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Titanium and Copper Oxide Based Catalysts for the *In situ* Reactions of Methanation and Desulfurization in the Removal of Sour Gases from Simulated Natural Gas

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ABSTRACT

The objective of this novel catalyst development is to achieve both low temperature and high conversion of sour gases. Supported mixed metal oxide catalysts were prepared by impregnating the catalysts on alumina beads for the *in-situ* reactions of H₂S desulfurization and CO₂ methanation from room temperature up to 200°C. The results showed that the 100% conversion of H₂S to elemental sulfur for all of the potential catalysts was achieved at 100°C. However, methanation of CO₂ in the presence of H₂S yielded 0.4% CH₄ over Fe/Zn/Cu/Ti-Al₂O₃ catalyst and 0.7% CH₄ over Fe/Zn/Cu-Al₂O₃ catalyst at maximum studied temperature of 200°C. XPS results indicated that spinel compounds of CuFe₂O₄ and Fe₃O₄ act as the active sites on the Fe/Zn/Cu-Al₂O₃ and Fe/Zn/Cu/Ti-Al₂O₃ catalysts. The appearance of Fe³⁺-OH on Fe/Zn/Cu/Ti-Al₂O₃ catalyst increased its H₂S desulfurization activity. N₂ adsorption-desorption analysis illustrated that 34% of the surface area of Fe/Zn/Cu-Al₂O₃ catalyst was reduced while Fe/Zn/Cu/Ti-Al₂O₃ catalyst showed reduction of 17% after catalytic testing, which indicated the deactivation of the catalysts resulted from sulfur poisoning.

| Titanium | copper | methanation | desulfurization | natural gas |

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1. INTRODUCTION

Crude natural gas is categorized as sour gas due to the contamination of carbon dioxide (CO₂) and hydrogen sulfide (H₂S). These corrosive elements may deteriorate the pipeline systems and become a safety hazard and also contribute to the environmental issue. Recently, the removal of these sour gases via chemical conversion techniques becomes the most promising technique. The catalysts for the CO₂ methanation have been extensively studied because of their application in the conversion of CO₂ gas to produce methane, which is the major component in natural gas. However, the presence of H₂S in certain industrial processes is known to cause poisoning of the commercial nickel based catalyst.

The essential requirement for the correct selection of the oxide system is its ability to accept and to activate CO₂ and H₂S. The acid nature of CO₂ and H₂S necessitates the employment of a catalytic system with basic properties. The acid and redox properties of transition metal oxides could be changed by adding other oxides [1]. Investigation done by Wang *et al.* [2] found that the adsorption strength of CO₂ is controlled by the Lewis basicity of a catalyst, d-band center of the metal surface, charge transfer from the metal surfaces to the chemisorbed CO₂. The major reason for the less reactive of mixed metal oxide is its significantly complexity possibly presence of multiple oxidation states, variable local coordination, coexisting bulk and surface phases as well as different surface termination functionalities such as M-OH, M=O or M-O-M [3]. Metal oxides are less active than metals, but they are stable in catalytic conditions.

Kulshreshtha *et al.* [4] have been reported that Fe-Ti-Sn intermetallics are capable of CO methanation and almost completely converted CO to methane at 323 °C. This investigation concluded that the catalytic activity of the intermetallics is significantly improved by Sn substitution. Later, Pineda *et al.* [5] reported when zinc oxide and zinc ferrite catalysts were doped with Cu and Ti, their catalytic performance on H₂S desulfurization process could be increased. The addition of Ti may increase the stability of ZnO towards reducing agent such as H₂. However, the addition of Cu do not affect the stability of catalyst but improve the catalyst performance by changing the surface of the catalyst during calcination and activation process. It has also been found that CO₂ strongly chemisorbs on the Fe (110) surface with the strongest binding energy, whereas CO₂ has moderate strength on the (111) surface of Co, Ni, Rh, Pd with slightly positive binding energies [2].

The selection of support is considered as important since it may influence both the activity and selectivity of the reaction. It has been discovered that the addition of alumina may increase the methanation activity although there is a presence of low concentration of H₂S [6]. Therefore, Al₂O₃ is considered as the support for all the studied catalysts in this research.

Efforts to search for efficient catalyst and to explore new technologies in order to meet the demands of the economical feasibility of *in-situ* reactions of methanation and desulfurization for the purification of natural gas has not been extensively studied. The objective of this novel catalyst development is to achieve both low temperature and high conversion of sour gas. At low temperature, application of the novel catalyst in gas industry is more likely. However, problem arises because exothermic reaction of conversion of CO₂ to CH₄ is unfavorable at low temperature due to its low energy content.

2. EXPERIMENTAL

2.1 Preparation of Catalysts

The catalysts were prepared by wet impregnation method. The respective metal nitrate salt was dissolved with minimum amount of distilled water. Mixed catalysts solution was prepared by mixing appropriate amount of metal nitrate salts according to the atomic ratio. Al₂O₃ supported catalyst was prepared by impregnating the catalyst solution on Al₂O₃ beads support for 15 minutes. It was then dried at 80°C for 24 hours and calcined in air at 400 °C for 5 hours. To prepare Ti⁴⁺ sol for the Ti based catalyst, 6 g of polyethylene glycol (PEG) was dissolved with 600 mL of ethanol. After that, 31.8 g diethanolamine (DEA) followed by 85.2 g titanium (IV) isopropoxide (Ti(ISO)₄) was added when PEG was completely dissolved. 5.4 mL of distilled water was added and stirred for 10 minutes to get a homogeneous solution. Al₂O₃ beads were dipped into the Ti⁴⁺ sol and then dried in the oven at 80 °C for 30 minutes. A mixed metal oxide with Ti sol was prepared by impregnating the resulted Al₂O₃ supported Ti with the respective metal oxide.

2.2 Catalytic Activity Measurements

The supported catalyst sample was packed into a cylindrical glass tube with diameter of 10 mm and length of 360 mm and was stored in the furnace of the home-built micro reactor. No pretreatment was done prior to beginning the heating experiment. Firstly, screening of the catalytic activity on individual reaction of CO₂ and H₂S conversion was performed under 760 Torr pressure. The conversion of CO₂ was screened from room temperature up to 500°C for the conversion of CO₂ and up to 200°C for the conversion of H₂S, with temperature rate of 5°C / min. After that, *in-situ* reactions of CO₂ methanation and H₂S desulfurization were performed from room temperature up to 200°C. CO₂ and H₂ gases were introduced into the reactor system in a stoichiometric ratio of 1: 4. About 2.5 mL/min H₂S gas was introduced into the gas stream. This composition is similar to the content of sour gases in Malaysian natural gas, which is 5 % of H₂S and 20 % of CO₂. Screening on the produced gas stream was done by using FTIR analysis. Percentage conversion of CO₂ and H₂S was obtained by calculating the peak area of their respective stretching band relative to the peak area of the gas during calibration without catalyst. Off line Gas Chromatography analysis was done on the product gas to determine the selectivity and yield of CH₄ gas due to the low sensitivity of FTIR towards stretching band of CH₄.

2.3 Characterization of Catalysts

2.3.1 X-rays Photoelectron Spectroscopy

The potential catalysts were characterized by using Kratos instrument XSAM HS surface analysis spectrometer with Mg K α x-rays source (1253.6 eV). Sample was introduced into the spectrometer in flowing argon atmosphere, and evaporated at least 6 \times 10⁹ Torr before spectrum was recorded. The spectrum was taken at 10 mA and 14 kV energy source at 2 sweeps.

2.3.2 Nitrogen Adsorption Analysis

The N₂ adsorption-desorption isotherms for the catalysts were measured by Micromeritics ASAP 2010. All samples were evacuated at 120°C prior to the measurement. The specific surface area was calculated using the BET method. The total pore volume was determined at a relative pressure of P/ P₀ = 0.99.

3. RESULTS & DISCUSSION

3.1 Catalytic Activity Measurement

3.1.1 Screening of the catalytic activity using FTIR spectroscopy

A series of Fe/Zn/Cu-Al₂O₃ catalyst containing three different ratio was prepared to optimize the copper content towards the catalyst. Table 1 compares the percentage conversion of CO₂ and H₂S catalyzed over Fe/Zn/Cu-Al₂O₃ catalyst with different ratios. According to Table 1, the optimum ratio for Al₂O₃ supported Fe/Zn/Cu-Al₂O₃ catalyst is 4: 16: 80. 100 % conversion of CO₂ was achieved over this catalyst at reaction temperature of 400 °C, whereas 100 % H₂S desulfurization was achieved at 100 °C. Fe/Zn/Cu(10:30:60)-Al₂O₃ and Fe/Zn/Cu (3: 7: 90)-Al₂O₃ catalysts only showed 98.9 % and 89.9 % conversion of CO₂ respectively, at maximum studied temperature of 500°C. It could be seen that high concentration of CuO in the catalyst could increase the amount of surface oxygen on the catalyst surface. Therefore, the percentage conversion of CO₂ over Fe/Zn/Cu (3: 7: 90)-Al₂O₃ catalyst was lowered. Relatively, smaller amount of CuO (Fe/Zn/Cu = 10: 30: 60) on the catalyst could increase the adsorption of H₂S. However, this catalyst is lack of surface oxygen that needed for desulfurization process as suggested in the previous study [7].

Table 1: Temperature for conversion of CO₂ and H₂S over Al₂O₃ supported Fe/ Zn/ Cu catalysts with different ratios using simulated natural gas.

Catalyst	T ₁₀₀ CO ₂ ^a (± 0.5°C)	T ₁₀₀ H ₂ S (± 0.5°C)
Fe/ Zn/ Cu (10:30:60)-Al ₂ O ₃	500 (98.9 %) ^b	120
Fe/ Zn/ Cu (4:16:80)-Al ₂ O ₃	400	100
Fe/ Zn/ Cu (3:7:90)-Al ₂ O ₃	500 (89.9 %) ^b	100

^a Temperature where 100 % conversion was achieved

^b Value in bracket is the % conversion of CO₂ at maximum studied temperature of 500 °C

It has been reported by Pineda *et al.* [5] the presence of Ti may increase the H₂S desulfurization process at lower temperature. Therefore, optimization of titanium content towards Fe/Zn/Cu/Ti-Al₂O₃ catalyst was done. Table 2 shows the comparison of percentage conversion of CO₂ and H₂S over Fe/Zn/Cu/Ti-Al₂O₃ catalyst with different ratios.

Table 2: Temperature for conversion of CO₂ and H₂S over Al₂O₃ supported Fe/ Zn/ Cu/ Ti catalyst with different ratios using simulated natural gas.

Catalyst	T ₁₀₀ CO ₂ ^a (± 0.5°C)	T ₁₀₀ H ₂ S (± 0.5°C)
Fe/ Zn/ Cu/ Ti (10:20:30:40)-Al ₂ O ₃	500 (64.2 %) ^b	100
Fe/ Zn/ Cu/ Ti (5:5:40:50)-Al ₂ O ₃	500 (75.2 %) ^b	100
Fe/ Zn/ Cu/ Ti (5:5:30:60)-Al ₂ O ₃	500 (62.5 %) ^b	100

^a Temperature where 100 % conversion was achieved

^b Value in bracket is the % conversion of CO₂ at maximum studied temperature of 500 °C

From Table 1 and 2, it could be concluded that Fe/Zn/Cu (4: 16: 80)-Al₂O₃ is the most potential catalyst for conversion of CO₂. This showed that copper oxide acts as a better based element for CO₂ conversion catalyst compared to TiO. Basu *et al.* [8] have proven that the addition of TiO at a high concentration may increase the surface oxygen storage. However, this property did not assist the adsorption of CO₂ on the catalyst surface. Besides that, the interaction between Ti and H₂ is weak because H₂ prefer to adsorb on the defect TiO lattice. Thus, prevent the adsorption of H₂ during CO₂ methanation [9]. Table 2 also shows that all the three catalysts achieved 100 % conversion of H₂S at reaction temperature of 100 °C. However, Fe/Zn/Cu/Ti (5: 5: 40: 50)-Al₂O₃ is considered as the most potential catalyst for desulfurization process due to its ability to convert higher percentage of H₂S at light off temperature (TLO = 60 °C) compared to the other catalysts (not showed). Fe/Zn/Cu/Ti(5: 5: 40: 50)-Al₂O₃ gave 96.2 % conversion of H₂S at TLO; Fe/Zn/Cu/Ti(10: 20: 30: 40)-Al₂O₃ catalyst gave

92.5 % while Fe/Zn/Cu/Ti (5: 5: 30: 60)-Al₂O₃ gave 87.3 % conversion of H₂S at TLO. It has been proven that TiO could influence the dissociation of H₂S to H⁺ and HS⁻ at the early stage due to its weak electron interaction in the *d* orbital [10].

3.1.2 In-situ reactions of CO₂ methanation and H₂S desulfurization

In order to elucidate the performance of the catalysts under *in-situ* reactions of CO₂ methanation and desulfurization condition, Al₂O₃ supported Fe/Zn/Cu and Fe/Zn/Cu/Ti catalysts with the optimum ratio were tested using simulated natural gas environment. The selectivity and yield of CH₄ was calculated by incorporating Gas Chromatography data due to the low sensitivity of FTIR towards stretching band of CH₄. Figure 1 shows the percentage conversion of H₂S over Fe/Zn/Cu/Ti(5: 5: 40: 50)-Al₂O₃ catalyst is higher than Fe/Zn/Cu(4: 16: 80)-Al₂O₃ catalyst. The graph shows a decrease on the conversion of H₂S from room temperature to 40°C. This phenomenon was assigned to the adsorption of H₂S by the catalyst. Both catalysts, completely removed H₂S at reaction temperature of 100°C. On the other hand, both catalysts gave a gradual increase for the conversion of CO₂ until maximum reaction temperature of 200 °C. Fe/Zn/Cu (4: 16: 80)-Al₂O₃ catalyst showed a higher conversion of CO₂ compared to Fe/Zn/Cu/Ti (5: 5: 40: 50)-Al₂O₃ catalyst. The catalytic activity of *in-situ* reactions over both catalysts slightly decreased compared to the individual reaction of CO₂ methanation and H₂S desulfurization.

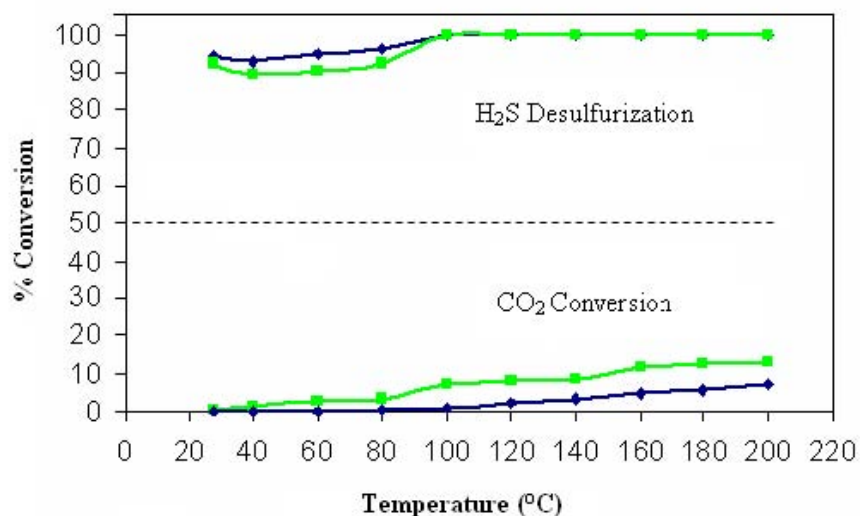


Figure 1: Percentage conversion of CO₂ and H₂S versus reaction temperature under *in-situ* reactions of CO₂ methanation and H₂S desulfurization over (■) Fe/Zn/Cu (4: 16: 80)-Al₂O₃ and (♦) Fe/Zn/Cu/Ti (5: 5: 40: 50)-Al₂O₃ catalysts.

Table 3: Selectivity products of *in-situ* reactions of CO₂ methanation and H₂S desulfurization over the catalysts.

Catalyst	Temperature (°C)	CO ₂ Conversion (%)		Unreacted CO ₂ (%)
		CH ₄	(CO + H ₂ O)	
Fe/ Zn/ Cu (4: 16: 80)-Al ₂ O ₃	100	0.6	5.9	93.5
	200	0.7	11.3	88.0
Fe/ Zn/ Cu/ Ti (5: 5: 40: 50)-Al ₂ O ₃	100	0.0	0.7	99.3
	200	0.4	6.2	93.4

* Calculation based on CO₂ detected *via* FTIR and CH₄ detected *via* GC.

From Table 3, Fe/Zn/Cu(4: 16: 80)-Al₂O₃ catalyst yielded 0.6% and 0.7% of CH₄ at reaction temperature of 100 °C and 200°C respectively. Fe/Zn/Cu/Ti(5: 5: 40: 50)-Al₂O₃ catalyst yielded no CH₄ at 100 °C and only 0.4% of CH₄ at 200 °C. The selectivity of CH₄ over TiO based catalyst is considered very low. From the result, it could be considered that the conversion of CO₂ to CH₄ in this research is incomplete because higher percentage of CO formed rather than CH₄ [11]. This

is due to the indirect conversion of CO₂ into C1 hydrocarbons, via intermediate formation of CO, as suggested by Silver *et al.* [12].

3.2 Characterization of the Catalysts

3.2.1 XPS

The surface active components on the fresh and after testing (spent) catalysts of Fe/Zn/Cu (4: 16: 80)- Al₂O₃ and Fe/Zn/Cu/Ti (5: 5: 40: 50)-Al₂O₃ was accomplished through XPS analysis. All data was corrected by using the binding energy of C 1s at 284.5 eV as standard. XPS analysis only detected the presence of Cu, Fe, Al and O on the surface. Even though the EDX analysis detected the weight percentage of Zn as 0.2 % in the Fe/Zn/Cu (4: 16: 80)-Al₂O₃ and 0.1 % in the Fe/Zn/Cu/Ti(5: 5: 40: 50)-Al₂O₃ catalyst, no peak assigned to Zn was detected from the deconvolution peak of Zn. This may be due to the agglomeration of the other elements, which thus pushed Zn into the lattice structure of the catalyst or poisoning from carbon compound during XPS analysis [13]. In addition, the presence of Ti in the Fe/Zn/Cu/Ti(5: 5: 40: 50)-Al₂O₃ catalyst also could not be detected due to the narrow diameter of Ti compared to Cu and Fe. It is believed that Ti was left inside the lattice structure of the catalyst. The interaction of electron from Ti was weak due to the distance of Ti inside the catalyst structure is comparably farer than those species on the surface.

The binding energy resulted from deconvolution peaks of Cu (2p) from the studied catalysts were tabulated in Table 4. Both fresh catalysts of Fe/Zn/Cu(4: 16: 80)-Al₂O₃ and Fe/Zn/Cu/Ti (5: 5: 40: 50)-Al₂O₃ contained normal spinel compound of CuFe₂O₄. The normal spinel of CuFe₂O₄ on the Fe/Zn/Cu(4: 16: 80)-Al₂O₃ catalyst turned to inverse spinel structure after the catalytic testing, while it remained as normal spinel structure for the spent Fe/Zn/Cu/Ti(5: 5: 40: 50)-Al₂O₃ catalyst. A normal spinel compound is the active site for the catalysts. Fe³⁺ made up the octahedral site while Cu²⁺ made up the tetrahedral site [14, 15]. Analysis showed that Fe/Zn/Cu(4: 16: 80)-Al₂O₃ and Fe/Zn/Cu/Ti (5: 5: 40: 50)-Al₂O₃ catalysts contain spinel compound of CuFe₂O₄ or Fe₃O₄ that are assumed to act as active species on the surface. Fe₃O₄ is considered as the most dominant structure compared to CuFe₂O₄ and it is also the active site for H₂S desulfurization.

Table 4: XPS data of Cu (2p) for Fe/ Zn/ Cu-Al₂O₃ and Fe/ Zn/ Cu/ Ti-Al₂O₃ catalysts.

Catalyst	Weight (%)	Binding Energy (eV) ^a		ΔE_{30} ^b (eV)	Peak Area ^c (2p _{3/2})	Peak Assignment
		2p _{3/2}	2p _{1/2}			
Fe/ Zn/ Cu (4:16:80)-Al ₂ O ₃ (fresh)	1.8	933.7	953.6	19.9	21.6	CuFe ₂ O ₄ (normal spinel)
Fe/ Zn/ Cu (4:16:80)-Al ₂ O ₃ (spent)	4.2	935.1	954.9	19.8	23.9	CuFe ₂ O ₄ (inverse spinel)
Fe/ Zn/ Cu/ Ti (5:5:40:50)-Al ₂ O ₃ (fresh)	3.6	933.6	953.5	19.9	247.6	CuFe ₂ O ₄ (normal spinel)
Fe/ Zn/ Cu/ Ti (5:5:40:50)-Al ₂ O ₃ (spent)	3.7	933.7	953.5	19.9	59.9	CuFe ₂ O ₄ (normal spinel)

^a Binding energy corrected by specific operation charge effect (284.5 eV)

^b ΔE_{30} (difference of 2 spin orbit) = $E_b(2p_{1/2}) - E_b(2p_{3/2})$

^c Peak Area = Peak Intensity x FWHM (Full Width Half Maximum)

Peaks referred to normal spinel compounds of CuFe₂O₄ or Fe₃O₄ appeared at binding energy of 710.1 eV (2p_{3/2}) and 723.7 eV (2p_{1/2}) for Fe/Zn/Cu (4: 16: 80)-Al₂O₃ catalyst, 709.7 eV (2p_{3/2}) and 723.2 eV (2p_{1/2}) for Fe/Zn/Cu/Ti (5: 5: 40: 50)-Al₂O₃ catalyst (Table 5). Peak area of these peaks is high enough, which indicated the formation of surface Fe in a large amount. This also proved that Fe₃O₄ is a more dominant structure compared to CuFe₂O₄. There are another peaks at binding energy of 712.4 eV (2p_{3/2}) and 726.1 eV (2p_{1/2}) for Fe/Zn/Cu/Ti (5: 5: 40: 50)-Al₂O₃ catalyst assigned to the Fe³⁺ bound to hydroxyl group (-OH) and is in agreement with Shah *et al.* [16]. The high binding energy of these peaks is due to the high electronegativity of hydroxyl group. -OH ligand is more electronegative than oxygen. The presence of hydroxyl ligand could increase the oxidation reaction over Fe/Zn/Cu/Ti (5: 5: 40: 50)- Al₂O₃ catalyst due to its high electron density nature. Morrison [13] also proved that TiO₂ in Fe/Zn/Cu/Ti (5: 5: 40: 50)-Al₂O₃ catalyst contributed to the presence of Fe³⁺-OH and thus active site for the H₂S desulfurization. Thus, the adsorption process of H₂S at low temperature that may inhibit H₂S desulfurization could be avoided.

On the other hand, the spent Fe/Zn/Cu (4: 16: 80)-Al₂O₃ catalyst showed the deconvolution peaks of CuFe₂O₄ or Fe₃O₄ at binding energy of 710.1 eV (2p_{3/2}) and 723.7 eV (2p_{1/2}) but with 85.3 % reduction of peak area. This is due to the occurrence of inverse spinel structure that contributed to the presence of larger amount of surface Cu. The spent catalyst of Fe/Zn/Cu/Ti (5: 5: 40: 50)-Al₂O₃ also showed a lower peak area for the deconvolution peaks of CuFe₂O₄ or Fe₃O₄ at 710.5 eV (2p_{3/2}) and 724.1 eV (2p_{1/2}). The formation of CuO obstructed the distribution of Fe on the catalyst surface.

Table 5: XPS data of Fe (2p) for Fe/ Zn/ Cu (4:16:80)-Al₂O₃ and Fe/ Zn/ Cu/ Ti (5:5:40:50)-Al₂O₃ catalysts.

Catalyst	Weight (%)	Binding Energy (eV) ^a		ΔE_{SO} ^b (eV)	Peak Area ^c (2p _{3/2})	Peak Assignment
		2p _{3/2}	2p _{1/2}			
Fe/ Zn/ Cu (4:16:80)-Al ₂ O ₃ (fresh)	3.6	710.1	723.7	13.6	66.7	CuFe ₂ O ₄ / Fe ₃ O ₄
Fe/ Zn/ Cu (4:16:80)-Al ₂ O ₃ (spent)	3.4	710.1	723.7	13.6	9.8	CuFe ₂ O ₄ / Fe ₃ O ₄
Fe/ Zn/ Cu/ Ti (5:5:40:50)-Al ₂ O ₃ (fresh)	3.8	709.7	723.2	13.5	12.5	CuFe ₂ O ₄ / Fe ₃ O ₄
		712.4	726.1	13.7	6.4	Fe ³⁺ -OH
Fe/ Zn/ Cu/ Ti (5:5:40:50)-Al ₂ O ₃ (spent)	2.8	710.5	724.1	13.6	10.0	CuFe ₂ O ₄ / Fe ₃ O ₄

^a Binding energy corrected by specific operation charge effect (284.5 eV)

^b ΔE_{SO} (difference of 2 spin orbit) = $E_b(2p_{1/2}) - E_b(2p_{3/2})$

^c Peak Area = Peak Intensity x FWHM (Full Width Half Maximum)

Table 6: BET surface area and BJH desorption average pore diameter of the fresh supported catalysts and after in-situ reactions testing catalysts

Catalyst	S_{BET} (m ² g ⁻¹)	d (nm)
Fe/ Zn/ Cu (4:16:80)-Al ₂ O ₃ (fresh)	184.8	5.1
Fe/ Zn/ Cu (4:16:80)-Al ₂ O ₃ (spent)	121.6	7.1
Fe/ Zn/ Cu/ Ti (5:5:40:50)-Al ₂ O ₃ (fresh)	259.2	2.6
Fe/ Zn/ Cu/ Ti (5:5:40:50)-Al ₂ O ₃ (spent)	215.6	3.2

Table 7: Elemental composition of Fe/ Zn/ Cu (4: 16: 80)-Al₂O₃ and Fe/ Zn/ Cu/ Ti (5: 5: 40: 50)-Al₂O₃ catalysts analyzed by Energy Dispersive X-rays Analysis.

Catalyst	Condition	Atomic Weight Percentage (%)						
		Ti	Cu	Zn	Fe	S	Al	O
Fe/ Zn/ Cu/ Ti (5: 5: 40: 50)-Al ₂ O ₃	Before testing	4.90	3.88	0.48	0.47	0.00	40.41	49.86
	After testing	4.82	3.80	0.43	0.41	1.43	39.94	49.17
	After regeneration	4.89	3.87	0.46	0.45	0.00	40.22	50.11
Fe/ Zn/ Cu (4: 16: 80)-Al ₂ O ₃	Before testing	0.00	14.83	3.68	0.74	0.00	49.12	31.63
	After testing	0.00	14.75	3.64	0.70	2.32	48.64	29.95
	After regeneration	0.00	14.84	3.65	0.73	0.00	50.06	30.72

3.2.2 Nitrogen Adsorption Analysis

One of the most characteristic properties of the surface of a solid is its ability to adsorb gases and vapours. Table 6 summarized the BET surface area and BJH desorption average pore diameter of the fresh supported catalysts and after in-situ reactions testing catalysts (spent catalysts). The fresh catalysts showed relatively narrow pore size compared to the spent catalysts. It could be seen that Fe/Zn/Cu/Ti (5: 5: 40: 50)-Al₂O₃ catalyst possesses higher surface area and narrower pore size. This was supported by Yamasaki *et al.* [17] that the addition of TiO₂ in the catalyst may increase the surface area

and decrease the particle size. These features improved the H₂S desulfurization activity but not the CO₂ methanation activity. However, the catalytic activity of a particular catalyst not only depends on the BET surface area and pore size, but also included other factors such as type of pores, shape of pores and the degree of porosity [18].

From the BET surface area analysis, the Fe/Zn/Cu(4: 16: 80)-Al₂O₃ catalyst showed reduction of 34 % and Fe/Zn/Cu/Ti(5: 5: 40: 50)-Al₂O₃ catalyst showed reduction of 17 % in surface area. This reduction was possibly due to the sulfur poisoning on the surface during H₂S desulfurization. This was also proven by the Energy Dispersive X-rays Analysis (Table 7). However, the isotherm plot of the fresh and spent catalysts did not show significant difference. All the catalysts showed Type IV isotherm plot and H3 type hysteresis loop resemblance with slit-shaped pores and with non-uniform shape and size.

4. CONCLUSION

The optimum ratio for Al₂O₃ supported CuO based catalyst obtained was Fe/Zn/Cu = 4: 16: 80, while for TiO based catalyst was Fe/Zn/Cu/Ti = 5: 5: 40: 50. Both of the catalysts completely converted H₂S to elemental sulfur at reaction temperature of 100°C. The aim to obtain high H₂S desulfurization rate at low temperature was achieved. The introduction of Fe, Zn, Cu and Ti intended to catalyze the CO₂/H₂ methanation reaction in the presence of H₂S proved ineffective in this case. However, it has been observed that Fe/Zn/Cu (4: 16: 80)-Al₂O₃ catalyst showed a higher conversion and also CH₄ formation compared to Fe/Zn/Cu/Ti(5: 5: 40: 50)-Al₂O₃. The catalytic activities of *in-situ* reactions over both catalysts showed a slightly decrease compared to the individual reaction of CO₂ methanation and H₂S. Therefore, further efforts are needed in the future work in the attempt to obtain catalysts that may increase the conversion rate of CO₂ and H₂S simultaneously.

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