First Row Transition Metal 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 of H2S and CO2 present in the natural gas. The results showed that the conversion of H2S to elemental sulfur on all of the potential catalysts was achieved 100 %. However, methanation of CO2 in the presence of H2S yielded 0.7 % CH4 over Fe/Zn/Cu/Ti-Al2O3 catalyst, 1.1 % CH4 over Fe/Zn/Cu-Al2O3 catalyst and the highest is 6.1 % CH4 over Pr/Co/Ni-Al2O3 catalyst at maximum studied temperature of 300 °C. The catalysts were further characterized by X-rays Photoelectron Spectroscopy and Nitrogen Adsorption analysis. XPS results revealed Ni2+ ion in the NiO and Ni3+ in Ni2O3 species, spinel compound of Co3O4 on the Pr/Co/Ni-Al2O3 catalyst. N2 adsorption-desorption analysis illustrated 7.9 % increment of surface area over the spent Pr/Co/Ni-Al2O3 catalyst, which assumed to be responsible for the dramatical increased of the methanation activity of this catalyst at the reaction temperature of 300 °C.

Keywords: Titanium, Copper, Nickel, Methanation, Desulfurization, Natural gas

1. Introduction
Crude natural gas is categorized as a 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 the natural gas and certain industrial processes is known to cause poisoning of the metal surface with both sulfur and hydrogen.

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. Such requirements are met with some transition metal oxides and apparently some Lanthanide oxides. Their acid and redox properties may be changed by adding other oxides (Krylov et al., 1998). Investigation done by Wang et al. (2007) 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 much slower of the catalyst science of mixed metal oxide is its significantly complexity compared with metal based catalyst, e.g. possible 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 (Wachs, 2005). Metal oxides are less active than metals, but they are stable in catalytic conditions.

Praseodymium oxide has been investigated as the most effective rare earth metal oxide when it was dopped onto NiO based catalyst for CO2 methanation reaction at 400 °C. Later, cobalt oxide was found as the most suitable dopant towards the Pr/ Ni catalyst (Wan Abu Bakar, 2005). Kulshreshtha et al. (1990) 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. (1997) found
out 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 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 (Wang et al., 2007). 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 (Happel & Hnatow, 1981). Therefore, Al₂O₃ is selected as the support for all of the studied catalysts in this research.

Efforts to search for efficient catalyst and to explore new technology in order to meet the demands of the economical feasibility of in-situ reactions of methanation and desulfurization for the purification of natural gas have not been extensively studied. The objective of this novel catalyst development is to achieve both low temperature and high conversion of sour gases. 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 impregnation method, namely, impregnating appropriate amount of metal nitrate salts on Al₂O₃ beads support for 15 minutes and dried at 80°C for 24 hours. It was then calcined in air at 400°C for 5 hours. Ti⁴⁺ sol for the Ti based catalyst was prepared by dissolving 6 g of polyethylene glycol (PEG) with 600 mL ethanol. Then, 31.8 g diethanolamine (DEA) followed by 85.2 g titanium (IV) isopropoxide (Ti(iso)₄) was added when PEG completely dissolved. After that, 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. The following metal oxides were impregnated onto the Al₂O₃ according to the above said method.

2.2 Catalytic activity measurements

In-situ reactions of methanation and desulfurization was performed from room temperature up to 300 °C with temperature rate of 5 °C/ min. 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. 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 Ka X-rays source (1253.6 eV). Sample was introduced into the spectrometer in flowing argon atmosphere, and evaporated at least 6 × 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 and Discussion

3.1 In-situ reactions of CO₂ methanation and H₂S desulfurization

Figure 1 shows the details trend on the percentage conversion of CO₂ and H₂S over the potential Pr/ Co/ Ni (5: 35: 60)-Al₂O₃, Fe/ Zn/ Cu (4: 16: 80)-Al₂O₃ and Fe/ Zn/ Cu/ Ti (5: 5: 40: 50)-Al₂O₃. Table 1 shows the yield of CH₄ which indicated the methanation activity of the studied catalysts.

Fe/ Zn/ Cu/ Ti (5: 5: 40: 50)-Al₂O₃ catalyst showed a relatively higher H₂S conversion activity than the other two catalysts at temperature lower than 200 °C. It could be assigned as the best H₂S desulfurization catalyst among the studied catalysts due to its ability to convert higher percentage of H₂S at light off temperature. Pineda et al. (1997) have reported the presence of Ti may increase the H₂S desulfurization process at lower temperature. It had been proven that TiO₂ could influence the dissociation of H₂S to H⁺ and HS⁻ at the early stage due to its weak electron interaction in the d orbital (Blesa et al., 1993). The graph in Figure 1 shows a decrease on the conversion of H₂S over Fe/ Zn/ Cu-Al₂O₃ and Fe/ Zn/ Cu/
Ti-Al2O3 catalysts from room temperature to 40 °C. This phenomenon was assigned to the adsorption of H2S by the catalysts at lower temperature. Both the catalysts, completely removed H2S at reaction temperature of 100 °C. At temperature higher than 200 °C, the H2S desulfurization activity decreased in a great order over Fe/ Zn/ Cu-Al2O3 and Fe/ Zn/ Cu/ Ti-Al2O3 catalysts. This may due to the uptake of H2 by sulfur deposited on the surface of the catalysts to form H2S. Therefore, H2S desulfurization reaction at temperature higher than 200 °C is unfavored over these two catalysts. On the other hand, Pr/ Co/ Ni-Al2O3 catalyst showed a totally different trend in the conversion of H2S compared to the copper and titanium oxide based catalysts. The conversion of H2S over this catalyst gradually increased by the increasing of temperature until 100 % conversion of H2S was achieved at reaction temperature of 280 °C.

During CO2 methanation in the presence of H2S, all the three catalysts showed a gradual increase until maximum studied temperature of 300 °C. Pr/ Co/ Ni-Al2O3 and Fe/ Zn/ Cu-Al2O3 catalysts yielded the same amount of CH4 at reaction temperature of 200 °C (0.7 %), but Pr/ Co/ Ni-Al2O3 catalyst performed dramatically high CO2 methanation and H2S desulfurization activities at 300 °C. Pr/ Co/ Ni-Al2O3 gave the highest conversion of CO2 where it converted 19.2 % of CO2 and yielded 6.1 % of CH4 at 300 °C. It is believed that Pr was able to generate active sites for the in-situ reactions of CO2 and H2S conversion at higher temperature. Rare earth metal oxides may increase the stability of catalyst at high temperature and avoid the sintering of nickel (Miao et al., 1997). At 300 °C, Fe/ Zn/ Cu-Al2O3 catalyst converted 12.7 % of CO2 and yielded 1.1 % of CH4, Fe/ Zn/ Cu/ Ti-Al2O3 catalyst yielded no CH4 at 100 °C and gave only 0.7 % of CH4 at 300 °C. The CO2 methanation activity over this catalyst is considered very low. Basu et al. (2004) have proven that the addition of TiO at a high concentration may increase the surface oxygen storage. However, this property did not assist the temperature and avoid the sintering of nickel (Miao (1975) who investigated on some coordination compounds; and Lorenz (1978), 1979) who studied ESCA on NiO/ SiO2 and NiO-Al2O3/ SiO2 catalysts. The existence of Ni (2p) peak at 856.8 eV (2p1/2) and 874.3 eV (2p3/2) was attributed to the presence of Ni3+ in NiO. Ni3+ shows a higher binding energy because the Eo of the metal increases when the covalency decreases (Vederine et al., 1978). As the ionic radius of Ni2+> Ni3+ and furthermore the covalency of Ni3+ decreases compare to Ni2+. It is known that Ni3+ is more reactive than Ni2+. It could be suggested that NiOx is responsible to be the active site for this catalyst. The lower percentage H2S desulfurization over Pr/ Co/ Ni (5: 35: 60)-Al2O3, Fe/ Zn/ Cu (4: 6: 80)-Al2O3 and Fe/ Zn/ Cu/ Ti (5: 5: 40: 50)-Al2O3 were accomplished through XPS. All data was corrected by using the binding energy, Eo, of C 1s at 284.5 eV as standard.

The Eb resulted from deconvolution peaks of Ni (2p) and Co (2p) from Pr/ Co/ Ni-Al2O3 was depicted in Table 2. The Eb of each species observed in Ni (2p) region for the fresh Pr/ Co/ Ni-Al2O3 catalyst are characteristic of the Ni2+ ion from the NiO at the Eb of 854.2 eV (2p3/2) and 871.8 eV (2p1/2), similar assignment to the data obtained by Nefedov et al. (1975) who investigated on some coordination compounds; and Lorenz et al. (1979) who studied ESCA on NiO/ SiO2 and NiO-Al2O3/ SiO2 catalysts. The existence of Ni (2p) peak at 856.8 eV (2p1/2) and 874.3 eV (2p3/2) was attributed to the presence of Ni3+ in NiO. Ni3+ shows a higher binding energy because the Eb of the metal increases when the covalency decreases (Vederine et al., 1978). As the ionic radius of Ni2+> Ni3+ and furthermore the covalency of Ni3+ decreases compare to Ni2+. It is known that Ni3+ is more reactive than Ni2+. It could be suggested that NiOx is responsible to be the active site for this catalyst. The lower percentage H2S desulfurization over Pr/ Co/ Ni (5: 35: 60)-Al2O3 at reaction temperature below 200 °C may be resulted from the lack of Ni2O3 present, which is an oxygen rich compound. XPS data also revealed the presence of spinel compound, Co3O4 on the surface of the catalyst, which is in accord with those reported by Kim (1975), Zeng et al. (1995), and Riedel & Schaub (2003) who worked with the CoO, CoO-ZrO2 and Co Fischer-Tropsch catalyst, respectively. The existence of the spinel compound in the catalyst was assigned to be good for the catalytic efficiency as it provides more active sites for the reaction and also it can easily change forms according to the environment, whether it is more to Co2+ or Co3+.

After the exposure to the in-situ reactions of CO2 methanation and H2S desulfurization environment, NiO was disappeared in the spent catalyst. Similar phenomenon also reported by Djaidja et al. (2000). NiO phase was disappeared in their used Ni/ Sm2O3 and Ni/ La2O3 catalysts. NiOx was detected in both of their fresh and used catalysts and they suggested that NiOx phase is needed in the oxidative transformation of methane reaction course. The absence of NiO was presumably contributed to the increasing of the catalytic performance over this catalyst at maximum study temperature of 300 °C. The Co (2p) peaks shifted to a lower Eb of 778.7 eV (2p3/2) and 782.8 eV (2p1/2) indicating no changes in the Co oxidation state on the surface.

According to the XPS analysis, 0.7 % of Pr was available on the fresh Pr/ Co/ Ni-Al2O3 catalyst, while only 0.2 % of Pr was available on the spent catalyst. This reduction may due to the agglomeration of other elements that forced the Pr element to move into the bulk of the catalyst.
Even though the EDX analysis revealed the weight percentage of Zn as 0.2 % in the Fe/ Zn/ Cu-Al2O3 catalyst, no peak assigned to Zn was detected from the deconvolution peak of Zn. This may 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. The lower loading of Zn that is insensitive to the XPS analysis is also a factor. The E_b resulted from deconvolution peaks of Cu (2p) and Fe (2p) from Fe/ Zn/ Cu-Al2O3 catalyst was tabulated in Table 3. The fresh Fe/ Zn/ Cu-Al2O3 catalyst contained normal spinel compound of CuFe2O4. This spinel compound turned to inverse spinel structure after the catalytic testing. A normal spinel compound is the active site for this catalyst. Fe3+ made up the octahedral site while Cu2+ made up the tetrahedral site (Ando et al., 1998a; 1998b) as illustrated in Figure 2. Peaks referred to normal spinel compounds of CuFe2O4 or Fe3O4 appeared at E_b of 710.1 eV (2p3/2) and 723.7 eV (2p1/2). CuFe2O4 and Fe3O4 were assumed to act as active species on the surface. Fe3O4 is considered as the more dominant structure compared to CuFe2O4 and it is also the active site for H2S desulfurization. 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. The spent Fe/ Zn/ Cu-Al2O3 catalyst showed deconvolution peaks of CuFe2O4 or Fe3O4 at E_b of 710.1 eV (2p3/2) and 723.7 eV (2p1/2) but with 85.3 % reduction of peak area. This may due to the inverse spinel structure that contributed to the presence of larger amount of surface copper.

Normal spinel compound of CuFe2O4 was revealed from the deconvolution peak of Cu (2p) for the fresh and spent Fe/ Zn/ Cu/ Ti-Al2O3 catalysts (Table 4). Peaks referred to normal spinel compounds of CuFe2O4 or Fe3O4 appeared at E_b of 709.7 eV (2p3/2) and 723.2 eV (2p1/2) on the fresh Fe/ Zn/ Cu/ Ti-Al2O3 catalyst. There are another peaks at E_b of 712.4 eV (2p3/2) and 726.1 eV (2p1/2) assigned to the Fe3+ bound to hydroxyl group (OH) in agreement with Shah et al. (2002). The higher 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-Al2O3 catalyst due to its high electron density nature. Morrison (1998) also proved that TiO2 in Fe/ Zn/ Cu/ Ti-Al2O3 catalyst contributed to the presence of Fe3+-OH and thus active site for the H2S desulfurization. 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/ Ti-Al2O3 catalyst also showed a lower peak area for deconvolution peaks of CuFe2O4/ Fe3O4 at 710.5 eV (2p3/2) and 724.1 eV (2p1/2). This may resulted from carbon coking on the surface of the catalyst during XPS analysis or the formation of CuO obstructed the distribution of Fe on the catalyst surface. Similar with Fe/ Zn/ Cu-Al2O3 catalyst, no peak assigned to Zn was detected even though 0.1% of Zn was revealed by EDX analysis. In addition, the presence of Ti in the Fe/ Zn/ Cu/ Ti-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 is weak due to the distance of Ti inside the catalyst structure is comparably farer than those species on the surface.

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 5 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 narrower pore size compared to the spent catalysts. It is believed that some of the pores collapsed during the in-situ reactions of CO2 methanation and H2S desulfurization leading to the enlargement of the pores. From the BET surface area analysis, the surface area of the spent Pr/ Co/ Ni-Al2O3 catalyst is higher than the fresh catalyst. This could explain the dramtical increased of the methanation activity of this catalyst at the reaction temperature of 300 °C. It is assumed that the increasing of the surface area with respect to temperature finally increase the catalytic activity of the Pr/ Co/ Ni-Al2O3 catalyst at higher temperature. By referring to the XPS analysis, Co ions were detected as spinel compound of Co3O4 on the surface. It is believed that Co3O4 contributed to the increment of surface area over this catalyst. Besides that, NiO might play a role too. NiO is present in the fresh Pr/ Co/ Ni-Al2O3 catalyst but absent in the spent Pr/ Co/ Ni-Al2O3 catalyst. It was observed that Fe/ Zn/ Cu/ Ti-Al2O3 catalyst posseses the highest surface area and narrowest pore size. This was supported by Yamasaki et al. (1999) that the addition of TiO2 in the catalyst may increase the surface area and decrease the particle size. These features increased 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 (Wan Abu Bakar, 2000). The Fe/ Zn/ Cu-Al2O3 catalyst showed reduction of 34 % and Fe/ Zn/ Cu/ Ti-Al2O3 catalyst showed reduction of 17 % in surface area after undergoing catalytic testing. This reduction is possibly due to the sulfur poisoning on the surface of the catalysts during H2S desulfurization, or collapsed of the pores during prolongs catalytic reaction. This was also proven by the Energy Dispersive X-rays Analysis, which indicated the appearance of sulfur element. However, the isothermal 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.
4. Conclusion

Nickel oxide based catalyst is the most potential for the in-situ reactions of CO₂ methanation and H₂S desulfurization compared to the copper oxide and titanium oxide based catalysts. It is capable of 100 % conversion of H₂S to elemental sulfur and yielded 6.1 % of CH₄ at reaction temperature of 300 °C. The aim to obtain high H₂S desulfurization rate at low temperature was achieved. However, improvement is needed for the CO₂ methanation reaction. 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 at much lower temperature.

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Table 1. Yields from in-situ reactions of CO₂ methanation and H₂S desulfurization over Al₂O₃ supported Pr/Co/Ni (5: 35: 60), Fe/Zn/Cu (4: 16: 80) and Fe/Zn/Cu/Ti (5: 5: 40: 50) catalysts

| Catalyst | Temperature (°C) | Converted CO₂ (%) | Unreacted CO₂ (%) |
|----------|-----------------|-------------------|-------------------|
|          |                 | CH₄   | CO + H₂O |                |
| Pr/Co/Ni (5: 35: 60)-Al₂O₃ | 100  | 0.4   | 10.7   | 88.9            |
|        | 200  | 0.7   | 14.1   | 85.2            |
|        | 300  | 6.1   | 13.1   | 80.8            |
| Fe/Zn/Cu (4: 16: 80)-Al₂O₃ | 100  | 0.6   | 5.9    | 93.5            |
|        | 200  | 0.7   | 11.3   | 88.0            |
|        | 300  | 1.1   | 11.6   | 87.3            |
| Fe/Zn/Cu/Ti (5: 5: 40: 50)-Al₂O₃ | 100  | 0.0   | 0.7    | 99.3            |
|        | 200  | 0.4   | 6.2    | 93.4            |
|        | 300  | 0.7   | 7.3    | 92.0            |

Table 2. XPS data of Ni (2p) and Co (2p) for fresh and spent Pr/Co/Ni (5: 35: 60)-Al₂O₃ catalysts

| Catalyst | Weight (%) | Binding Energy (eV) | ΔE<sub>SO</sub> (eV) | Peak Area <sup>c</sup> (2p<sub>3/2</sub>) | Peak Assignment |
|----------|------------|--------------------|----------------------|-----------------------------|-----------------|
|          |            | 2p<sub>3/2</sub>   | 2p<sub>1/2</sub>     |                             |                 |
| Pr/Co/Ni (5:35:60)-Al₂O₃ (fresh) | 5.1 | 854.2 | 871.7 | 17.5 | 167.9 | Ni²⁺ in NiO |
| | 1.6 | 856.8 | 874.3 | 17.5 | 115.6 | Ni³⁺ in Ni₂O₃ |
| |             | 779.8 | 794.0 | 14.2 | 127.6 | Co₃O₄ |
| Pr/Co/Ni (5:35:60)-Al₂O₃ (spent) | 7.6 | 856.8 | 874.3 | 17.5 | 233.3 | Ni³⁺ in Ni₂O₃ |
| | 1.6 | 781.7 | 796.1 | 14.4 | 92.9 | Co₃O₄ |

<sup>a</sup> Binding energy, E<sub>b</sub> corrected by specific operation charge effect (284.5 eV)

<sup>b</sup> ΔE<sub>SO</sub> (difference of 2 spin orbit) = E<sub>b</sub>(2p<sub>1/2</sub>) - E<sub>b</sub>(2p<sub>3/2</sub>)

<sup>c</sup> Peak Area = Peak Intensity × FWHM (Full Width Half Maximum)
Table 3. XPS data of Cu (2p) and Fe (2p) for fresh and spent Fe/ Zn/ Cu (4: 16: 80)-Al₂O₃ catalysts

| Catalyst | Weight (%) | Binding Energy (eV) | ∆Eₕₒ b (eV) | Peak Area c (2p₃/2) | Peak Assignment |
|----------|------------|---------------------|--------------|---------------------|----------------|
| Fe/ Zn/ Cu (4:16:80)-Al₂O₃ (fresh) | 1.8 | 933.7 | 953.6 | 19.9 | 21.6 | CuFe₂O₄ (normal spinel) |
| | 3.6 | 710.1 | 723.7 | 13.6 | 66.7 | CuFe₂O₄/ Fe₃O₄ (normal spinel) |
| Fe/ Zn/ Cu (4:16:80)-Al₂O₃ (spent) | 4.2 | 935.1 | 954.9 | 19.8 | 23.9 | CuFe₂O₄ (inverse spinel) |
| | 3.4 | 710.1 | 723.7 | 13.6 | 9.8 | CuFe₂O₄/ Fe₃O₄ (normal spinel) |

a Binding energy, Eₖ corrected by specific operation charge effect (284.5 eV)
b ∆Eₕₒ (difference of 2 spin orbit) = Eₖ(2p₁/₂) - Eₖ(2p₃/2)
c Peak Area = Peak Intensity × FWHM (Full Width Half Maximum)

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

| Catalyst | Weight (%) | Binding Energy (eV) | ∆Eₕₒ b (eV) | Peak Area c (2p₃/2) | Peak Assignment |
|----------|------------|---------------------|--------------|---------------------|----------------|
| Fe/ Zn/ Cu/ Ti (5:5:40:50)-Al₂O₃ (fresh) | 3.6 | 933.6 | 953.5 | 19.9 | 247.6 | CuFe₂O₄ (normal spinel) |
| | 3.8 | 709.7 | 723.2 | 13.5 | 12.5 | CuFe₂O₄/ Fe₃O₄ (normal spinel) |
| | 712.4 | 726.1 | 13.7 | 6.4 | Fe³⁺-OH |
| Fe/ Zn/ Cu/ Ti (5:5:40:50)-Al₂O₃ (spent) | 3.7 | 933.7 | 953.5 | 19.9 | 59.9 | CuFe₂O₄ (normal spinel) |
| | 2.8 | 710.5 | 724.1 | 13.6 | 10.0 | CuFe₂O₄/ Fe₃O₄ (normal spinel) |

a Binding energy, Eₖ corrected by specific operation charge effect (284.5 eV)
b ∆Eₕₒ (difference of 2 spin orbit) = Eₖ(2p₁/₂) - Eₖ(2p₃/2)
c Peak Area = Peak Intensity × FWHM (Full Width Half Maximum)
Table 5. BET surface area and BJH desorption average pore diameter of the fresh and after in-situ reactions testing catalysts

| Al₂O₃ Supported Catalyst | Condition | $S_{BET}$ (m² g⁻¹) | $d$ (nm) |
|--------------------------|-----------|---------------------|--------|
| Pr/ Co/ Ni = 5: 35: 60    | Fresh     | 166.2               | 5.6    |
| Pr/ Co/ Ni = 5: 35: 60    | Spent     | 180.4               | 5.9    |
| Fe/ Zn/ Cu = 4: 16: 80    | Fresh     | 184.8               | 5.1    |
| Fe/ Zn/ Cu = 4: 16: 80    | Spent     | 121.6               | 7.1    |
| Fe/ Zn/ Cu/ Ti = 5: 5: 40: 50 | Fresh | 259.2               | 2.6    |
| Fe/ Zn/ Cu/ Ti = 5: 5: 40: 50 | Spent | 215.6               | 3.2    |

a BET surface area  

b BJH desorption average pore diameter

Figure 1. Percentage conversion of CO₂ and H₂S versus reaction temperature under in-situ reactions of CO₂ methanation and H₂S desulfurization over (♦) Pr/ Co/ Ni (5: 35: 60)-Al₂O₃; (■) Fe/ Zn/ Cu (4: 16: 80)-Al₂O₃; (▲) Fe/ Zn/ Cu/ Ti (5: 5: 40: 50)-Al₂O₃ catalysts.
Figure 2. An illustration diagram of normal spinel compound of CuFe$_2$O$_4$.