Preparation and Characterization of Ruthenium Oxides Doped Catalysts for Catalytic Oxidative Desulfurization of Diesel Oil

Nur Izzati Jailani[a], Wan Nur Aini Wan Mokhtar[b], Susilawati Toemen[a]*

[a]Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 Johor Bahru, Malaysia
[b]Centre for Advanced Materials and Renewable Resources, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia
*Corresponding author: susilawatitoemen@utm.my

Abstract
Diesel fuel widely used in transportation due to its wide range of performance, efficiency and safety features. However, sulfur compounds present in commercial diesel fuel have been the primary sources of industrial problems and environmental pollution. In order to lower the sulfur content, diesel fuel can be treated using green technology such as catalytic oxidative desulfurization (Cat-ODS). In Cat-ODS reaction, the parameter studied were different calcination temperatures and based ratios. For the oxidation reaction step, the tert-butyl hydroperoxide (TBHP) was used as oxidant with reaction conditions of TBHP to sulfur ratio of 3:1, the temperature of $45^{\circ}C$ and period time 30 minutes. Meanwhile for the extraction process, the condition for the reaction involve using N,N-dimethylformamide (DMF) as the solvent, with a DMF to diesel ratio of 1.0 and conducting the reaction at ambient temperature of $29^{\circ}C$ for 30 minutes. A total of five bimetallic catalyst were analyse using Cat-ODS method to determine the best catalyst for the desulfurization process. The bimetallic RuO_2-NiO_2 catalyst supported on Al_2O_3 calcined at $500^{\circ}C$ with 30 wt.% of Ni loading was proven to be the best catalyst in this reaction. Based on Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) analysis, the percentage of sulfur removal observed was 56.93% reduce the sulfur content from 70.10 ppm to 32.23 ppm. From the XRD analysis, it is confirmed the presence of Al_2O_3, RuO_2, NiO_2 species for RuO_2-NiO_2 (3:30)/Al_2O_3 catalyst. The crystallite size of RuO_2-NiO_2 (3:30)/Al_2O_3 catalyst found to be 11.72 nm. TGA analysis identified that $500^{\circ}C$ as the best calcination temperature in the reaction. NA analysis discovered that BET surface area of 251.73 m^2/g. In summary, this study proves that Cat-ODS is the best method to reduce sulfur compound in commercial diesel sample.
Keywords: Catalytic oxidative desulfurization; Catalyst; Diesel oil; Metal oxide

1. Introduction

Sulfur in transportation fuels is a major sources of air pollution. The removal of sulfur from transportation fuel is gaining more attention due to its awareness of the adverse effects of burning sulfur containing oils on the environment and human health. Diesel fuel, primarily used in high-performance diesel engines because of the unique combination of alkanes, cycloalkanes, and aromatic hydrocarbons, as well as trace amounts of sulfur and nitrogen compounds. To enhance air quality and reduce harmful emissions from diesel engines, many countries have implemented regulations to significantly reduce sulfur content in diesel fuel (Stanislaus, A. et al., 2010a). In 2009, the Euro 5 standard for diesel fuel was introduced, specifying a maximum sulfur content of 10 parts per million (ppm). However, certain petrol pumps still provided diesel fuel that did not comply with these standard regulations. Consequently, a desulfurization process has been developed to address this issue.

The ultra-deep desulfurization of fuels has accumulated significant attention, not only due to growing environmental concerns and legal requirements but also because it is crucial for producing ultra-low sulfur fuels, which are essential for fuel cell applications. However, the levels of organic sulfur presents in the diesel fuel are sufficient to considerably reduce the activity and lifetime of catalyst used in fuel processor. The organic sulfur compound presents such as mercaptans, thiophene (T), benzothiophenes (BT), and dibenzothiophene (DBT) can cause corrosion and deactivation of catalyst during the desulfurization process. Desulfurization is a chemical method employed to remove sulfur from various materials, predominantly fuels.

In the case of diesel fuel, desulfurization typically involves a two-stage deep desulfurization process. This process not only prevents contamination but also enhances the efficiency of petroleum products.

The existing hydrodesulfurization (HDS) process for reducing sulfur require harder than desired processing condition to remove the last 100 ppm of sulfur. However, the utilization of catalysts in a catalytic oxidative desulfurization (Cat-ODS) process can facilitate the selective oxidation of sulfur compounds. In general, catalysts promote the formation of reactive oxygen species from the most desired oxidants, such as H_2O_2 and O_2, and thus accelerate the ODS process.

Metal oxides are highly desirable catalysts for desulfurization processes due to their straightforward synthesis, stability, ready availability, and insolubility in common organic solvents. Metal oxide synthesis is simple and usually involves precipitation followed by calcination. The catalytic activity of a metal oxide in oxidative desulfurization (ODS) is determined by the specific characteristics of the metal. The noble transition metals which the earth-abundant first row transition metal such as Fe, Mn, Co, and Ni have high unique catalytic characteristics. Due to their abundance of earth, the capabilities to form bond of the d subshell that are partially filled with electrons for the transition metal also high. Thus, it was easier for this transition metal to form stable oxidation state in the reaction. Ce, on the other hand, exhibits sufficient kinetic stability. All these metal oxides offer the advantage of low operational and production costs (Zhang, G. et al., 2009). They serve as catalysts and extraction solvents due to their ease of preparation, environmental friendliness, cost-effectiveness, regenerability, and non-toxic nature.

This research aims to (1) to synthesize and characterize the RuO_2-x/ Al_2O_3 (x=NiO_2, MnO, Fe_2O_3, CoO, CeO_2) catalysts for desulphurization reaction, (2) to optimize the catalytic oxidative desulfurization activity in different based ratios and calcination temperature towards catalytic oxidative desulfurization reaction, (3) to analyze the percentage of sulfur content in treated commercial diesel by using Inductively Couple Plasma-Optical Emission Spectroscopy (ICP-OES). The higher the percentage of sulfur removal, the better the diesel fuel will be.

2. Materials and Methods

2.1 Catalyst Preparation

A series of metal nitrate salts of cobalt, nickel, cerium, iron, and manganese, were initially chosen for the aqueous incipient wetness impregnation (IWI) method supported on alumina, Al_2O_3. Firstly, a ruthenium nitrate salts and nickel nitrate salts with ratio (3:30) were weight and dissolved in 5 mL of distilled water each. The catalyst solutions were then mixed together and the mixture was stirred for 30 minutes with a magnetic stirrer. The alumina was immersed in the catalyst solution for 1 hour after a solution produced a homogeneous mixture. The catalyst was then dried at room temperature before being aged at 90°C in an oven overnight to remove water and provide a good coating of metal onto the exterior of the alumina. To remove impurities from precursor salts and excess water, all catalysts were calcined in the furnace at a rate of 5°C/min from the furnace temperature up to 500°C and kept at this temperature for 5 hours in the presence of air. The procedures were repeated for other metal nitrate salts of cobalt, cerium, iron, manganese. Then, the catalysts were further investigated with different based ratios (20% - 40 wt.%) and calcination temperatures (400 °C – 600 °C).

2.2 Catalytic Oxidative Desulfurization Reaction (Cat-ODS)

All reactions were carried out in a round bottom flask fitted with a magnetic stirrer and a condenser as shown in Figure 1. The paraffin oil bath was first heated and stabilized at a constant temperature of 45°C [18]. The flask was then filled with commercial diesel (10 mL), followed by a tert-butyl hydroperoxide (TBHP) oxidant to sulfur ratio of 3 mol (O/S=3). 0.1g of RuO_2-x/Al_2O_3 catalysts, x represents the metal oxide of cobalt, cerium, iron, nickel, or manganese was added inside the mixture solution. At 45°C and atmospheric temperature, the mixture was refluxed for 30 minutes with vigorous stirring. Next, the oxidized diesel was extracted using liquid-liquid extraction techniques under optimal extraction conditions. In each extraction experiment, 10 mL of oxidized diesel and N,N-dimethylformamide (DMF) were poured into a 250 mL conical flask with a diesel solvent ratio of 1.0. After that, the mixture was vigorously stirred for 30 minutes at room temperature (29°C) and atmospheric pressure. The mixture was then separated in a funnel until two distinct layers of treated diesel (upper layer) and extracted solvent formed in bottom layer. Finally, the upper layer (treated diesel) was taken and the sulfur content was collected.
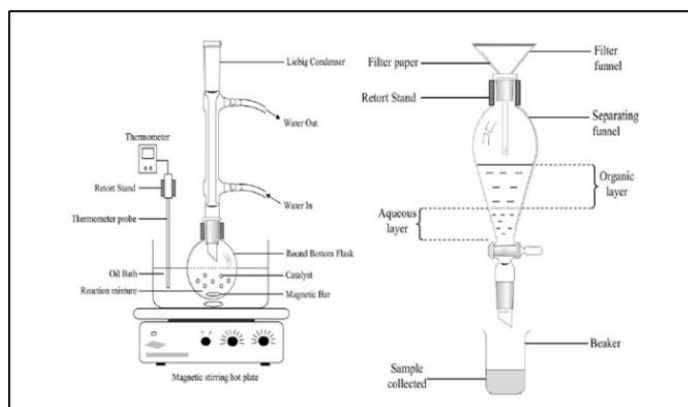
Figure 1. Experimental set up for catalytic oxidative desulfurization reaction and extraction process

2.3 Sulfur Measurement of Cat-ODS Process

The treated diesel obtained was analyzed by using inductively couple plasma-optical emission spectroscopy (Perkin Elmer Avio 200 ICP model) equipped with RF Power of 1300W and flow rate of 1.50 mL/min. Argon gas was used as the carrier gas. The gas flow for plasma, auxiliary and nebulizer were 1.0 L/min, 0.2 L/min and 0.6 L/min respectively. The initial temperature programmed was $160^{\circ}C$ and hold for 10 minutes. It was then ramped to $200^{\circ}C$ at $5^{\circ}C/min$ and hold for 20 minutes. The treated diesel collected was diluted in volumetric flask until 25 mL using ultra pure water. 0.1 g of sample was injected into the ICP system.

2.4 Characterization of Prepared Catalyst

The physicochemical characteristics of synthesized catalysts were investigated through characterization techniques such as X-ray diffraction spectroscopy (XRD), and thermogravimetric analysis–differential thermal analysis (TGA-DTA). XRD pattern was measured by using Rigaku SmartLab X-ray Diffractometer equipped with Cu-Kα radiation over 2θ values between 20° to 80°. The data was analyzed by using software, SmartLab Studio II. Thermogravimetric analysis was carried out by using TGA Q500 V20.13 Build 39 and Universal V4.5A TA Instruments. 0.3 – 0.5 g of catalyst sample was heated at temperature of 60°C to 900°C at 15°C/min in the flow 50 µL/min of nitrogen gas. Nitrogen Adsorption Analysis (NA) was used with Micromeritics ASAP 2010 to figure out the average catalyst's pore size, diameter, volume, type, shape, and surface area. The sample was degassed at 120°C and then cooled to room temperature using a vacuum pump to remove any remaining air.

3. Results and discussion

3.1 Diesel Fuel concentration

Sulfur content of commercial diesel was analyzed using ICP-OES. The total sulfur content in commercial diesel sample was 70.10 ppm, which higher than the sulfur limit for Euro 5 diesel. As stated, the standard regulation for Euro 5 diesel is supposed to be a maximum of 10-15 ppm, but the commercial diesel shows higher results.

3.2 Catalytic Oxidative Desulfurization Activity

3.2.1 Effect of bimetallic metal oxide

Figure 2 illustrates the effect of incorporation of bimetallic metal oxides on Cat-ODS activity. To study this parameter, the calcination temperature was kept constant at $500^{\circ}C$ with calcination time of 5 hours. The composition of based NiO_2, MnO, Fe_2O_3, CoO, CeO_2 were 30 wt.%. Among all tested catalyst, RuO_2-NiO_2 (3:30)/Al_2O_3 shows the higher performance desulfurization activity which decreased to 30.19 ppm from 70.10 ppm with the removal percentage is 56.93%. Meanwhile, RuO_2-CeO_2 (3:30)/Al_2O_3 present slightly higher elimination of sulfur (37.53%) after nickel, followed by RuO_2-Fe_2O_3 (3:30)/Al_2O_3 with 35.61% of sulfur removal. The percentage of sulfur removal for RuO_2-CoO (3:30)/Al_2O_3 was 35.14%. Lastly, RuO_2-MnO (3:30)/Al_2O_3 show the least sulfur removal percentage of 33.71%. From the results, it showed MnO was not suitable metal oxide for Cat-ODS. The activity of the catalyst for oxidation reaction of commercial diesel for Cat-ODS reaction follow the order of Ni > Ce > Fe > Co > Mn. These results were not in line with the work of Wan Mokhtar et al. who proved that Mn and Ce shows the highest performance catalyst towards Cat-ODS (Wan Mokhtar, W. N. A. et al., 2015).
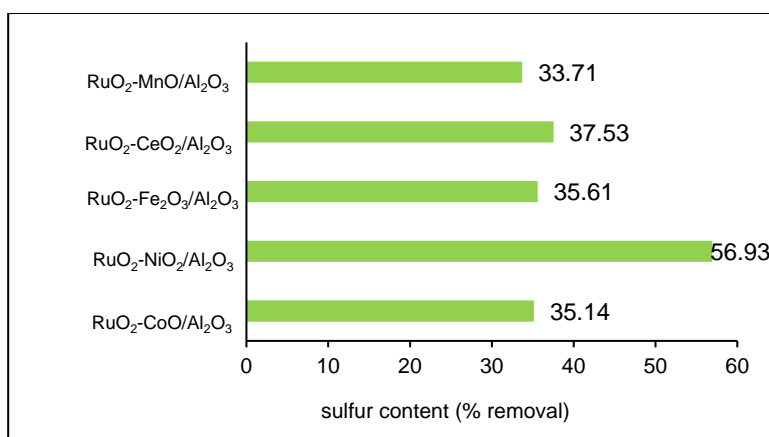
Figure 2. Effect of bimetallic metal oxide on Cat-ODS reaction on commercial diesel (Reaction conditions: Calcination temperature = 500 °C for 5 hrs, reaction time = 30 min, based ratios = 30 wt.%, diesel/solvent ratio = 1.0)

3.2.2 Effect of Calcination Temperature

The calcination temperature had an effect on the characteristics of catalyst including specific surface area and crystallinity. In this study, RuO_2-NiO_2 (3:30)/Al_2O_3 catalyst was calcined at 400-600°C for 5 hrs. To study this parameter, the reaction time of 30 minutes was kept constant throughout the reaction. Figure 3 shows the trend for the effect of calcination temperature towards catalytic oxidative desulfurization. Overall, percentage of sulfur removal increase with increasing temperature.

As shown in Figure 3, RuO_2-NiO_2 (3:30)/Al_2O_3 catalyst was calcined at 400°C shows very low desulfurization activity (41.63%). From XRD analysis, different type of alumina species (γ-AlOOH) was found in the catalyst calcined at 400°C, which may inhibit the active species of RuO_2 and NiO_2 and thus deactivating the catalyst as well as catalytic activity. The calcination temperature increased up to 500°C, the percentage removal of sulfur was up to 56.93%. The sulfur removal slightly increased to 58.23% after calcination at 600°C. Sulfur removal was notably related to the dispersion of RuO_2 and NiO_2 species on the catalyst surface (Wan Mokhtar, W. N. A. et al., 2015). At 500-600°C, RuO_2 and NiO_2 might well-dispersed in the catalyst (Hasan, Z. et al., 2012). From Figure 3, only small different of 1.3% of sulfur removal observed after increase the temperature from 500°C to 600°C. Overall, the analysis of Cat-ODS reaction was not proceed for RuO_2-NiO_2 (3:30)/Al_2O_3 catalyst calcined at temperature higher than 600°C.
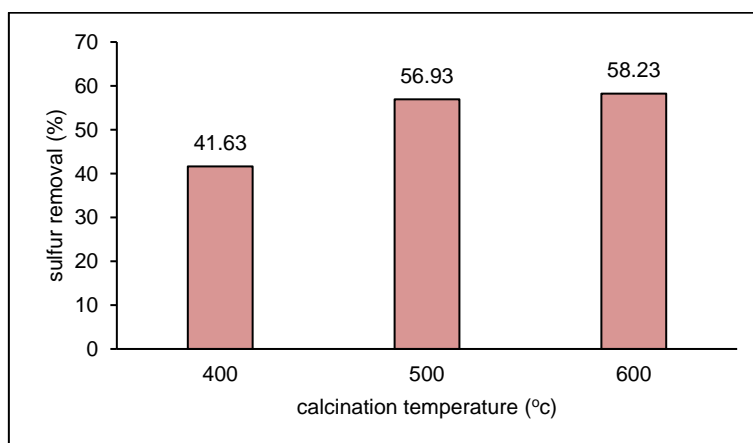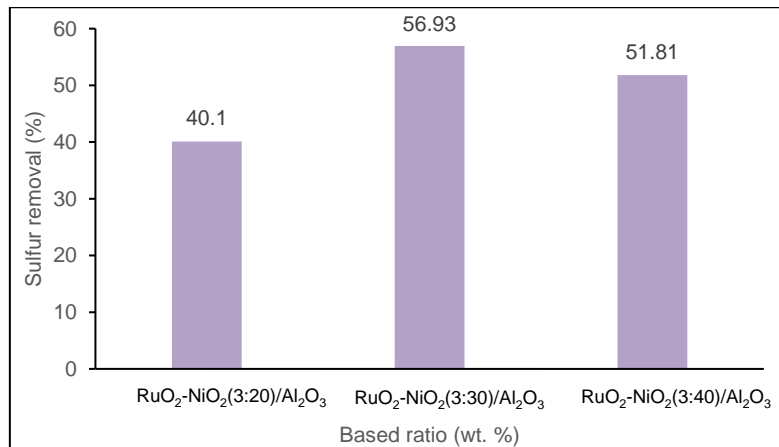

Figure 3. Effect of different temperature for RuO_2-NiO_2 (3:30)/Al_2O_3 catalyst (Reaction conditions: time = 30 min, based ratios = 30 wt.%, diesel/solvent ratio = 1.0)

3.2.3 Effect of Based Ratios

The based ratios of RuO_2-NiO_2/Al_2O_3 catalyst was studied to evaluate the optimal based ratios in for desulfurization reaction. The study was performed at different based ratios (20, 30, and 40 wt.%). The calcination temperature of 500°C was kept constant throughout the reaction. Figure 4 shows the effect of based ratios towards catalytic oxidative desulfurization. Overall, percentage of sulfur removal increase with increasing based ratios to 30 wt.% and decrease back after 40 wt.%. The decreasing activity of

desulfurization was due to the coverage effect of catalyst surface and cause the agglomeration, hence decrease the active sites (Ibrahim, S. et al., 2016).

As shown in Figure 4, RuO_2-NiO_2 (3:20)/Al_2O_3 catalyst were able to remove 40.1%. The removal of sulfur was increased with the increase of nickel ratio up to 30 wt.% (56.93%). The result was attributed to the higher dispersion of active sites on the surface of catalyst, which contributed to high surface area. However, it was found the catalytic activity of the RuO_2-NiO_2/Al_2O_3 catalyst dropped as based ratios was increased to 40 wt.% (51.81%). Further increase of NiO_2 decrease the conversion of sulfur compound and deactivated the catalyst. An excess NiO_2 in the catalyst cause agglomeration on the catalyst surface which lowered the dispersion of active sites, thus possessed weak catalytic activity. As conclusion, RuO_2-NiO_2 (3:30)/Al_2O_3 showed the best for Cat-ODS activity and nickel was one of the active species that contributed to the high performance of catalytic activity.


Figure 4. Effect of different based ratios on Cat-ODS reaction for RuO_2-NiO_2/Al_2O_3 catalyst (Reaction conditions: time = 30 min, temperature = 500 °C, diesel/solvent ratio = 1.0)

3.3 Characterization of Catalyst

3.3.1 X-Ray Diffraction (XRD)

XRD diffractograms over RuO_2-NiO_2/Al_2O_3 catalysts with different calcination temperatures and different based ratios are shown in Figure 5. From the figure, RuO_2-NiO_2/Al_2O_3 catalysts with different calcination temperature (400°C, 500°C, 600°C) and different based ratios (20-30 wt%) display polycrystalline state dominated by Al_2O_3 support.
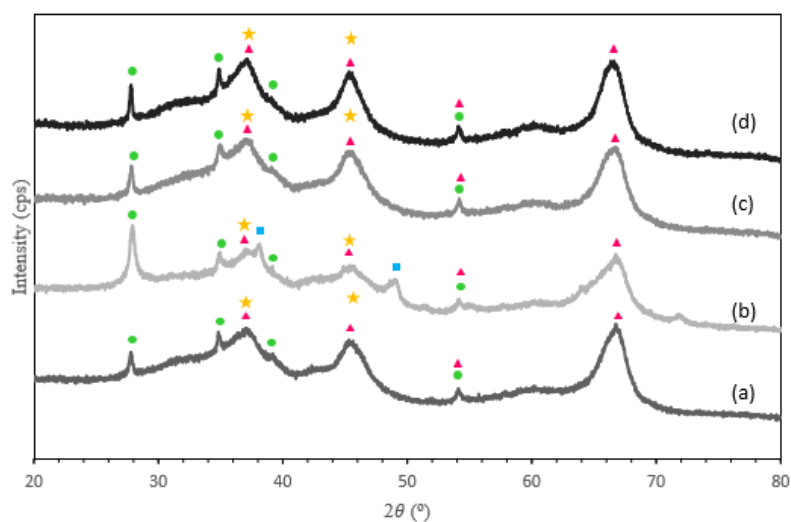

Figure 5. XRD diffractogram for (a) RuO_2-NiO_2 (3:20)/Al_2O_3 for temperature 500°C, (b) RuO_2-NiO_2 (3:30)/Al_2O_3 for temperature 400°C, (c) RuO_2-NiO_2 (3:30)/Al_2O_3 for temperature 500°C and (d) RuO_2-NiO_2 (3:30)/Al_2O_3 for temperature 600°C [▲ Al_2O_3, ● RuO_2, ★ NiO_2, ■ γ-AlOOH]

According to XRD result, the broad diffraction peaks for cubic alumina at ($2\theta=37°$, $45°$, $54°$ and $66°$) and tetragonal RuO_2 species at $2\theta = 27°$, $34°$, $39°$ and $54°$ were almost unchanged in all the catalyst samples. In addition, monoclinic NiO_2 species compounds was found at $2\theta = 37°$, and $45°$. Some peaks were overlapped to each other due to the effect of amorphous behavior of the prepared catalyst that could not enough to separate the peak. However, the new peak was observed at $2\theta= 38°$, and $49°$ for the catalyst calcined at 400°C (Figure 5b) which probably because of the contaminant of γ-AlOOH active species that inhibit the active species of RuO_2 and NiO_2 and thus deactivating the catalyst as well as catalytic activity. This is in line with the results in Figure 3.

3.3.2 Thermogravimetric Analysis

The thermal behavior of prepared catalyst showed two mass losses in TG-DTA curve according to Figure 6. Initial mass loss of the RuO_2-NiO_2 (3:20)/Al_2O_3 and RuO_2-NiO_2 (3:30)/Al_2O_3 catalysts which both around 8% in the range of temperature between 60°C to 150°C corresponding to the evaporation of surface free water molecules. The second significant mass loss was 12% for both catalyst which occurred at temperature range 150°C to 450°C due to the decomposition of surface hydroxyl molecules and nitrate precursors was observed [4]. From 450°C onwards, the impurities from synthesized catalyst have been removed and pure metal oxide could be obtained.
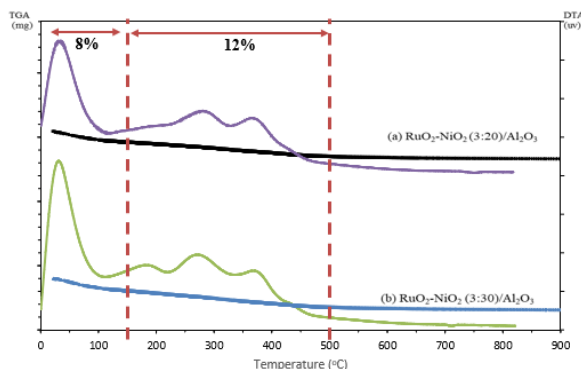
**Figure 6**. TG-DTA curve for (a) RuO_2-NiO_2 (3:20)/Al_2O_3, (b) RuO_2-NiO_2 (3:30)/Al_2O_3 uncalcined catalyst

3.3.3 Nitrogen Sorption Analysis

The textural characteristics of RuO_2-NiO_2 (3:30)/Al_2O_3 catalyst on BET surface area, average pore diameter, and total pore volume is shown in Table 1, while the isotherm plot is shown in Figure 7. It can be seen that the RuO_2-NiO_2 (3:30)/Al_2O_3 catalyst calcined at 500°C have high surface area of 251 m^2/g with average pore diameter of 5.65 nm and total pore volume of 0.48 cm^3/g. The high surface area may contribute to the high performance of the catalyst (Einaga, H., & Ogata, A. (2009). On the basis of IUPAC classification, the sample displayed type IV sorption isotherms with hysteresis loop type H3, indicating that the catalyst was typically mesoporous structure. The hysteresis loop in relative pressure was from P/P$_o$ 0.4 to 1.0 which explained that the degree of mesoporosity of the catalyst.

Table 1 . Textural characteristics of for RuO_2-NiO_2 (3:30)/Al_2O_3 catalyst at calcination temperature of 500°C.

Catalyst	Calcination temperature (°C)	BET Surface Area (m^2/g)	Average Pore Diameter (nm)	Total Pore Volume (cm^3/g)
RuO_2-NiO_2 (3:30)/Al_2O_3	500	251.73	5.6586	0.4827
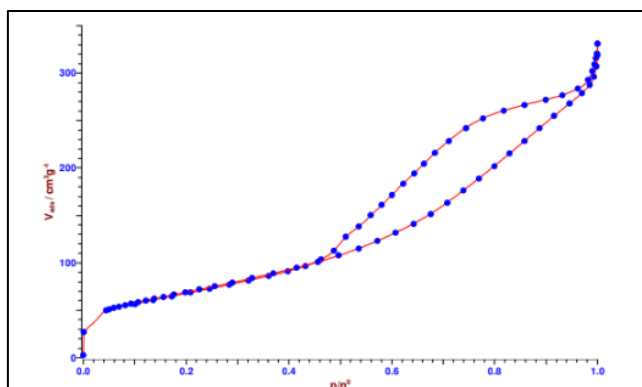
Figure 7. Nitrogen adsorption-desorption isotherm of RuO_2-NiO_2 (3:30)/Al_2O_3 catalyst at calcination temperature of 500^oC

4. Conclusion

This research focuses on synthesizing bimetallic metal oxide catalyst that can be used to catalyse the desulfurization process. RuO_2-x/ Al_2O_3 (x=NiO_2, MnO, Fe_2O_3, CoO, CeO_2) catalysts were successfully synthesized by using wetness impregnation method at different calcination temperatures of 400, 500 and 600^oC for 5 hours and different based loadings of 20, 30 and 40wt%. Desulfurization activity of the synthesized catalysts was successfully monitored using ICP-OES to determine the sulfur percentage of diesel. The constant reaction conditions of Cat-ODS was done at temperature 45^oC reaction temperature, 3:1 diesel to solvent (DMF) ratio, TBHP as oxidant with sulfur ratio of 3 mol and 30 minutes for reaction time. Based on the result obtained, RuO_2-NiO_2 (3:30)/Al_2O_3 catalyst with calcination temperature of 500^oC shows the ideal characteristics with percentage of sulfur removal of 56.93%. Furthermore, the potential RuO_2-NiO_2/Al_2O_3 catalysts calcined at different temperature and different based ratios selected were successfully characterized using X-Ray diffraction (XRD), thermogravimetric analysis (TGA) and nitrogen sorption analysis (NA). XRD analysis of RuO_2-NiO_2/Al_2O_3 catalysts showed polycrystalline structure with the presence of active species such as RuO_2, NiO_2, Al_2O_3 that contribute to the high catalytic activity of the catalyst. RuO_2-NiO_2 (3:30)/Al_2O_3 catalysts has highest crystallite size of 11.72 nm and 500^oC was identified as sufficient calcination temperature for decomposition of nickel nitrate precursor in the catalyst. In NA analysis, the dispersion of RuO_2-NiO_2 (3:30)/Al_2O_3 catalysts resulted in surface area of 251.73 m^2/g with mesoporous characteristic.

References
Stanislaus, A., Marafi, A., & Rana, M. S. (2010a). Recent advances in the science and technology of ultra low sulfur diesel (ULSD) production. Catalysis today, 153(1-2), 1-68.

Zhang, G., Yu, F., & Wang, R. (2009). Research advances in oxidative desulfurization technologies for the production of low sulfur fuel oils. Petroleum Coal, 51(3), 196-207.

Wan Mokhtar, W. N. A., Wan Abu Bakar, W. A., Ali, R., Abdul Kadir, A. A. J. C. T., & Policy, E. (2015). Catalytic oxidative desulfurization of diesel oil by Co/Mn/Al_2O_3 catalysts—tert-butyl hydroperoxide (TBHP) system: preparation, characterization, reaction, and mechanism. 17(6), 1487-1497.

Hasan, Z., Jeon, J., & Jhung, S. H. (2012). Oxidative desulfurization of benzothiophene and thiophene with WO_x/ZrO_2 catalysts: effect of calcination temperature of catalysts. *Journal of hazardous materials*, *205*, 216-221

Ibrahim, S., Charinpanitkul, T., Kobatake, E., & Sriyudthsak, M. (2016). Nanowires nickel oxide and nanospherical manganese oxide synthesized via low temperature hydrothermal technique for hydrogen peroxide sensor. Journal of Chemistry, 2016.

Einaga, H., & Ogata, A. (2009). Benzene oxidation with ozone over supported manganese oxide catalysts: effect of catalyst support and reaction conditions. Journal of Hazardous materials, 164(2-3), 1236-1241.