Deactivation mechanism of the simultaneous removal of carbonyl sulphide and carbon disulphide over Fe–Cu–Ni/MCSAC catalysts

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Abstract. The deactivation mechanism of the simultaneous removal of COS and CS₂ over a Fe–Cu–Ni/MCSAC catalyst was investigated using SEM/EDS, XPS and *in situ* DRIFTS methods. The results show that the catalytic hydrolysis of COS and CS₂ over the Fe–Cu–Ni/MCSAC catalyst involves two steps: hydrolysis of COS/CS₂ and oxidation of H₂S. The SEM/EDS and XPS results indicate that that catalytic hydrolysis of CS₂ can be achieved by the actions of alkaline groups and active components. When O₂ was introduced into the system, oxidation of H₂S occurred *via* $\text{H}_2\text{S} \rightarrow \text{S} \rightarrow \text{SO}_4^{2-}$ /sulphate. *In situ* DRIFTS experiments indicated that the formation of sulphate may occur as follows: (a) $\text{H}_2\text{S} + \text{O}_2 \rightarrow \text{S} + \text{H}_2\text{O}$, (b) $\text{S} + \text{O}_2 \rightarrow \text{S-O}$, (c) $-\text{COO} + \text{H}_2\text{S} \rightarrow -\text{CH} + \text{S-O}$, (d) $\text{C-OH} + \text{H}_2\text{S} \rightarrow -\text{CH} + \text{S-O}$. The *in situ* DRIFTS experiments also indicated that the C–OH groups, –COO groups and O₂ played important roles in the deactivation of the catalyst, which was consistent with the XPS results. Meanwhile, the SO_4^{2-} /sulphate content increased during the reaction, which led to its occupancy of the catalyst's surface activity sites. Additionally, the alkaline groups and active components were removed, which could also result in the deactivation of the catalysts.

Keywords. Deactivation mechanism; simultaneous catalytic hydrolysis of CS₂ and COS; Fe–Cu–Ni/MCSAC catalyst; closed carbide furnace tail gas.

1. Introduction

As the by-products in the industrial production, such as closed carbide furnace tail gas, carbonyl sulphide (COS) and carbon disulphide (CS₂) corrode pipeline equipment and influence the purity of the raw material gas.^{1–3} During various industrial productions, the presence of COS and CS₂ negatively affects the performance of catalysts, reducing their activity and lifespan.^{4–6} To address this issue, catalytic hydrolysis has been shown to provide lower levels of by-products under mild reaction conditions and has thus become the most commonly used method to remove COS and CS₂ from industrial processes.^{7–11} With the advantages of being cost-effective and having good adsorption, activated carbons have become a promising type of catalyst carrier.^{12–14} Several previous studies from our group

have examined the hydrolysis of COS and CS₂ over modified activated carbon catalysts.^{2,15–18} For example, we have shown that Fe–Cu–Ni/MCSAC (i.e., microwave coconut shell activated carbons supported Fe₂O₃, CuO and NiO) has a high catalytic hydrolysis activity and 100% COS conversion and 100% CS₂ conversion for approximately 540 min and 600 min, respectively (reaction conditions: 400 ppm COS; 10 ppm CS₂; GHSV = 10000 h^{–1}).¹⁷ However, its catalytic ability gradually decreased over the reaction time. Although the deactivation was attributed to the deposition of sulphur (S) on the catalyst's surface, the hydrolysis reaction and deactivation mechanisms remained unclear.¹⁷ Accordingly, these unresolved issues require further attention to improve the performance of the catalyst and its industrial application in the hydrolysis reaction.

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Recently, many reports have detailed the hydrolysis reaction mechanism of COS and CS₂. However, the results have varied for different catalysts and reaction paths. For instance, Guo *et al.*, reported the COS hydrolysis mechanism without the use of a catalyst.¹⁹ The results indicated that OH and H in H₂O first attack the C=O and C=S bonds in COS. In addition, Yi *et al.*, reported that the hydroxyl groups and oxygen free radicals on the catalyst's surface could enhance the catalytic performance for CS₂.²⁰ Li *et al.*, also investigated the COS hydrolysis mechanism. The results indicated that the nucleophilic additions of water across the C=O or C=S bonds of COS were competitive.²¹ Further, Wang *et al.*, investigated the reactivation of the catalyst for COS hydrolysis. The results demonstrated that the main source of the catalyst's strong basicity was the presence of alkaline ions.²² A study from the 1870s on the hydrolysis of COS using a Co-Mo catalyst indicated that the catalyst's surface was partially covered by -OH and H₂O and that COS was adsorbed on the catalyst's surface resulting in ion-dipole interactions. Moreover, the reaction centre was alkaline and played a key role in the COS hydrolysis reaction.²³ Akimoto *et al.*, reported that the catalyst would inactivate rapidly if strongly alkaline organic species were introduced to the reaction system. The results also indicated that COS would first become adsorbed at the active sites of the catalyst's surface and would then react with the adsorbed H₂O.²⁴ Guanju Shang *et al.*, demonstrated that the type of alkaline centre, alkaline strength and the number of alkaline functional groups all influence COS hydrolysis.²⁵ In recent years, Hoggen *et al.*, analysed the hydrolysis reaction of COS on the surface of γ -Al₂O₃ using FTIR analysis and quantum chemical calculations and obtained similar results.²⁶ Wilson *et al.*, studied the potential energy of the system surface and found that the rotatable -OH moieties provided hydrogen atoms for the close-in sulphur atom to generate hydrolysate (CO₂ and H₂S).²⁷ Hanaoka *et al.*, studied the reaction mechanism of COS removal over activated carbon. The results showed that the activated carbon could eliminate COS and that some COS could be converted into CO₂.²⁸ Additionally, the mechanism of CS₂ hydrolysis is identical to that of COS, and COS is an intermediate the hydrolysis of CS₂. Xiaofeng Guo *et al.*, studied the adsorption process of CS₂ on an Al₂O₃ catalyst with two possible outcomes: CS₂ reacted directly with the adsorbed water on the surface of the catalyst, and CS₂ generated the intermediate COS initially and then the COS reacted with H₂O. Therefore, the hydrolysis mechanism of CS₂ may be summarized as CS₂ → COS → H₂S → S/SO₄²⁻.²⁹

However, little research has focused on the deactivation mechanism of the simultaneous removal of COS and CS₂. Our group has prepared a good catalyst (Fe-Cu-Ni/MCSAC) to simultaneously remove COS and CS₂; however, the corresponding deactivation mechanism remains unknown. Determining the detailed steps of the deactivation mechanism is necessary because they can provide a theoretical foundation for the future application and development of the "simultaneous removal of COS and CS₂ over Fe-Cu-Ni/MCSAC" field. Therefore, this work characterizes the Fe-Cu-Ni/MCSAC catalyst of deactivated samples under different conditions using SEM/EDS, XPS, *in situ* DRIFTS methods to investigate the deactivation mechanism of the simultaneous removal of COS and CS₂.

2. Experimental

2.1 Material preparation

Microwave coconut shell activated carbon (MCSAC) was from the Faculty of Materials and Metallurgical Engineering, Kunming University of Science and Technology. The main preparation parameters: activation temperatures were 850–900 °C, microwave processing time was 40 min and water vapour activation flow was 5 g/min. First, the MCSAC was crushed and sieved to a 40–60 mesh size and washed 5–7 times with tap water and then 5–7 times with distilled water to remove the suspended substances. The MSCAC was dried at 100 °C for 3–5 h in a drying box and was then boiled in a 1 mol/L KOH solution for 2 h. Subsequently, the MSCAC was washed with distilled water to a constant pH and then dried at 100 °C for 3–5 h in a drying box.

The Fe-Cu-Ni/MCSAC catalyst was then prepared by the sol-gel method, which was similar to our previous reports.^{15–17} The MCSAC was impregnated in a colloid solution that contained Fe(NO₃)₃, Cu(NO₃)₂, Ni(NO₃)₂ and Na₂CO₃ in a n(Fe):n(Cu):n(Ni) molar fraction of 10:2:0.5. The sample was then ultrasonicated for 30 min and dried at 120 °C for 3–4 h in a drying box. The sample was calcined at 300 °C for 3 h under atmospheric conditions (82.4 kPa) and then impregnated in a 13% (mass fraction) KOH solution under ultrasonic conditions for 30 min and dried at 120 °C for 3–4 h in a drying box. The catalyst obtained after these procedures is designated as Fe-Cu-Ni/MCSAC.

2.2 Material characterization

A QUANTA200 scanning electron microscope was used in this work, which can observe the morphology changes of the catalysts. Beryllium (Be) was the metal probe, and the samples were pretreated by vacuum and gold plating methods. Energy dispersive X-ray spectrometry (EDS) was used to determine the chemical composition of the catalysts. An ESCALAB 250 X-ray photoelectron spectrometer

from Thermo Fisher Scientific was used in this work. The resolution ratio is 0.45 eV (Ag), 0.82 eV (PET), and the sensitivity is 180 kcps (200 μm , 0.5 eV) with an image resolution of 3 μm . In-situ DRIFTS were recorded on a Nicolet iS50 FTIR spectrometer equipped with a Smart Collector. Mass flow controllers and a sample temperature controller were used to simulate the reaction conditions. The IR spectra were recorded by accumulating 100 scans at a resolution of 4 cm^{-1} .

2.3 Test of catalytic activity

The desulfurization tests were performed in a fixed-bed quartz reactor under atmospheric pressure. CS_2 and COS from a gas cylinder (0.3% CS_2 in N_2 ; 1% COS in N_2 ; (O_2 : 99.999%, when used)) were diluted with N_2 (99.99%) to the required concentration (i.e., CS_2 : 30 mg/m^3 ; COS: 980 mg/m^3 ; O_2 content: 0–10.2%). The overall gas hourly space velocity (GHSV) was 18000 h^{-1} . The water came from a saturator system in which the water temperature was 0.3–35 $^\circ\text{C}$ and the corresponding relative humidity (RH) was 17–96%. The reaction temperature of the reactor was 30–70 $^\circ\text{C}$. The CS_2 and COS concentrations in the mixture gas feed and effluent from this reactor were analysed using an HC-6 sulphur phosphorus microscale analyser. Figure S1 (in Supplementary Information) shows a schematic diagram of the apparatus for the catalytic activity measurements. The CS_2 and COS removal rates were determined by calculating the inlet and outlet CS_2 and COS concentrations:

$$\begin{aligned} & \text{CS}_2 (\text{COS}) \text{ removal rate (\%)} \\ &= \frac{\text{CS}_2 (\text{COS})_{\text{in}} - \text{CS}_2 (\text{COS})_{\text{out}}}{\text{CS}_2 (\text{COS})_{\text{in}}} \times 100 \end{aligned}$$

When the CS_2 and COS conversions were below 90%, the catalysts were regarded as being deactivated. The sulphur capacity was defined as the quantity of sulphur per unit mass of a catalyst (terminating at 90% CS_2 conversion and 90% COS conversion).

3. Results and Discussion

3.1 SEM/EDS analysis

The changes of the surface morphologies and elemental compositions can be observed by SEM/EDS. SEM images (20000 $\times$ and 5000 $\times$) of fresh and deactivated catalysts are presented in Figure 1 and the EDS results are presented in Table 1.

As seen, there were some metal oxides distributed on the surface. Most of the pores on the deactivated catalyst surface are blocked and there are relatively few pores on its surface (Figure 1c and Figure 1d). Meanwhile, there were more luminous white substances on the deactivated catalyst than on the fresh catalyst. Further, agglomeration was evident on the deactivated catalyst, suggesting a large amount of metal salt compounds on its surface,

which blocked most of the pores, leading to deactivation.

EDS analyses of these catalysts were performed to illustrate the composition changes on the deactivated catalyst surface (Table 1). The mass fraction changes of Na, Fe, Cu and Ni were not obvious for the fresh and deactivated catalysts. However, the S content on the deactivated catalyst increased from 1.20% to 12.88%, which can be attributed to the generation of elemental S or sulphate. These products can block the catalyst's pores and lead to a decrease of its specific area and lead to its deactivation. In contrast, the C content on the catalyst's surface decreased from 54.51% to 39.42%, which can be attributed to the sulphate on the deactivated catalyst surface. In summary, the EDS analysis indicates that deactivation may occur because of the presence of sulphate on the catalyst's surface.

3.2 XPS analysis

3.2a XPS analysis of fresh and deactivated catalysts:

The elemental contents of the fresh and deactivated catalysts are shown in Table 1, and the XPS data of the catalysts are given in Figure 2 and Table 2.

The C, Fe, Cu, and Ni contents of the deactivated catalyst decreased compared with the fresh catalyst. The reason may be that metal oxides could be converted into some other metal sulphates or sulphites, and metal sulphates or sulphites could cover the catalyst's surface. The S content on the deactivated catalyst increased to 3.10%, which we attribute to the formation of various sulphate substances.

As seen in Table 2, the $\text{Fe}_2(\text{SO}_4)_3$ content on the surface of deactivated catalyst increased, while the Fe_2O_3 content decreased from 1.04% to 0.79%. The interactions between H_2S , O_2 , H_2O and Fe_2O_3 led to the decreasing and conversion of Fe_2O_3 .

Compared with the deactivated catalyst, the S content of the fresh catalyst was not detected. The S chemical states on the deactivated catalyst varied. First, elemental S (163.95 eV) was only found on the deactivated catalyst, which was generated from the oxidation of H_2S in the presence of O_2 . Second, the peak at 168.83 eV on the deactivated catalyst was obvious, which was attribute to $\text{Fe}_2(\text{SO}_4)_3$ /sulphate. This peak indicates that H_2S can be oxidized to $\text{Fe}_2(\text{SO}_4)_3$ /sulphate.

3.2b XPS analysis of deactivated catalysts at different O_2 contents:

The above analysis of fresh and deactivated catalysts indicates that the deactivated catalysts surface is covered by S and sulphate species. Clearly, oxidation plays a critical role in the process, and changing the O_2 content may lead to differences in the type

Figure 1. SEM images of fresh Fe–Cu–Ni/MCSAC (a: 20000×; b: 5000×) and deactivated Fe–Cu–Ni/MCSAC (c: 20000×; d: 5000×). (a) 20000× (b) 5000× (c) 20000× (d) 5000×.

Table 1. EDS and XPS results of fresh and deactivated catalysts.

Element	Element content (mass fraction)/% in EDS results		Element	Element content (atom fraction)/% in XPS results	
	Fresh catalyst	Deactivated catalyst		Fresh catalyst	Deactivated catalyst
C	54.51	39.42	C	75.84	74.18
O	12.80	14.86	O	20.69	20.32
Na	3.47	3.77	Fe	1.04	0.79
S	1.20	12.88	S	0.00	3.10
K	11.73	12.02	Cu	0.34	0.26
Fe	12.59	12.88	Ni	0.15	0.14
Ni	1.10	1.54	N	1.54	1.21
Cu	2.60	2.63			

of products generated. Figure S2 (in Supplementary Information) shows the effect of the O_2 content on the simultaneous catalytic hydrolysis of COS and CS_2 . As shown in Figure S2a, the conversion efficiency of COS decreased as the O_2 content increased. Figure S2b shows

that the conversion efficiency of CS_2 initially increased but then decreased as the O_2 content increased. Further, the sulphur capacity was highest (57.33 mgS/g) when the O_2 content was 0% (Figure S2c). The sulphate capacity decreased with an increase in O_2 , and the sulphate

Figure 2. XPS characterization of the fresh catalyst and deactivated catalysts (Fe2p, S2p).

Table 2. XPS data of the fresh and deactivated catalysts (Fe2p, S2p).

Catalyst	Elements	Binding Energy (eV)	At. %	Chemical Speciation
Fresh catalyst	Fe2p	711.42	1.04	Fe ₂ O ₃
	S2p	—	—	—
Deactivated catalyst	Fe2p	711.46	0.79	Fe ₂ O ₃
	S2p	163.95	0.73	S
	S2p	168.83	2.37	Fe ₂ (SO ₄) ₃ /Sulphate

capacity remained above 45 mgS/g when the O₂ content was 3.6%, which indicates that the catalyst can function in an environment with a small amount of O₂.

XPS analyses of the deactivated catalysts at 2.2% and 10.2% O₂ content are presented in Figure 3 and Table 3.

There is a clear difference in the XPS data of Fe2p between the deactivated catalysts at 2.2% and 10.2% O₂ contents. The Fe₂O₃ content on the catalyst at an O₂ content of 10.2% decreased from 0.79% to 0.63% compared with the sample at an O₂ content of 2.2%, which indicates that most of the Fe₂O₃ participated in the oxidation of H₂S, especially at high O₂ content.

Compared with the elemental S content on the catalyst at 2.2% O₂ content (0.29%), the elemental S content on the catalyst at 10.2% O₂ content was low (0.08%). Clearly, a high O₂ content leads to the oxidation of elemental S to sulphate. We assign the peak at approximately 169.64 eV to Fe₂(SO₄)₃/sulphate. It is clear that the Fe₂(SO₄)₃/sulphate content on the catalyst at an O₂ content of 10.2% is higher than it is on the catalyst at an O₂ content of 2.2%. On one hand, the high O₂ content promotes the oxidation of H₂S; on the other hand,

elemental S derived from the oxidation of H₂S can be converted into sulphate more quickly under a high O₂ content. Thus, the increase of H₂S oxidation and fast generation of Fe₂(SO₄)₃/sulphate occurs, which is consistent with previous conclusions. FeS and CuS may be formed during the reaction process, but because of the existing of O₂ and H₂O in the reaction system, FeS and CuS could be turned to the metal sulphates or sulfites. The Fe₂(SO₄)₃/Sulphate could be found from the XPS results. Furthermore, the contents of Cu was so low that it was difficult to find the Cu₂(SO₄)₃/Sulphate. Besides, the stability of metal carbonate is poor, so the metal sulphates or sulfites could be generated more easily than metal carbonate under the condition of sulfate radical existing. Thus, metal carbonate could not be detected from XPS results.

3.2c XPS analysis of deactivated catalysts at different RH: The previous section describes the changes of the surface species on the catalyst as a function of O₂ content. Water is a reactant in catalytic hydrolysis, so relative humidity (RH) is an important factor in this process. Figure S3 (in Supplementary Information) shows

Figure 3. XPS characterization of the deactivated catalysts at 2.2% and 10.2% O₂ contents (Fe2p, S2p).

Table 3. XPS data of the deactivated catalysts at 2.2% and 10.2% O₂ content (Fe2p, S2p).

Catalyst	Elements	Binding Energy (eV)	At. %	Chemical Speciation
Deactivated catalyst (2.2% O ₂)	Fe2p	711.37	0.79	Fe ₂ O ₃
	S2p	164.01	0.29	S
	S2p	169.64	0.96	Fe ₂ (SO ₄) ₃ /Sulphate
Deactivated catalyst (10.2% O ₂)	Fe2p	711.39	0.63	Fe ₂ O ₃
	S2p	164.09	0.08	S
	S2p	169.67	1.26	Fe ₂ (SO ₄) ₃ /Sulphate

the effect of RH on the simultaneous catalytic hydrolysis of COS and CS₂. As seen in Figure S3a and Figure S3b, the conversion efficiency of CS₂ and COS initially increased but then decreased as the RH increased, and the highest catalytic efficiency was achieved when the RH was 32%. Excess H₂O may compete with COS and CS₂ for adsorption sites, which decreased the hydrolysis efficiency.³⁰ Meanwhile, excess H₂O led to the formation of a water film, which may inhibit the diffusion and adsorption of COS and CS₂ on the catalyst's surface.³⁰ As seen in Figure S3c, the sulphur capacity initially increased but then decreased as the RH increased, and it was highest (63.5 mgS/g) when the RH was 32%. Further, the sulphate capacity remained above 60 mgS/g when the RH was 17%–49%, which indicates that the RH range was favourable for catalytic activity.

The XPS results of the deactivated catalysts at 0% and 96% RH are presented in Figure 4 and Table 4.

There is a difference in the XPS data of Fe2p for the catalysts at 0% and 96% RH. The Fe₂O₃ content on the catalysts at 96% RH was low. The reason may be that the water film affected the reaction and Fe₂O₃ was decreased

and converted. More water film was produced on the catalyst's surface when the RH was 96% and inhibited the hydrolysis reaction. It indicates that excessive water film was not conducive to the hydrolysis of COS/CS₂.

Compared with the Fe2p changes, the changes of S2p were complex. We assign the peak at approximately 163.28 and 164.11 eV to elemental S. The S content on the catalyst at 96% RH was low, as elemental S could be more easily oxidized to sulphate at this RH. We assign the peak at approximately 168.67 eV to Fe₂(SO₄)₃/sulphate. Clearly, the Fe₂(SO₄)₃/sulphate content on the catalyst at 96% RH was higher than the other sulphur species. At high RH (96%), H₂O can provide O free radicals, which would promote the oxidation of H₂S and the formation of Fe₂(SO₄)₃/sulphate. These results agree with the changes of S. Therefore, the oxidation products of H₂S were relatively more at high RH (96%).

3.2d XPS analysis of deactivated catalysts at different inlet concentrations: The inlet concentration has a

Figure 4. XPS characterization of the deactivated catalyst at 0% RH and 96% RH (Fe2p, S2p).

Table 4. XPS data of the deactivated catalysts at 0% and 96% RH (Fe2p, S2p).

Catalyst	Elements	Binding Energy (eV)	At. %	Chemical Speciation
Deactivated catalyst (0% RH)	Fe2p	711.32	0.77	Fe ₂ O ₃
	S2p	163.28	0.03	S
		164.11	0.07	S
		168.67	0.92	Fe ₂ (SO ₄) ₃ /Sulphate
Deactivated catalyst (96% RH)	Fe2p	711.41	0.58	Fe ₂ O ₃
	S2p	164.06	0.02	S
		168.98	1.65	Fe ₂ (SO ₄) ₃ /Sulphate

clear effect on the hydrolysis process. Figure S4 (in Supplementary Information) shows the effect of the inlet concentration ratio of COS/CS₂ on the simultaneous catalytic hydrolysis of COS and CS₂. As seen in Figure S4a and Figure S4b, the conversion efficiency of COS and CS₂ decreased as the COS/CS₂ ratio decreased. This result suggests that the CS₂ increase inhibits the catalytic activity of the catalyst when the total concentration of COS and CS₂ is constant. Additionally, Figure S4c shows that the sulphur capacity decreased as the COS/CS₂ decreased. One of the reasons for these results may be that the hydrolysis of CS₂ is the rate-limiting step. Indeed, COS is a type of intermediate product in the hydrolysis of CS₂, and low COS/CS₂ may produce more COS, which decreases the catalytic activity. Further, low COS/CS₂ may produce more H₂S and sulphate, which may block the active sites and decrease the catalytic activity. To examine these issues more fully, XPS analyses of deactivated catalysts at 1:1 and 1:40 CS₂/COS content were performed and are presented in Figure 5 and Table 5.

There are two different peaks between the catalyst at 1:1 and 1:40 CS₂/COS content in the XPS data of O1s. The peak at approximately 531.58 eV belongs to the C=O bond, and its content on the catalyst at 1:1 CS₂/COS content was clearly higher than that at the 1:40 CS₂/COS content. A large number of COS intermediates generated from the hydrolysis at high CS₂ concentration did not fully participate in the hydrolysis reaction. It is possible that the C=O bonds became adsorbed on the catalyst's surface and led to the deactivation of the catalyst. The peak at approximately 533.37 eV belongs to the –COOH bond, and its content on the catalyst at 1:1 CS₂/COS was slightly lower than it was at 1:40 CS₂/COS. We attribute this difference to the lack of H₂O that could react with a high concentration of COS. Thus, more –OH free radicals were generated from the cleavage of the –COOH bond when the CS₂/COS ratio was 1:1.

There was a difference between the catalyst at 1:1 and 1:40 CS₂/COS in the XPS data of Fe2p. The peak at approximately 711.43 eV belongs to Fe₂O₃. Clearly,

Figure 5. XPS characterization of the deactivated catalyst at a 40:1 COS/CS₂ content and a 1:1 COS/CS₂ content (O1s, Fe2p, S2p).

Table 5. XPS data of the deactivated catalysts at 40:1 and 1:1 COS/CS₂ content (Fe2p, S2p).

Catalyst	Elements	Binding Energy (eV)	At. %	Chemical Speciation
Deactivated catalyst (40:1 COS/CS ₂)	O1s	531.58	15.87	C=O bond
		533.37	3.35	-COOH bond
	Fe2p	711.43	0.45	Fe ₂ O ₃
		164.16	0.41	S
	S2p	165.37	0.25	S
Deactivated catalyst (1:1 COS/CS ₂)	O1s	169.19	0.59	Fe ₂ (SO ₄) ₃ /Sulphate
		169.19	0.59	C=O bond
	Fe2p	533.39	1.92	-COOH bond
		711.45	0.79	Fe ₂ O ₃
	S2p	164.22	0.03	S
		169.12	1.26	Fe ₂ (SO ₄) ₃ /Sulphate

its content on the catalyst at 1:1 CS₂/COS was higher than it was at 1:40 CS₂/COS. These results indicate that a high COS content promotes the conversion of Fe₂O₃.

Figure 6. *In situ* DRIFTS experiment over the catalyst (Reaction temperature = 50 °C; RH = 49%; O₂ = 0.5%; GHSV = 20000 h⁻¹; CS₂ = 30 mg/m³; COS = 980 mg/m³).

Compared with the changes of O1s and Fe2p, the changes of S2p were complex, and the types of S2p on the two catalysts are not completely similar. We assign the peak at approximately 164.16 and 165.37 eV to elemental S. Its content on the catalyst at 1:1 CS₂/COS was clearly lower than it was at 1:40 CS₂/COS, which may result from it being oxidized to other intermediate products or sulphate. We assign the peak at approximately 169.19 eV to Fe₂(SO₄)₃/sulphate. The total sulphate content on the catalyst at 1:1 CS₂/COS was higher than it was on the catalyst at 1:40 CS₂/COS. Meanwhile, the Fe₂(SO₄)₃/sulphate species on the catalyst at 1:1 CS₂/COS were more because the metal oxides participated in the reaction and produced different types of sulphates.

3.3 *In situ* DRIFTS results

To better understand the hydrolysis reaction and investigate the hydrolysis reaction mechanism, *in situ* DRIFTS experiments were performed to show the change of the surface functional groups in the hydrolysis reaction of COS and CS₂ over the Fe–Cu–Ni/MCSAC catalyst. As seen in Figure 6, there were a small amount of –C=O groups, –COO groups, –CH groups and C–OH

Figure 7. Deactivation mechanism of the simultaneous removal of CS₂ and COS.

groups on the surface of the catalyst at 0 min (fresh catalyst). The increase of the CO_2 molecule indicated that the hydrolysis reaction occurred. Meanwhile, the amount of $-\text{C}=\text{O}$ groups, $-\text{COO}$ groups, $-\text{CH}$ groups and $\text{C}-\text{OH}$ groups in the reaction were obviously higher than that at 0 min (fresh catalyst). It indicated that these functional groups mainly formed from the reaction process, especially by the interaction of metal oxide with CO_2 and H_2O . The decreasing amounts of H_2O (3495 cm^{-1}), the $\text{C}-\text{OH}$ groups (1040 cm^{-1} , 1065 cm^{-1}) and the $-\text{CH}$ groups (1155 cm^{-1}) indicate that these species were involved in the hydrolysis reaction. The increase of the $\text{S}-\text{O}$ groups (815 cm^{-1}) indicates that sulphate was generated and accumulated on the catalyst. The bond energies of different chemical bonds are shown in Table S1.^{31–34} As seen, the $\text{C}=\text{O}$ bond energy is higher than that of $\text{S}-\text{O}$, and the bond energies of $\text{C}-\text{O}$ and $\text{O}-\text{H}$ are lower than that of $\text{S}-\text{O}$, which indicates that the $\text{S}-\text{O}$ bond may originate from $\text{C}-\text{O}$ and $\text{O}-\text{H}$. The decreasing amounts of $-\text{COO}$ groups (1435 cm^{-1}) supports the above assumption. Meanwhile, the $\text{S}-\text{O}$ groups are also derived from the direct oxidation of H_2S in the environment with 0.5% O_2 . According to these results, the formation of sulphate may be as follows: (a) $\text{H}_2\text{S} + \text{O}_2 \rightarrow \text{S} + \text{H}_2\text{O}$, (b) $\text{S} + \text{O}_2 \rightarrow \text{S}-\text{O}$, (c) $-\text{COO} + \text{H}_2\text{S} \rightarrow -\text{CH} + \text{S}-\text{O}$, (d) $\text{C}-\text{OH} + \text{H}_2\text{S} \rightarrow -\text{CH} + \text{S}-\text{O}$. Combined with the previous XPS results, the formation of sulphate and the decreasing and conversion of Fe_2O_3 are the main reasons for the deactivation of the catalyst.

3.4 Deactivation mechanism

On the basis of this work, the deactivation mechanism of the simultaneous removal of CS_2 and COS is shown in Figure 7. Overall, the process includes two steps: the hydrolysis of CS_2 and COS , and the oxidation of H_2S . Initially, COS , CS_2 and H_2O are adsorbed onto the catalyst's surface. H_2S and CO_2 are then generated by Fe_2O_3 through $\text{C}=\text{S}$ bond cleavage and $\text{S}-\text{H}$ bond formation. The O_2 molecule, the $\text{C}-\text{OH}$ groups, the $-\text{COO}$ groups and Fe_2O_3 promote the oxidation of H_2S . The generation of sulphate occupies the active sites and inhibits the active components of Fe_2O_3 , which decreases the hydrolytic efficiency and leads to the deactivation of the catalyst.

4. Conclusions

In this study, the deactivation mechanism of the simultaneous catalytic hydrolysis of COS and CS_2 over a $\text{Fe}-\text{Cu}-\text{Ni}/\text{MCSAC}$ catalyst was investigated with

SEM/EDS, XPS methods. On the basis of the SEM/EDS and XPS results, the reaction mechanism appears to include two steps: the hydrolysis of COS and CS_2 and the oxidation of H_2S . COS and CS_2 can be catalytically hydrolysed to H_2S , which is an intermediate product of CS_2 hydrolysis, including COS . However, COS can be further hydrolysed to H_2S , which could subsequently be oxidized to sulphate in the presence of O_2 . The catalytic hydrolysis of CS_2 is achieved *via* alkaline groups and active components. When O_2 was introduced into the system, the oxidation of H_2S occurred *via* $\text{H}_2\text{S} \rightarrow \text{S}/\text{RSOR} \rightarrow \text{RSO}_2\text{R} \rightarrow \text{RSO}_2\text{OR} \rightarrow \text{SO}_4^{2-}/\text{sulphate}$. Meanwhile, the contents of $\text{SO}_4^{2-}/\text{sulphate}$ increased during the reaction, and they could occupy the activity sites on the catalyst's surface. Additionally, the alkaline groups and active components were removed, which caused the deactivation of the catalysts. In-situ DRIFTS experiments indicated that the formation of sulphate may occur as follows: (a) $\text{H}_2\text{S} + \text{O}_2 \rightarrow \text{S} + \text{H}_2\text{O}$, (b) $\text{S} + \text{O}_2 \rightarrow \text{S}-\text{O}$, (c) $-\text{COO} + \text{H}_2\text{S} \rightarrow -\text{CH} + \text{S}-\text{O}$, (d) $\text{C}-\text{OH} + \text{H}_2\text{S} \rightarrow -\text{CH} + \text{S}-\text{O}$. The $\text{C}-\text{OH}$ groups, $-\text{COO}$ groups and the O_2 molecule played important roles in the deactivation of the catalyst.

Supplementary Information

Figures S1–S4 are available as Supplementary Information at www.ias.ac.in/chemsci.

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