

A SUPPORTED TITANIUM BASED CATALYST FOR *IN-SITU* HYDROGEN SULPHIDE DESULPHURIZATION AND CARBON DIOXIDE METHANATION REACTION IN NATURAL GAS

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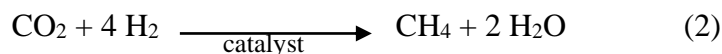
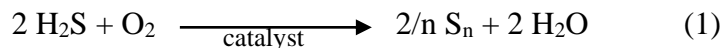
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ABSTRACT

Malaysian crude natural gas contains various gases components including methane (40-50%), ethane (5-10%) and propane (1-5%). However, this crude natural gas also contain H₂S (1-5%) and CO₂ (20-30%) which have the ability to corrode carbon steel used in the natural gas pipeline system and material in the processing plant. Fe³⁺/Zn²⁺/Cu²⁺/Ti⁴⁺/Al₂O₃ with the ratio 0.1:0.1:0.8:1 was prepared to produce the best catalyst for *in-situ* reaction of H₂S desulphurization and CO₂ methanation. This catalyst was produced via modified sol-gel and impregnation methods and was calcined at 400 °C for 5 hours. The results of catalytic activity testing for the Fe³⁺/Zn²⁺/Cu²⁺/Ti⁴⁺/Al₂O₃ showed H₂S desulphurization percentage of 100% and 0.9% methanation at a workable plant reaction temperature of 100 °C. This catalyst also had the lowest H₂S adsorption with 1.9% at the range of room temperature to 40 °C and it also could oxidize the highly concentration of H₂S with 94.3% at the low temperature of 40°C. Importantly, this catalyst could be regenerated via heating at 200 °C for 3 hours under compressed air flow at the rate of 100 mL min⁻¹. The XRD analysis only showed the present three peaks due to cubic phase of γ-Al₂O₃. The Ti, Cu, Zn and Fe elements present in the catalyst matrix system were presumably to be homogeneously dispersed on the surface of alumina support besides their presence in very low concentration. The SEM micrograph showed that this catalyst had homogeneous size particles.

INTRODUCTION

Catalytic of H₂S desulphurization and CO₂ methanation are an important stage of the process of gas purification from natural gas. The investigation of low-temperature *in-situ* H₂S desulphurization with O₂ (Eqn. 1) and CO₂ methanation with H₂ (Eqn. 2) over a supported titanium based catalyst revealed periodic changes in the gases ratio at O₂/H₂S = 0.5 and H₂/CO₂ = 4, which entailed changes in the product composition and temperature in the catalyst bed [1,2].



In this study, we investigated the catalytic technique for selective removal of H₂S and CO₂ will form methane when reacted with H₂ in the natural gas. Hydrogen sulphide was completely converted to the elemental of sulphur. This would possibly offer a new solution for the treatment of toxic gas present in crude natural gas.

EXPERIMENTAL DETAILS

Catalyst Preparation

The catalyst sample of titanium (IV) was doped with copper (II), zinc (II) and iron (III) nitrates according to their ratio of 1:0.8:0.1:0.1 respectively. TiO₂ sol solution was prepared by dissolving titanium isopropoxide in 500 mL of ethanol and the solution stirred continuously until the transparent solution was formed. In the separate round-bottomed flask, copper, zinc and iron nitrates, were prepared according to required atomic weight of metals by dissolving the salt with minimum amount of distilled water and stirred continuously. Then, copper (II), zinc(II) and iron(III) nitrate solutions were mixed together and stirred continuously. Alumina beads with diameter of 4 mm to 5 mm were used as supported material. The supports were dipped into the TiO₂ sol solution until the solution was evenly adsorbed on the surface of the support and dried in oven at 80 - 90°C for 24 hours. After that, the supports were dipped in mixture of copper (II), zinc (II) and iron (III) nitrates solution until the solution was evenly adsorbed on the surface of the support. The supported catalyst was dried at 80 - 90°C for 24 hours and calcined in furnace at 400°C for 5 hours.

Catalytic Activities Measurement

The catalytic measurement data were derived from the deduction of peak areas. Once the gas mixture flow rate was steady and the recorded peak areas were stable, the gas mixture was then passed through the catalyst. The FTIR spectrum was recorded several times to reach a steady state. Then, the temperature was increased gradually and the scanning procedure was repeated. The reaction reached its completion once the peak shown by the FTIR had diminished. The determination of peak area that correlate to the percentage degradation of H₂S and CO₂ were accomplished in the wavelength range of 2078 – 2022 cm⁻¹ and 2097 – 2075 cm⁻¹ respectively.

Catalyst Characterization

Characterization of catalyst provides the chemistry underlying the physical properties of the material pertaining to its catalytic performance. In this research, XRD analysis was conducted using the Diffractometer D5000 Siemens Crystalloflex using Cu K_α radiation ($\lambda = 1.54060 \text{ \AA}$). Scans were performed in step mode of 0.20/step and 0.4 seconds/step in the range of the 2-theta was from 10 to 70°. The obtained data was analysed by a PC interfaced to the diffractometer using software called Diffrac. Plus. Peaks position, width and intensity were then identified by comparison with accumulated Powder Diffraction File (PDF) data.

RESULTS AND DISCUSSION

Catalytic Activities

Figure 1 shows the *in-situ* reactions of H₂S desulphurization and CO₂ methanation in the presence of O₂ and H₂ by Fe³⁺/Zn²⁺/Cu²⁺/Ti⁴⁺/Al₂O₃ and commercial puraspec catalysts using the mixture of simulated gases.

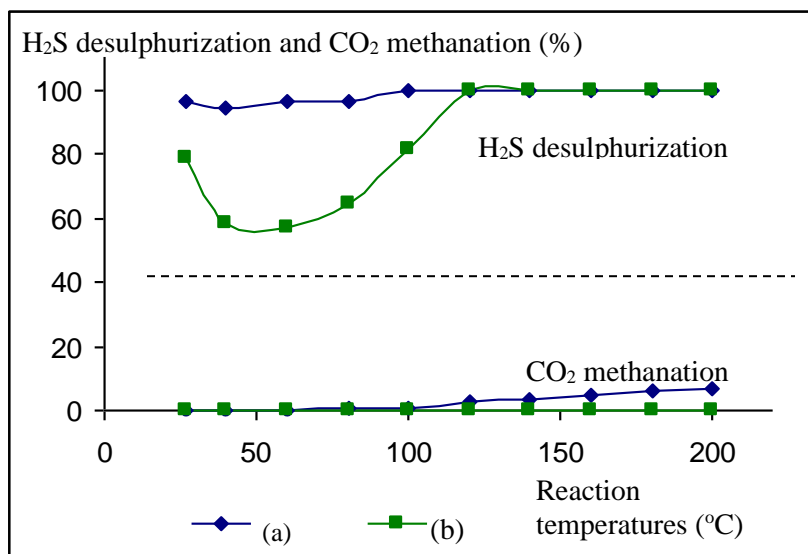


Figure 1: *In-situ* reactions of H₂S desulphurization and CO₂ methanation of the (a) Fe³⁺/Zn²⁺/Cu²⁺/Ti⁴⁺/Al₂O₃ and (b) commercial puraspec catalysts using the mixture of simulated gases against reaction temperatures

Fe³⁺/Zn²⁺/Cu²⁺/Ti⁴⁺/Al₂O₃ indicated high catalytic activity with 100% H₂S desulphurization and 0.9% CO₂ methanation at 100°C. However, at the reaction of temperature, 40°C, the supported catalyst revealed the high percentage of 94.3% H₂S desulphurization and 0.2% CO₂ methanation. The Fe³⁺/Zn²⁺/Cu²⁺/Ti⁴⁺/Al₂O₃ catalysts also could convert CO₂ to CH₄ for 6.9% at 200°C of reaction temperature. However, the commercial catalyst (puraspec) indicated 100% H₂S desulphurization at 120°C but no CO₂ methanation reaction occurred at below 200°C. Obviously, Fe³⁺/Zn²⁺/Cu²⁺/Ti⁴⁺/Al₂O₃ and the commercial catalysts also underwent adsorption phenomenon of 1.9 and 21.6% of H₂S at the low temperature range of room temperature to 40°C.

Figure 2 shows the H₂S desulphurization and CO₂ methanation in the presence of O₂ and H₂ by Fe³⁺/Zn²⁺/Cu²⁺/Ti⁴⁺/Al₂O₃ and commercial puraspec catalyst using the crude natural gas sample was obtained from Bergading Platform,

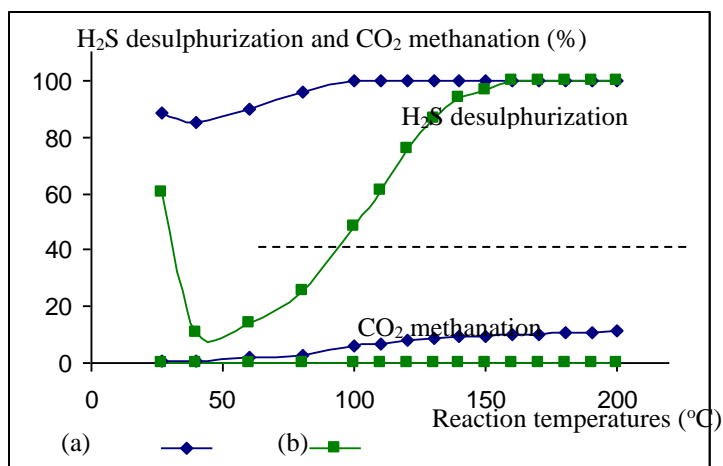


Figure 2: The *in-situ* H₂S desulphurization and CO₂ methanation reactions of the (a) Fe³⁺/Zn²⁺/Cu²⁺/Ti⁴⁺/Al₂O₃ and (b) commercial puraspec catalysts using the crude natural gas sample Bergading Platform, Petronas Carigali Sdn. Bhd against reaction temperatures

Petronas Carigali Sdn. Bhd. The Fe³⁺/Zn²⁺/Cu²⁺/Ti⁴⁺/Al₂O₃ catalyst indicated 100% H₂S desulphurization and 0.7% CO₂ methanation at 100°C. However, the supported catalyst revealed the first CO₂ methanation reaction with 0.1% at 80°C and it could convert CO₂ to CH₄ with 5% at light off temperature at 200°C. The supported catalyst showed only 3.3% H₂S adsorption phenomena at the low temperature of room temperature to 40°C and 85.3% H₂S desulphurization at light off temperature of 40°C. In comparison, the commercial puraspec catalyst indicated 100% H₂S desulphurization at 160°C and CO₂ methanation reaction did not occurred at below 200°C. The commercial catalyst revealed only 10.5% H₂S desulphurization at light off temperature of 40°C. It also indicated the highest of H₂S adsorption phenomena with 50% at the low temperature range of room temperature to 40°C.

The comparison of both catalysts showed the supported catalyst is better than the commercial puraspec catalyst in H₂S desulphurization and CO₂ methanation using the crude natural gas sample. It could be noted that the percentage of H₂S desulphurization using supported and commercial catalysts towards crude natural gas sample decreased at the low temperature compared to H₂S desulphurization of the supported catalyst and commercial catalyst using mixture of simulated gases. Among the contribution factors are the catalytic testing using crude natural gas sample contained various gases such as methane, ethane, propane, CO₂ and H₂S that can prevent the H₂S desulphurization reaction on the surface of both catalysts. Other than that, the highest H₂S adsorption phenomena by the commercial catalyst using crude natural gas sample at low temperature range of room temperature to 40°C compared to this catalyst using the

mixture of simulated gases. However, for CO₂ methanation reaction, the supported and commercial catalysts gave no changed.

Catalyst Characterization

X-ray diffraction analysis for Fe³⁺/Zn²⁺/Cu²⁺/Ti⁴⁺/Al₂O₃ catalyst indicates three broad peaks due to γ-Al₂O₃ cubic phase and was most probably contributed by the present of amorphous property in the catalyst (Table 1). No peaks due to the present of Fe³⁺, Zn²⁺, Cu²⁺ and Ti⁴⁺ was observed due to very low loading of these elements. This was proven by EDX analysis as shown in Table 1.

Table 1: The X-ray powder diffraction data of Fe³⁺/Zn²⁺/Cu²⁺/Ti⁴⁺/Al₂O₃ catalyst

| Catalyst | 2θ | d (Å) | d (Å) references | Peaks |
|--|-------|-------|---------------------|--------------------------------------|
| Fe ³⁺ /Zn ²⁺ /Cu ²⁺ /Ti ⁴⁺ /Al ₂ O ₃ | 39.08 | 2.39 | 2.39 | γ-Al ₂ O ₃ (c) |
| | 45.19 | 1.97 | 1.96 | γ-Al ₂ O ₃ (c) |
| | 68.50 | 1.39 | 1.39 | γ-Al ₂ O ₃ (c) |

(c) = Cubic phase

Table 2 shows the SEM-EDX analysis of Fe³⁺/Zn²⁺/Cu²⁺/Ti⁴⁺/Al₂O₃ supported catalyst which possesses 4.90% of titanium element, 4.32% of copper element, 1.47% of zinc element, 1.30% of iron element, 40.41% of aluminium element and 47.60% of oxygen element. This analysis proved the present Fe, Zn, Cu and Ti species in the supported catalyst which was undetected by x-ray powder diffraction analysis.

Table 2: The SEM-EDX analysis of Fe³⁺/Zn²⁺/Cu²⁺/Ti⁴⁺/Al₂O₃ catalyst

| Catalyst | Ti | Cu | Zn | Fe | Al | O |
|--|------|------|------|------|-------|-------|
| Fe ³⁺ /Zn ²⁺ /Cu ²⁺ /Ti ⁴⁺ /Al ₂ O ₃ | 4.90 | 4.32 | 1.47 | 1.30 | 40.41 | 47.60 |

Figure 3 illustrated the SEM micrograph of the Fe³⁺/Zn²⁺/Cu²⁺/Ti⁴⁺/Al₂O₃ catalyst which revealed irregular shape with homogenous smaller particle size ranging 4 to 7 μm. This catalyst indicated larger pore sizes that may contribute to increase the surface area of the catalyst.

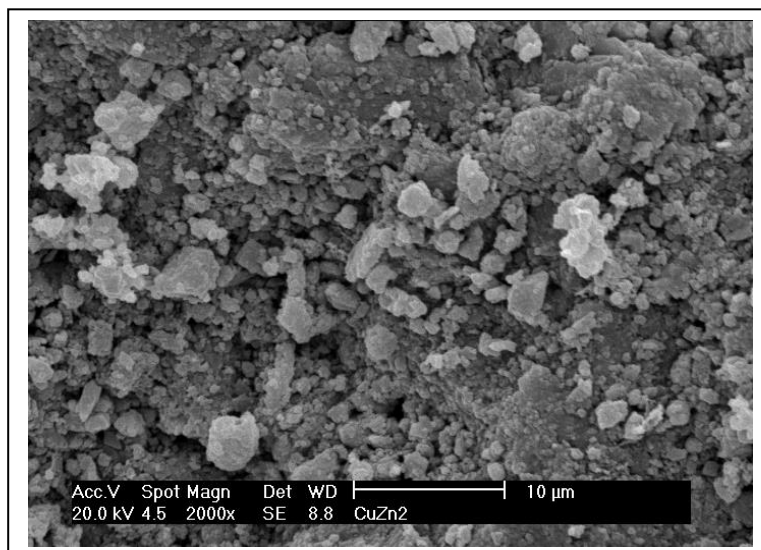


Figure 3: The SEM micrograph of $\text{Fe}^{3+}/\text{Zn}^{2+}/\text{Cu}^{2+}/\text{Ti}^{4+}/\text{Al}_2\text{O}_3$ with magnification of 2000 X and scale bar 10 μm

CONCLUSION

The $\text{Fe}^{3+}/\text{Zn}^{2+}/\text{Cu}^{2+}/\text{Ti}^{4+}/\text{Al}_2\text{O}_3$ catalyst revealed the highest catalytic activity with 100% H_2S desulphurization and 0.9% CO_2 methanation at 100°C. Furthermore this catalyst possesses very low of H_2S adsorption phenomena with 1.9% at low temperature. Other than that, it also indicated 0.2% and 6.9% CO_2 methanation at 60 and 200°C respectively. The XRD analysis of the supported catalyst only showed peaks due to $\gamma\text{-Al}_2\text{O}_3$ cubic phase. The SEM analysis revealed that the supported catalyst morphology was comprised of homogeneous smaller sized particles.

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