2$ and H$_2$S exit concentration, which is analyzed every hour. The final sulfurizing temperature is 400 °C which is held for 3 h. The sulfurizing gas is then stopped, and switched to coal gas, whose composition is as follows: CO 44%, CO$_2$ 5%, H$_2$S 0.4−1.2%, H$_2$, 50%; dry gas GHSV: 10 000 h^{-1}; H$_2$O/CO 1.0; catalyst is used as received, trilobe shape, pressure 3.6 MPa.

In the industrial plant, there is normally annual maintenance, which provides an opportunity to withdraw some catalyst sample from the side stream. Because the sulphide is air-sensitive and may catch fire, the catalyst in the side stream was passivated using a small amount of leaked air at 200 °C to convert the sulphide form into oxide form. The catalyst before test was regarded to be fresh, the one withdrawn after 1 year side stream test is marked as 1y, the sample with the 2 year test is marked as 2y. The remarks of the catalyst sample in this study are shown in Table 1. The image of the industrial reactor for the sour water−gas shift catalyst is shown in Figure 1. The industrial catalyst samples were collected from the side stream reactor of the first industrial reactor.
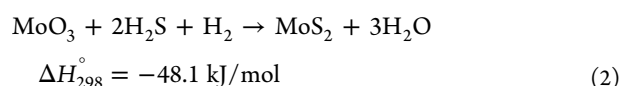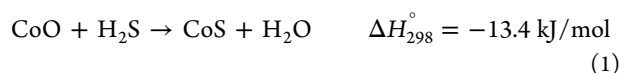
2.3. Catalyst Intrinsic Activity Test. The catalyst samples at various stages were tested in a microreactor system at lab

scale for comparison. The catalyst samples were crushed and sieved into particle size between 0.3 and 0.5 mm, each time 0.3 g catalyst was loaded in a stainless steel reactor and sulfurized at 400 °C using H$_2$S/H$_2$ mixture before testing, then switched to reactants composed of CO 44%, CO$_2$ 5%, H$_2$S 0.5%, and H$_2$ 50%; at GHSV of 10 000 h^{-1}; H$_2$O/CO = 1.0. The exit gas was analyzed using an online GC, and the catalyst activity is calculated according to the following equation:

$$X_{CO}\% = (Y_{CO} - Y'_{CO})/[Y_{CO} \times (1 + Y'_{CO})] \times 100\%$$

In which, Y_{CO} is the volume concentration of CO in the feed gas (dry base) and Y'_{CO} is CO content in the exit gas after the shift catalyst (dry base).

2.4. Temperature Programmed Sulfurization (TPS) Study of the Catalyst. The CoMo catalyst showed high catalytic activity in its sulphide form, the sulfurization process can be expressed by the following reactions:

$$CoO + H_2S \rightarrow CoS + H_2O \qquad \Delta H^{\circ}_{298} = -13.4 \text{ kJ/mol} \tag{1}$$

$$MoO_3 + 2H_2S + H_2 \rightarrow MoS_2 + 3H_2O$$
$$\Delta H^{\circ}_{298} = -48.1 \text{ kJ/mol} \tag{2}$$

In our TPS experiment, the H$_2$S in a gas stream (30 mL/min, 0.7 vol% H$_2$S/H$_2$) before and after flowing through the catalyst bed is monitored. Each time, 0.2 g of 40−60 mesh catalyst sample is load in a quartz reactor and first purged with flowing Ar (99.999%) gas to 200 °C to remove the moisture, then cooled down to room temperature, before switching to the H$_2$S/H$_2$ stream, and held at room temperature for 30 min while monitoring the H$_2$S in the exit gas stream. After 30 min when a constant H$_2$S is shown in the exit gas, the reactor is heated at 10 °C/min to 700 °C.

Low or nondetectable H$_2$S levels in the gas stream after the catalyst suggest the absorption or consumption of the H$_2$S. Higher H$_2$S content in the exit gas stream means desorption of H$_2$S or the yield of H$_2$S from the catalyst. When H$_2$S is consumed, it is expected that reaction 1 or 2 occurs, where H$_2$O is generated, therefore leading to sulfurization of the catalyst.

2.5. Catalyst Characterization. The catalyst samples were measured using X-ray diffraction (XRD) with a Rigaku D/max 2550 diffractometer using Cu Kα radiation (l = 0.1541 nm) over a 2θ range from 10° to 80° at a 0.02 step.

The surface areas of the catalysts were measured using nitrogen adsorption−desorption isotherms at −196 °C with an ASAP 2020 surface area and porosity analyzer. The specific surface areas were calculated using BET equation. The total pore volumes were evaluated from the nitrogen uptake at a relative N$_2$ pressure around 0.99.

The Raman spectra of the catalysts were recorded in an Yvon Jobin Labram spectrometer with a 514 nm HeNe laser running in a backscattered cofocal arrangement. The samples were pressed in a microscope slide with 1 h scanning time in the range of 100−2000 cm^{-1} resolution.

3. RESULTS AND DISCUSSION

The industrial side steam test results of the catalysts are shown in Figure 2. The CoMo/Al$_2$O$_3$−TiO$_2$ has been mostly stable for 2 years, although the CO conversion changes due to the H$_2$S content variations in the feed gas. The CO conversion is mostly above 88% even when H$_2$S is nearly 0. Increasing H$_2$S can increase the catalyst activity, which reaches 92% when H$_2$S

Table 1. Remarks on the Catalyst Samples at Different Stages

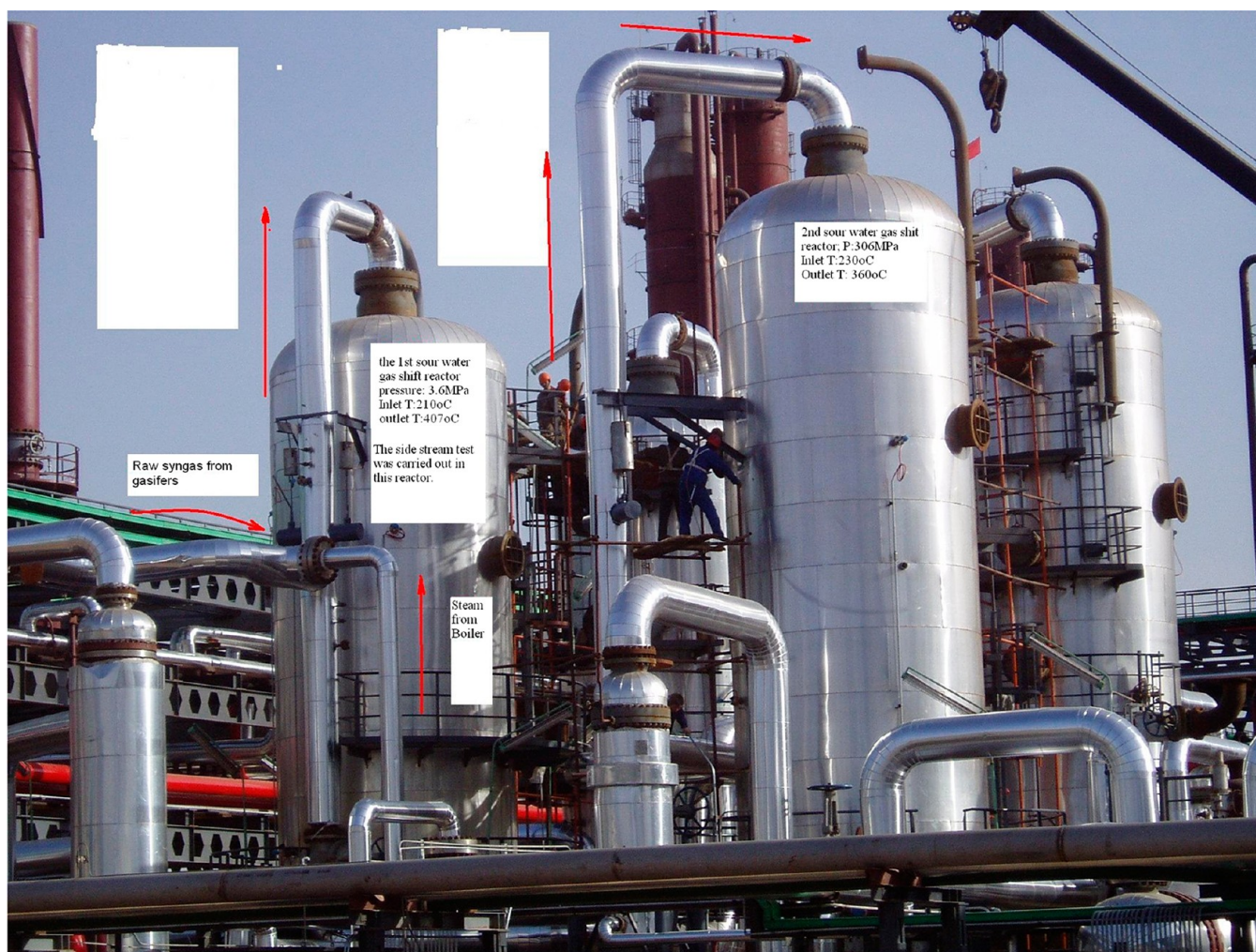|	fresh	1 year industrial test	2 year industrial test
sample with NO TiO$_2$	CoMo/Al$_2$O$_3$	CoMo/Al$_2$O$_3$-1Y	CoMo/Al$_2$O$_3$-2Y
with TiO$_2$ modification	CoMo/Al$_2$O$_3$−TiO$_2$	CoMo/Al$_2$O$_3$−TiO$_2$-1Y	CoMo/Al$_2$O$_3$−TiO$_2$-2Y

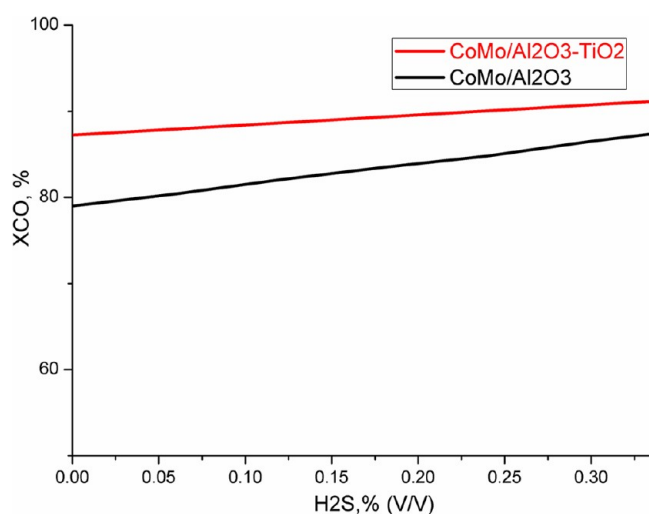**Figure 1.** Industrial operation of the sour water−gas shift catalyst.

Figure 2. Performance of the CoMo shift catalyst during the 2-year industrial application.

content is up to 0.3 vol % in the feed gas; although there have been variations in the CO conversion, the catalyst performance has been stable and CO conversion can meet the industrial requirements. This can be achieved by adjusting the reactor temperatures. .

For the $CoMo/Al_2O_3$, it is shown that CO conversion is significantly lower compared to the $CoMo/Al_2O_3$−TiO_2 when H_2S is lower than 0.06 vol %. However, the catalyst activity increases faster with the rise of H_2S in the feed gas, and even when the H_2S reaches 0.35 vol %, the CO conversion is still lower than that over $CoMo/Al_2O_3$−TiO_2 .Because this catalyst showed lower activity, especially with the low H_2S content in the feed gas, the feed gas has H_2S added when H_2S is lower than 0.3 vol %.

Industrial operation results also showed that for $CoMo/Al_2O_3$ catalyst, CO conversion drops more than 10% when H_2S is below 0.06%. However, for the TiO_2 modified shift catalyst, when the catalyst bed temperature is above 630 °C and $H_2O/$ gas is changes from 1.0 to 1.2, and H_2S varies from 0.01% to 0.3%, in the 2 year operation. In this case, CO conversion is around 90% with very small changes. This is the reason that several companies replace the original $CoMo/Al_2O_3$ with Co−Mo/Al_2O_3−TiO_2.

3.1. Intrinsic Activity Calibration of the Used CoMo/ Al_2O_3 and CoMo/Al_2O_3−TiO_2. In industrial operation, a trace amount of dust may flow with the gas stream onto the catalyst bed, physically covering the catalyst surface. To eliminate the surface impurities effect and particle size effect, the used catalyst samples at different stages have been grounded and sieved to 20−40 meshes, and their intrinsic activities are tested in a microreactor system, the results are given in Table 3.

Table 3. Comparison of the Catalyst Intrinsic Activity at Different Stages

	CO conversion, X_{CO}%		
catalysts	523 K	623 K	723 K
$CoMo/Al_2O_3$	5.7	33.7	61.8
$CoMo/Al_2O_3$-2y	1.3	16.2	47.6
remaining activity (%)	22.3	48.2	77.0
$CoMo/Al_2O_3-TiO_2$	7.8	41.6	67.8
$CoMo/Al_2O_3-TiO_2$-2y	3.3	28.2	56.6
remaining activity (%)	41.8	67.7	83.5

It can be seen that the fresh catalyst always has higher CO conversion than that of the used catalyst at all the tested temperatures. Increasing the temperature improves the catalyst activity. For $CoMo/Al_2O_3$ without TiO_2 modification, the catalyst conversion activity after 2 years at 523 K is 22.28%, but increases to 48.18% and 76.98% when the temperature is increased to 623 and 723 K, respectively. This suggests that the industrial operation may damage the most active catalyst sites, which enables CO shift at low temperatures. However, increasing the temperature enables the active site to recover.

For the $CoMo/Al_2O_3-TiO_2$, the CO conversion over the fresh catalyst at different temperatures are 7.8%, 41.6%, and 67.8%, which are all higher than the catalyst without TiO_2 modification at the same temperature. After 2 years of industrial usage, the remaining activity of this TiO_2 modified catalysts is 41.8%, 67.7%, and 83.5% at 523, 623, and 723 K, respectively. These are all higher than the catalyst without TiO_2 modification. Also the TiO_2 modification increases the catalyst initial activity.

3.2. Physical Property Changes of the Industrial Used Samples. The physical properties of the fresh and the used catalysts are given in Table 4. It is shown that the surface areas

Table 4. Physical Properties of the $CoMo/Al_2O_3$ and $CoMo/Al_2O_3-TiO_2$ Catalyst before and after Industrial Applications

	$CoMo/Al_2O_3$		$CoMo/Al_2O_3-TiO_2$	
	fresh	2 year use	fresh	2 year use
strength, N/cm	168	81	171	116
surface area m^2/g	162.6	47.9	164.1	97.4
pore volume mL/g	0.41	0.21	0.41	0.31
average pore diameter (nm)	84.2	23.1	96.1	56.7
pore distribution <25 nm	77.0	86.2	74.2	78.2
25–50 nm	9.1	6.1	9.2	5.4
50–150 nm	5.2	5.7	7.0	6.8
>150 nm	8.6	2.0	9.7	8.7

of fresh catalysts with and without TiO_2 modification are very close, both around 162 m^2/g, so are the strength and pore volumes, although the pore diameters change from 84.2 to 96.1 nm when TiO_2 is added to the support. After 2 years of industrial application, the surface area of $CoMo/Al_2O_3$ drops to 47.9 m^2/g, while the one with TiO_2 additive only drops to 97.4 m^2/g. This may be the reason for the relative catalyst activity drop. Another important change is the catalyst strength. The TiO_2 modified catalyst pellet has a strength of 116 N/cm while the one without TiO_2 has strength of 47.9 N/cm. This is because the TiO_2 modifier helps to resist the hydration of the alumina support, which enables it to maintain the pellet

strength and catalyst surface area, as pointed out in the literature.[35]

3.3. Characterization of the Industrial Catalysts. The bulk crystalline phases and the surface properties of catalyst samples at different stages have been characterized using XRD and laser Raman spectroscopy. Figure 3 shows the laser Raman
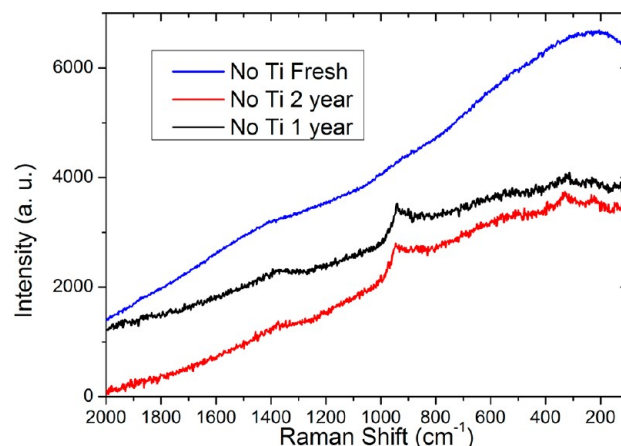
Figure 3. Laser Raman of $CoMo/Al_2O_3$ at different stages.

spectra of the $CoMo/Al_2O_3$ catalysts at various stages. With the fresh catalyst, no Raman scattering peaks are seen, although there are more than 8 wt % of MoO_3 supported over the alumina support, suggesting that the catalyst surface be mainly covered with Al_2O_3, which is not Raman sensitive. When the catalysts is used for one year, a Raman band at about 928 cm^{-1} is seen, which is characteristic of the stretching vibration of $Mo=O$ bond,[36] and a weak broad band at 1380 cm^{-1} in the sample, which is assigned to the D band of carbon deposit over the catalyst.[37] This suggests that the active component, e.g., MoO_3 may migrate to the catalyst surface or the surface alumina may be hydrated and leached away during the reaction, which leaves the active components in the internal surface exposed to the external surface, and therefore detected by Raman surface scattering technology. When the catalyst has been used for 2 years in the industrial side stream reactor, the Raman bands at 928 and 1380 cm^{-1} become more intense, suggesting that the longer industrial applications of the catalysts leads to more surface Al_2O_3 leached away and more carbon deposition. This can explain the catalyst strength deterioration for the Al_2O_3 supported catalysts.

Figure 4 gives the Raman spectra in the ranges from 100 to 1000 cm^{-1} of the $CoMo/Al_2O_3-TiO_2$ at different stages. The Raman modes are typical Raman resonances of anatase crystalline ~145.7 (Eg), 198 (Eg), 395.4 (B1g), 515.2 (A1g), and 639 cm^{-1} (Eg).[38,39] With the catalyst used for 1 and 2 years, no shift of the Raman bands were observed, while the band intensities grow slightly, suggesting more TiO_2 exposes the catalyst surface which may be due to the leaching of the Al_2O_3 by the hydration of the steam. In the range of 700–2000 cm^{-1}, of the Raman band of the $CoMo/Al_2O_3-TiO_2$, the signal is much weaker compared to these of TiO_2, it is therefore separately drawn and shown in Figure 5. There is a very weak Raman band of MoO_3, in the 1-year used sample, which is not seen in the fresh sample, but with increasing slightly in the 2-year used sample. This is in agreement with the physical properties of the sample. The TiO_2 catalyst has few changes in the surface area and strength, which is tentatively assigned to
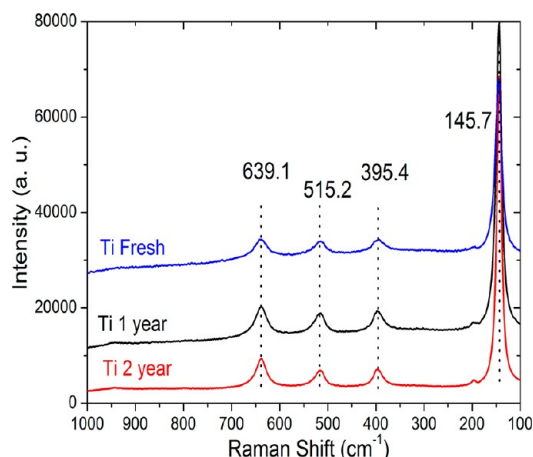
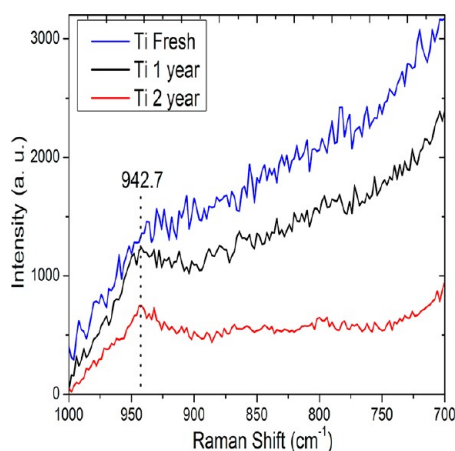**Figure 4.** Laser Raman spectrum of the TiO_2 containing supported CoMo catalysts.

Figure 6. XRD patterns of the $CoMoO_x/Al_2O_3$ catalysts at different stages.

Figure 5. Laser Raman spectra of the TiO_2 containing supported CoMo catalysts in the range of 700−1000 cm^{-1}.
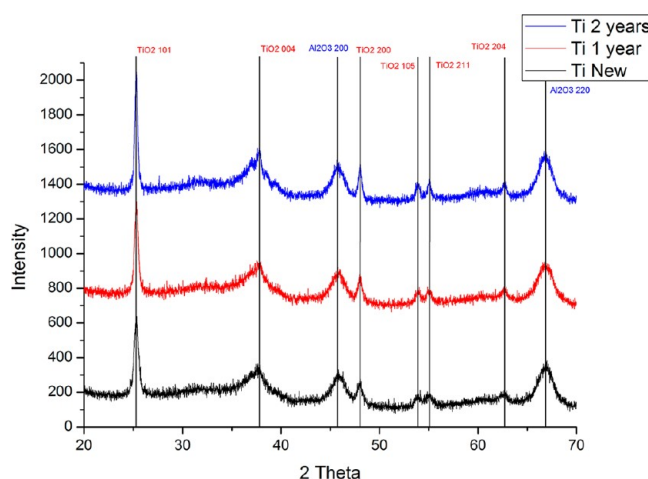
Figure 7. XRD patterns of the TiO_2 containing supported CoMo WGS catalysts.

the less surface leaching of Al_2O_3 and lower hydration activity of TiO_2. In terms of carbon deposition, the Raman peak at 1380 cm^{-1} is too weak to be seen over it, suggesting less carbon deposition over the TiO_2 modified catalysts.

The XRD patterns of the $CoMo/Al_2O_3$ catalysts are shown in Figure 6. In the fresh catalyst, no crystalline MoO_3 or Co oxides have been detected, suggesting a very high dispersion of the active components.[12,40] The diffraction peaks of the fresh sample are due to the alumina support. When the catalyst is used for 1 year, the active components are still not detected, suggesting they are not aggregated during the industrial usage, but there is a very weak peaks shown at 29.01°, which is tentatively assigned to the [220] plane of Co_2AlO_4, where Co is in Co^{2+} and Co^{3+} form, as suggested by the blue color of the samples. The intensity of the diffraction peak of Co_2AlO_4 increases slightly with the catalyst test extended to 2 years, where it is shown that the catalyst intrinsic activity drops (shown in Table 3), it is therefore inferred that the formation of Co_2AlO_4 may be responsible for the catalyst activity drops, which is generally present in the industrial catalyst used for 2 years

The XRD patterns of the $CoMo/Al_2O_3−TiO_2$ catalysts at different stages are shown in Figure 7. There have been sharp diffraction peaks of anatase TiO_2 and broad Al_2O_3 peaks. Small or nondetectable Co_2AlO_4 have been detected in the fresh
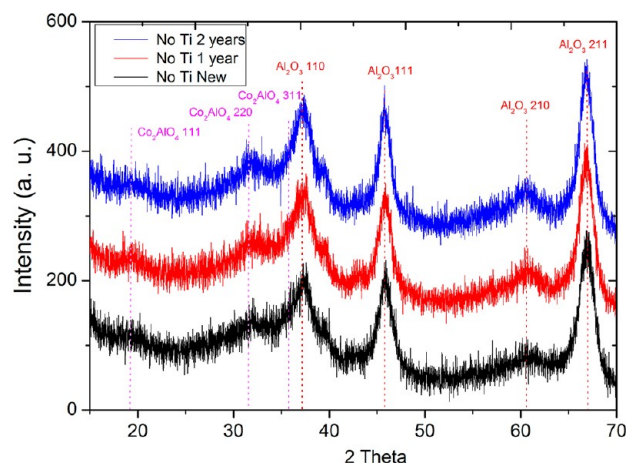
catalyst and also the industrially used catalyst, suggesting that the activity decrease of the TiO_2 modified catalysts may not be due to the formation of inert phase of Co_2AlO_4. It can be seen from Figure 7 that the TiO_2 diffraction peaks become sharper in the used samples, which suggests that the TiO_2 crystallite may grow larger in the catalyst during the application, however, basically no significant changes occur to the crystalline structure of the TiO_2 modified catalysts, which may be the reason for the higher remaining activity of the TiO_2 modified catalyst system.

3.4. TPS Study of the TiO_2 Promoting Effect on the CoMo/Al$_2$O$_3$ Catalysts. *TPS Profiles of Co−Mo/Al$_2$O$_3$ and Co−Mo/Al$_2$O$_3$−TiO$_2$.* Figure 8 showed the TPS profiles of the fresh CoMo based shift catalyst with and without TiO_2 modification. The first 60 min is the changes of the H_2S in the flowing gas stream over the two catalysts system. Less H_2S is detected in the TiO_2 modified catalysts during the absorption period, suggesting that TiO_2 modified catalyst has higher H_2S sorption capacity. When the exit H_2S content reaches the level as the inlet gas stream, the temperature is then increased, there are H_2S desorption peaks at about 328 K, which may be due to the physisorption of H_2S over the support. The desorption peak of H_2S over the $CoMo/Al_2O_3$ fresh catalyst is higher than that on fresh $CoMo/Al_2O_3−TiO_2$ catalyst, suggesting that less H_2S is emitted from the TiO_2 modified catalyst. When the
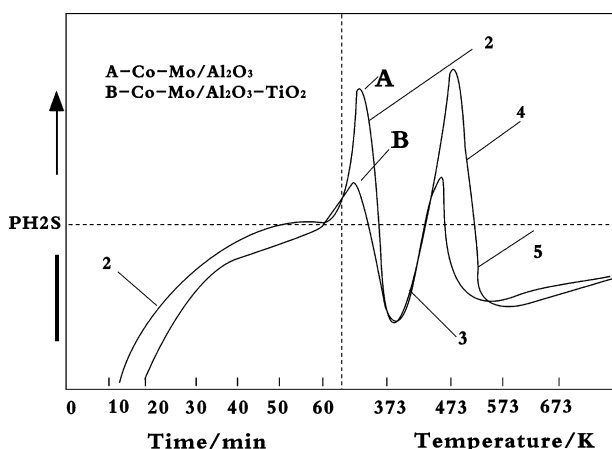
Figure 8. TPS profiles of the fresh $CoMo/Al_2O_3$ shift catalyst with and without TiO_2 modification.

temperature is further increased, peak 3 is observed, which is due the sulfurization of the active components. The catalysts with or without TiO_2 have almost the same sulfurization peak intensity. When the sulfurization temperature further rises, another H_2S desorption peaks appeared (peak 4) followed by sulfurization (peak 5, less H_2S is detected in the sulfurization stream). The TiO_2 modified catalyst has lower sulfurization peak intensity, suggesting that the Co and Mo oxides are easier to be sulfurized. The TPS profiles of the fresh catalysts showed that the TiO_2 modification gave higher H_2S sorption capacity and makes the Co and Mo oxide easier to sulfurize.

The industrially used CoMo catalyst with and without TiO_2 are also studied using TPS; the results are shown in Figure 9.
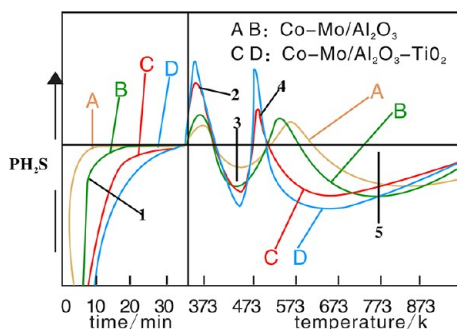

Figure 9. TPS profiles of the industrially used catalysts: (A) CoMo/Al_2O_3-2y; (B) CoMo/Al_2O_3-1Y; (C) CoMo/Al_2O_3–TiO_2-2y; (D) CoMo/Al_2O_3–TiO_2-1y.

Curves A and B are the TPS profiles of CoMo/Al_2O_3-1y and CoMo/Al_2O_3-2y. It is shown that longer industrial running time decreases the H_2S sorption capacity; the H_2S sorption reaches the saturated capacity in only 30 min, nearly half of the fresh catalysts. The TiO_2 modified catalyst has higher H_2S capacity than the one without TiO_2, but the H_2S capacity also drops after 1 and 2 year use. Generally the longer running time of the catalyst has lower H_2S capacity which also has less remaining activity. These results suggest that the H_2S capacity may be related to the catalyst activity. However, the temperature of the sulfurization peak in the CoMo/Al_2O_3 significantly increases, suggesting that the industrial use makes the active components more difficult to sulfurize. While in the TiO_2 modified catalyst system, the sulfurization

peaks corresponds to lower temperatures (peaks 3 and 5 in Figure 9), suggesting that the TiO_2 can ease the Co and Mo oxide interaction with the support, leading to less loss of the active component, which is in agreement with the XRD results.

4. CONCLUSION

CoMo/Al_2O_3 and CoMo/Al_2O_3–TiO_2 catalyst have been prepared and tested for sour water gas shift for use in coal gas conversion. Both Co and Mo oxide are highly dispersed over the supports, and in the internal surface of the catalyst pellets.

The modification of the catalyst with TiO_2 makes the active components easy to sulfurize and have higher H_2S capacity. The TiO_2 promoting effect may be due to its higher resistance to the hydration than Al_2O_3.

The TiO_2-promoted catalyst has higher shift activity, stable performance, and fewer changes in physical properties after 2 years of industrial operation.

There is aggregation of MoO_3 and carbon deposition over the shift reaction during the industrial operation, and the presence of TiO_2 in the catalyst support can reduce carbon deposition and stabilize the Mo active phase.

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Notes

The authors declare no competing financial interest.

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