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Research note

Catalytic Reduction of SO_2 with CH_4 to Elemental Sulfur: A Comparative Analysis of Alumina, Copper-Alumina, and Nickel-Alumina Catalysts

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ABSTRACT

The catalytic reduction of sulfur dioxide with methane to form elemental sulfur was studied. Al_2O_3, Cu-Al_2O_3, and Ni-Al_2O_3 were examined as catalysts whose performances were compared in terms of SO_2 conversion and selectivity. Performance of the catalyst extremely improved when nickel and copper were added as promoters. The effects of temperature, SO_2/CH_4 molar ratio, and reaction time on SO_2 reduction were studied. The operating temperature range was 550–800 °C, and it was observed that the reaction was strongly temperature dependent. At temperatures lower than 700 °C, Al_2O_3-Cu (10 %) catalyst showed the best performance of all the catalysts. However, at 700 °C and higher, performances of Al_2O_3-Cu (10 %) and Al_2O_3-Ni (10 %) catalysts were similar. Complete conversion and selectivity (more than 99.5 %) was achieved by Al_2O_3-Cu (10 %) and Al_2O_3-Ni (10 %) catalyst, at 750 °C. Effect of molar feed ratio of SO_2/CH_4= 1-3 was studied, and stoichiometric feed ratio showed the best performance. In addition, the investigation of reaction time for Al_2O_3-Cu (10 %) and Al_2O_3-Ni (10 %) catalysts showed good long-term stability for SO_2 reduction with methane.

1. Introduction

Today, air pollution is one of the most important environmental problems of industrialized and developing countries, since it directly affects human health. While it is possible to prevent human from using contaminated water or soil, currently there is no way to prevent human from directly breathing the polluted air.

Carbon dioxide, sulfur oxides, nitrogen oxides, carbon monoxide, volatile organic compounds, etc. are the main agents of air pollution. Among sulfur oxides, sulfur dioxide is the most important one and is the main cause of acid rain.

Sulfur dioxide has serious effects on human

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health, reduces agricultural productivity, causes mortality of fishes by reducing the pH of rivers, and creates many other hazardous effects. Due to its damaging effects, development of appropriate methods for controlling these emissions is essential. Flue Gas Desulfurization (FGD) methods are divided into two groups: throwaway and regenerative [1].

The lime sorption methods can reduce SO_2 emission to the atmosphere as the throwaway. These methods are usually appropriate for small amounts of SO_2 in flue gas; however, for a large amount of SO_2, a vast amount of non-usable waste material is produced, which is a great problem for landfill disposal.

The regenerative methods are mainly used for high SO_2 mole fractions, such as copper converting and zinc roasting plants. Production of sulfuric acid and elemental sulfur by catalytic reaction of SO_2 is the most important regenerative method that converts SO_2 to the desired industrial products.

When there is a good demand for this sulfuric acid, its production by SO_2 is a good option; however, due to highly corrosive nature of this acid, its storage and transportation are difficult. Concerning simple transportation of solid sulfur, this method is very interesting and promising.

For reduction of SO_2 to elemental sulfur, several reductants were used; CO [2, 3], CH_4, and H_2 [4, 5] are important reductants used for this reaction; however, syngas ($CO+H_2$) [6] and carbon were also used.

The advantage of SO_2 reduction with carbon monoxide and hydrogen is the low operating temperatures. However, production of CO an H_2 is significantly expensive.

Lower price and better accessibility of CH_4, in comparison with CO or H_2, make it a very interesting choice. For the countries with a large amount of natural gas reservoirs (such as Iran, Russian and etc.), CH_4 can be the best choice.

SO_2 reduction by methane can be performed as follows:

$$CH_4 + 2SO_2 \rightarrow 2S + CO_2 + 2H_2O \quad (1)$$

This reaction is a complete methane oxidation by SO_2, produced water, carbon dioxide, and elemental sulfur. However, for this process, various side reactions may occur.

Partial methane oxidation by SO_2 is one of the significant side reactions that produces H_2S as follows:

$$2CH_4 + SO_2 \rightarrow H_2S + 2CO + 3H_2 \quad (2)$$

Hydrogen may result from the above as well as methane decomposition reaction:

$$CH_4 \rightarrow C + 2H_2 \quad (3)$$

H_2 produced may react with SO_2 and form H_2S and water, as shown in the following reaction:

$$3H_2 + SO_2 \rightarrow H_2S + 2H_2O \quad (4)$$

Because of Reactions (2) and (4), H_2S is the most important undesirable byproduct of this process.

However, on the other hand, SO_2 and produced H_2S can react according to reaction (5) and produce elemental sulfur.

$$SO_2 + 2H_2S \rightarrow 3S + 2H_2O \quad (5)$$

This reaction is commonly used in Claus unit in the natural gas refineries.

Bauxite [7], alumina [8-10], metal oxides and sulfides supported on alumina and activated carbon [11-15] are used for catalytic reduction of SO_2 to form elemental sulfur with CH_4. In addition, transition metal sulfide [16], ferromanganese nodules [17], and cobalt oxide on different supports [18] for this reaction are used.

Cerium oxide is also among the catalysts that worked well for this reaction [19-22].

Copper and nickel on ceria-based catalyst show good performance for SO_2 reduction [19-22]; however, given the high cost of cerium, in terms of industries, it is not a suitable choice.

That is the reason for selecting alumina as a support for catalyst in this investigation. On the other hand, the alumina surface is much higher than cerium, and in the solid-gas reactions, the surface area of catalyst is a very important factor; thus, this choice can be a very appropriate option.

In this study, alumina and two kinds of modified alumina with copper and nickel are examined and compared for SO_2 reduction by CH_4. Cu-Al_2O_3 and Ni-Al_2O_3 catalysts with different concentrations (5 and 10 %) were prepared and characterized by a wet impregnation technique. After synthesis of the catalysts, reactor tests at the temperature range of 550–800 °C were accomplished and the best catalyst according to conversion, and selectivity was determined. Then, for the best catalyst, effect of feed ratio was investigated.

Finally, stability effect of the catalysts, with regard to the importance of this parameter in industrial applications, was studied.

2. Experimental

2.1. Catalyst preparation

In this work, wet impregnation technique was used for catalyst preparation [23].

An aqueous solution of copper nitrate trihydrate ($Cu(NO_3)_2.3H_2O$, from Merck) or nickel nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$, from Merck) was used as precursors for impregnation onto commercial γ-Al_2O_3 support.

A well-impregnated catalyst precursor was then put aside for 1 h, dried overnight at 120 °C in an oven, and finally was calcined at 550 °C for 4 h.

Copper-alumina and nickel-alumina catalysts used in this study are of 5 and 10 % loading by weight over γ-alumina and are represented as Al_2O_3-Cu (5 %), Al_2O_3- Cu (10 %), Al_2O_3-Ni (5 %), and Al_2O_3-Ni (10 %), respectively.

2.2. Catalyst characterization

BET specific surface area, pore size distributions, and adsorption isotherms of the catalysts were measured using nitrogen adsorption method by Autosorb-1MP apparatus from Qantachrome at 77 K.

2.3. Catalyst performance tests

The experiments were conducted in a fixed-bed stainless steel tubular reactor. In every reactor test, 1 g catalyst sample was mounted on the reactor. The experiments were carried out with alumina granules sized 2.5-3.0 mm.
The flow diagram of the system is shown in Fig. 1.

At first, the reactor is purged by an inert gas stream (gas 1). Then, the system is heated to reach the desired temperatures under a mixture of reaction gases. This reacting gas (gas 2) is a combination of CH_4, SO_2, and inert (argon) streams with predefined concentrations.

SO_2, CH_4, and argon inlet concentrations in the mixture were adjusted by three mass flow controllers. The reaction outlet was analyzed online by a Mass Spectrometer (MS) from Leda Mass.

After converting base peak heights to partial pressures, it is possible to plot mole fractions of up to 12 different gases versus time with ppm sensitivity by the mass spectrometer [24].

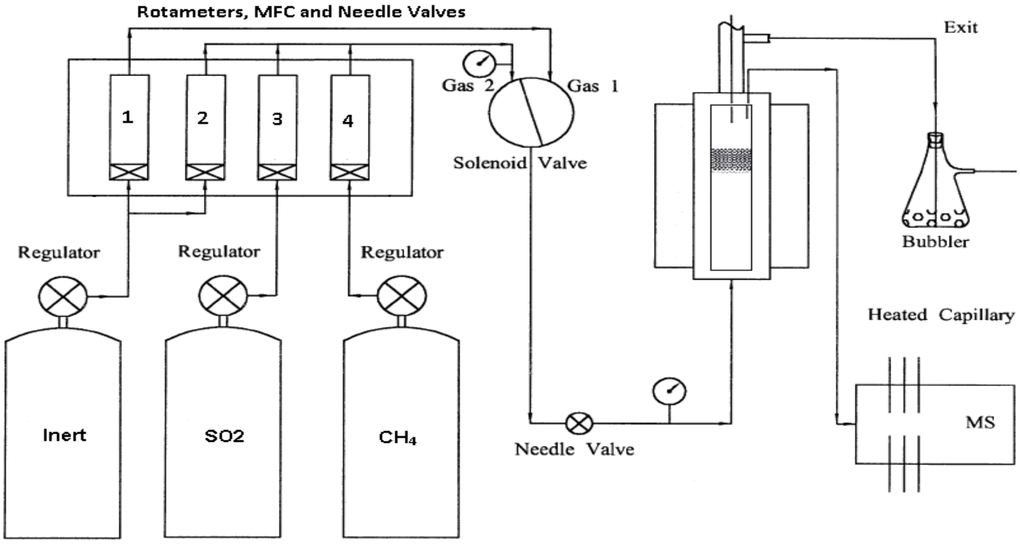

Figure 1. Flow diagram of the reaction test system.

3. Results and discussion

3.1. Catalyst characterization

Table 1 shows the results of BET (Brunauer, Emmett and Teller) specific surface area, total pore volume, and average pore diameter of the catalysts.

Table 1
BET specific surface area, total pore volume, and average pore diameter of the synthesized catalysts.

Sample	S_{BET} (m^2/g)	V_{total} (pore volume) (cm^3/g)	Average pore diameter (Å)
Al_2O_3	347.1	0.3786	43.62
Al_2O_3-Cu (5 %)	237.6	0.3630	61.10
Al_2O_3-Ni (5 %)	236.2	0.3705	69.63
Al_2O_3-Cu (10 %)	207.8	0.3499	67.35
Al_2O_3-Ni (10 %)	221.7	0.3641	69.68

The results show that impregnation of copper and nickel (as a promoter on Al_2O_3) decreases the surface area of the catalysts.

This is due to blockage of the support pores during impregnation by copper and nickel nanoparticles. That is the reason why the amount of surface area decreases with increasing amount of metal on support. However, on the other side, copper and nickel nanoparticles (as active metals) showed good performance on catalyst activity.

N_2 adsorption-desorption isotherms of the synthesized catalysts are shown in Fig. 2.

Alumina support catalyst has the highest N_2 adsorption and desorption. With increasing amount of metals on the support, the amount of N_2 adsorbed by the catalyst decreases.

This is quite consistent with a decrease in specific surface area (Table 1). In addition, reduction of total pore volume of the catalysts is a proof to this (Table 1).

BJH pore size distributions of various catalysts are shown in Fig. 3.

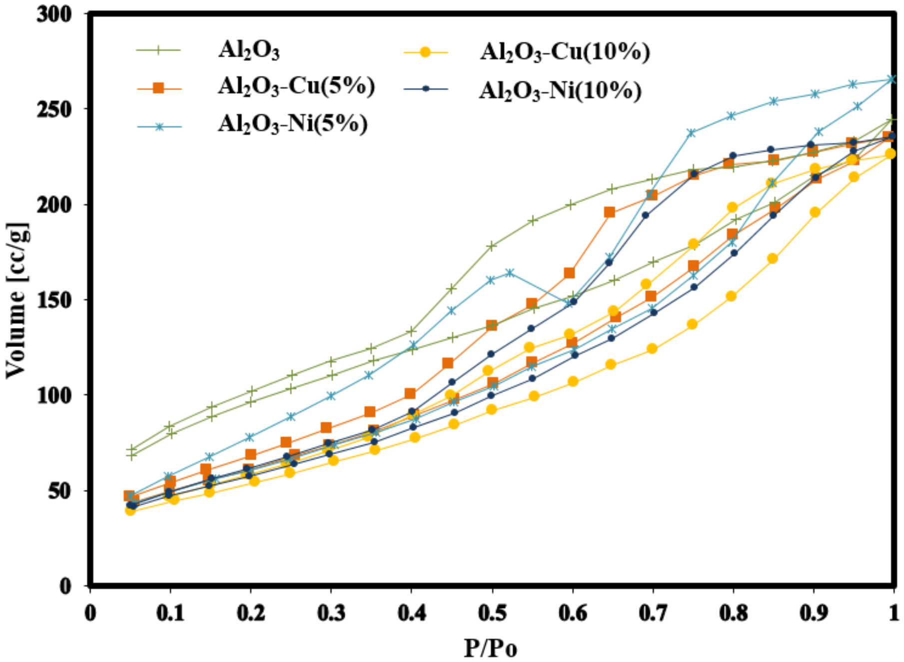

Figure 2. N_2 adsorption-desorption isotherms of the synthesized catalysts.

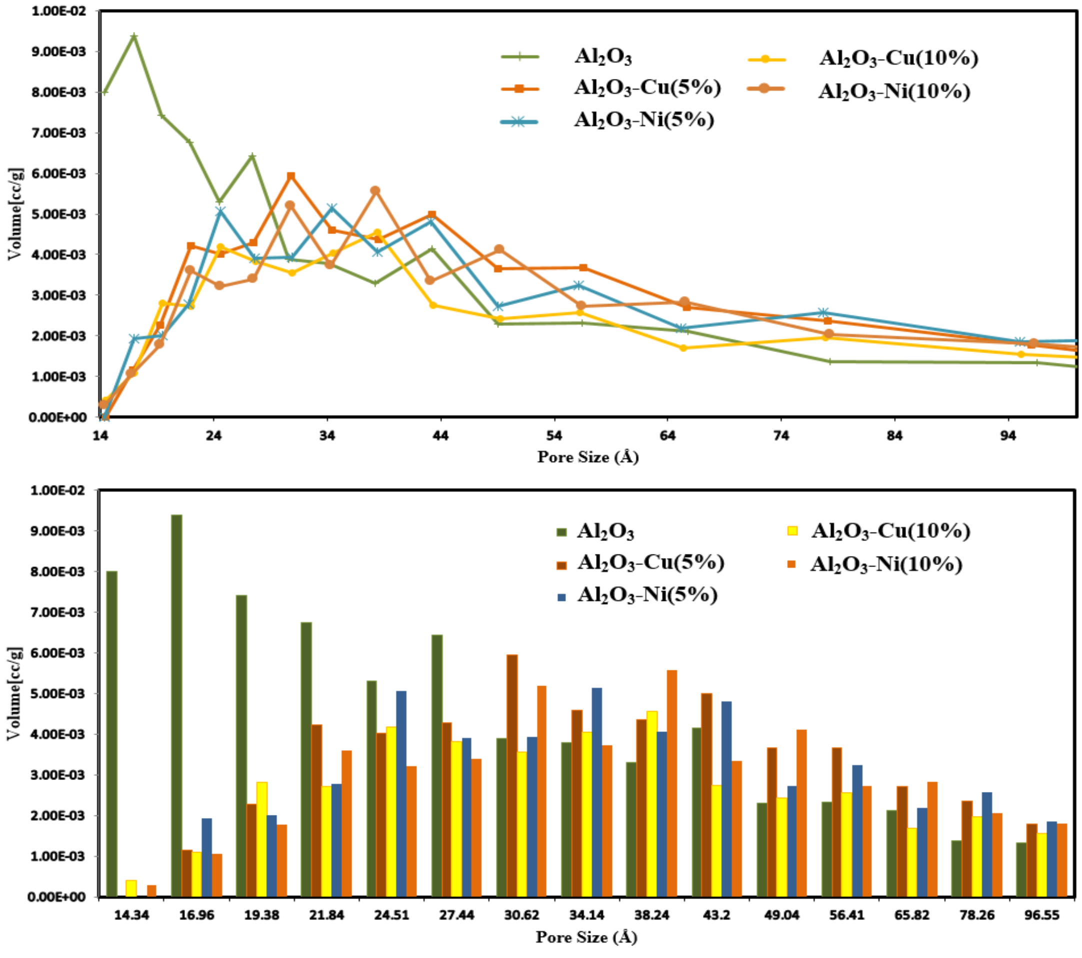

Figure 3. BJH pore size distribution of synthesized catalysts.

This figure indicates that, by adding Cu and Ni, some of the fine pores of alumina are filled because of which Cu-alumina and Ni-alumina catalysts have less total pore volume than alumina (Table 1).

It is quite clear that alumina pores are more evident at low pore sizes than Cu-alumina and Ni-alumina catalysts.

Average pore diameter of catalysts (as shown in Table 1) is completely consistent with Fig. 3.

By adding copper and nickel, the particles penetrate into the alumina pores through impregnation to alumina. This reduces the surface area, pore volume, and N_2 adsorption, yet increases the average pore diameter of the catalysts. However, these metal nanoparticles on the surface and pores of alumina will become active sites for the reaction.

Consequently, total pore volume of alumina is 0.3786 cm^3/g, while this amount is reduced to 0.3499 and 0.3641 for Al_2O_3-Cu (10 %) and Al_2O_3-Ni (10 %), respectively. Similarly, average pore diameters of the catalysts increased from 43.62 Å for alumina to about 67.35 Å for Al_2O_3-Cu (10 %) and 69.68 for Al_2O_3-Ni (10 %).

3.2. Catalysts activity tests

The principal reaction for SO_2 reduction by CH_4 can be represented as Eq. (1). The main side-reaction that may occur between sulfur dioxide and methane is illustrated through Eq. (2).

While the first reaction produces a suitable sulfur product, the second reaction produces toxic H_2S and CO gases.

Conversion of SO_2 was calculated from inlet and outlet SO_2 volume fractions.

The following expression was used to calculate SO_2 conversion:

$$X_{SO2} = \frac{V_{SO2_{in}} - V_{SO2_{out}}}{V_{SO2_{in}}} * 100$$

where $V_{SO2_{in}}$ and $V_{SO2_{out}}$ are volumetric velocity of SO_2 at the reactor inlet and outlet, respectively.

Sulfur yield was estimated from the difference of all sulfur compound mole fractions (including H_2S, COS, CS_2, and unreacted SO_2) from inlet SO_2 mole fraction.

SO_2 conversions for various catalysts are presented in Fig. 4 versus operating temperature.

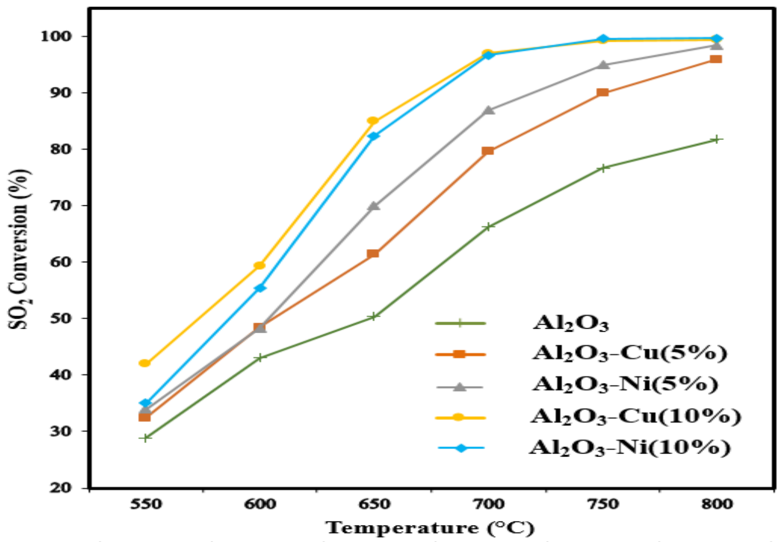

Figure 4. SO_2 conversion as a function of temperature for different catalysts (2 % SO_2–1 % CH_4–Ar; S.V. =3000 mL/h^{-1}).

At 550 °C, SO_2 conversation rate is very low. When the temperature increases, SO_2 conversion rate extremely increases for all catalysts. This shows that the reaction is strongly temperature dependent.

In the temperature range of 550-800 °C, all the Cu-alumina and Ni-alumina catalysts perform much better than alumina. This indicates that metal has a very good effect on catalyst performance. In addition, the choice of copper and nickel, as a prompter for this reaction, is very suitable.

By increasing the amount of metal from 5 to 10 % for both catalysts, the conversions greatly increased.

As shown in Fig. 4, Al_2O_3-Cu (10 %) catalyst has a much better performance than other catalysts at 550 °C. At 600 and 650 °C, Al_2O_3-Cu (10 %) performance is slightly better; however, Al_2O_3-Cu (10 %) and Al_2O_3-Ni (10 %) show similar performance at 700, 750, and 800 °C. For Al_2O_3-Cu (10 %) and Al_2O_3-Ni (10 %), the conversion was almost complete at 750 °C and higher temperatures, which was a very good result for these catalysts.

Regarding the addition of copper and nickel to alumina, these nanoparticles are to be placed on the surface of alumina. Moreover, like nanoparticles, they penetrate into alumina pores, reducing the surface area and total pore volume of the catalyst (Table 1). After placing nickel and copper nanoparticles on alumina, density of moderate and weak acids increased significantly [25]. This is due to replacement of nickel and copper with bronsted strong acid sites. Whereas nickel and copper created weak and moderate acid sites, leading to an increase in weak and moderate acid sites after modification with this metals.

In addition, it is mutually observed that amount of strong acid site is reduced. Weak and moderate acid sites are more suitable for SO_2 reduction with methane, while their increase results in increased activity of the catalyst. Accordingly, catalyst activity of Al_2O_3-Cu (10 %) and Al_2O_3-Ni (10 %) increased greatly, compared to Al_2O_3. Similarly, for Al_2O_3-Cu (5 %) and Al_2O_3-Ni (5 %), catalyst activity increased due to an increase in weak and moderate acid sites.

However, because of minor increase in amounts of weak and moderate acid in them, compared to Al_2O_3-Cu (10 %) and Al_2O_3-Ni (10 %), their catalytic activity is less than Al_2O_3-Cu (10 %) and Al_2O_3-Ni (10 %). Partial pressure curves of H_2S produced from the reactions for different catalysts are compared in Fig. 5.

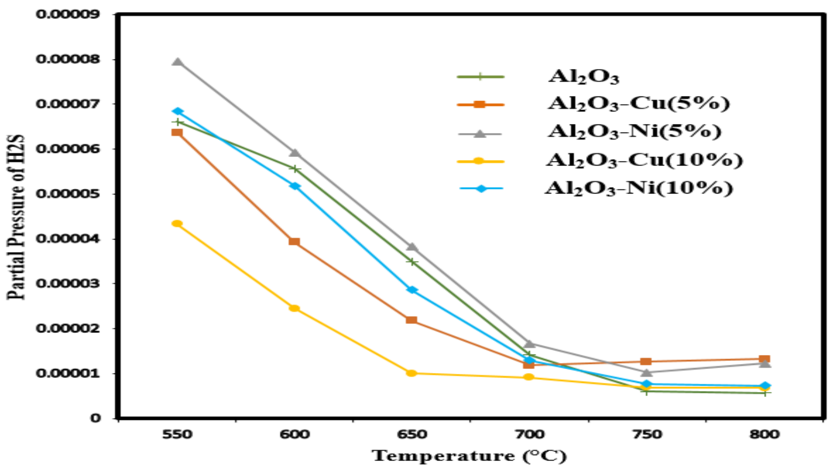

Figure 5. Partial pressures of H_2S versus temperature for different catalysts.

At the temperatures lower than 700 °C, copper-alumina catalyst has a better performance than nickel-alumina and produces lower amount of H_2S. However, at 750 and 800 °C, Al_2O_3-Cu (10 %) and Al_2O_3-Ni (10 %) catalysts show similar performance, and the amount of produced H_2S is very low for both catalysts. At high temperatures, Al_2O_3-Cu (5 %) produces H_2S more than other catalysts.

For all the catalysts, by increasing the temperature, the amount of H_2S decreased.

This is contrary to the increased SO_2 conversion with temperature. Because, at lower temperatures, the conversion is incomplete and there is large amount of unreacted CH_4 and SO_2. The unreacted CH_4 can be decomposed, according to Eq. (3). According to Eq. (4), it is likely that H_2 is reacted catalytically with SO_2 to form H_2S and water.

Given that no significant amount of hydrogen is produced and that H_2S is decreased with increased conversation rate, this possibility is confirmed [13].

It is noteworthy that, at all temperatures, the amount of produced H_2S is very low.

COS partial pressure profiles from the reaction versus temperature for different catalysts are illustrated in Fig. 6.

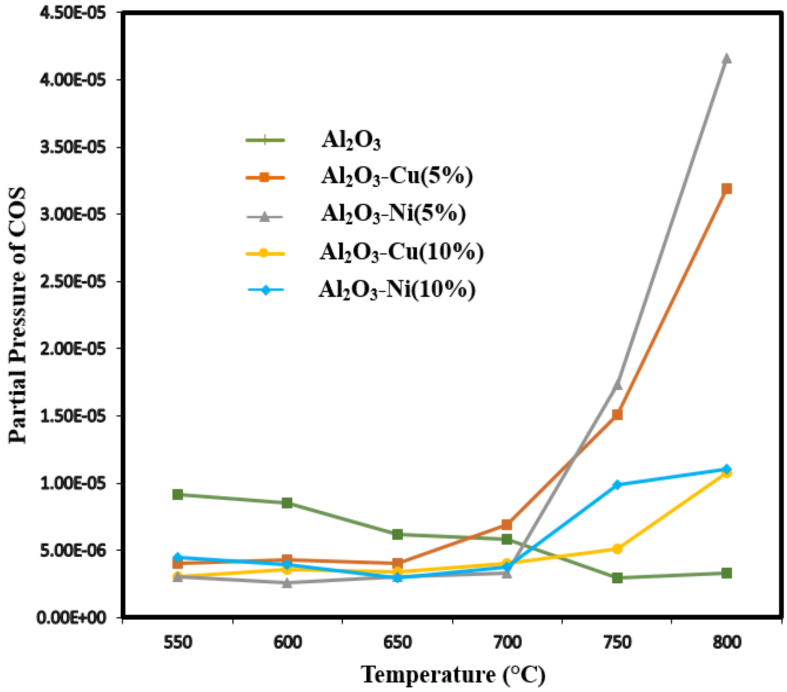

Figure 6. Partial pressures of COS versus temperature for different catalysts.

The amounts of COS produced for Cu-alumina and Ni-alumina catalysts are less than alumina at temperatures lower than 700 °C, while the amount of COS produced by Cu-alumina and Ni-alumina catalysts increases at higher temperatures, and they produce more COS than Al_2O_3.

At temperatures below 700 °C, the amount of COS produced by Cu-alumina and Ni-alumina catalysts is very low. However, when the temperature passes 700 °C, COS production increases. This increase in Al_2O_3-Cu (5 %) and Al_2O_3-Ni (5 %) catalysts is much more severe. Pure alumina catalyst shows quite opposite behavior. This may be due to the fact that the amount of CS_2

production increases [22], while such an increase does not occur for Al_2O_3, and this CS_2 reacts with CO_2 to produce COS, as shown in the following reaction:

$$CS_2 + CO_2 \rightarrow 2COS \quad (6)$$

Of note, Al_2O_3-Cu (10 %) and Al_2O_3-Ni (10 %) catalysts have almost similar performances. Moreover, complete conversion for these catalysts prevents production of CS_2 and, thus, COS.

In general, the important thing is that total amount of H_2S and COS is negligible and catalyst selectivity is more than 99.5 %.

Formation of CS_2, as the reaction by-product, was not observed in the experiments. This is probably due to reaction (6) which converts this gas to COS.

The effects of changing molar SO_2/CH_4 ratio on the conversion of SO_2 as well as production of H_2S and COS are shown in Figs. 7 and 8(a-b), respectively.

When SO_2/CH_4 ratio is equal to 3, SO_2 is in excess of stoichiometric ratio required for reaction, and the conversion efficiency drops drastically.

This is completely rational because there is not enough methane for the reduction of all SO_2. By reducing SO_2/CH_4 ratio from 3 to 2, the conversion rate increased rapidly to make the conversion almost complete, which was quite expected. In addition, at SO_2/CH_4 ratio of 1, the conversion is complete. This is due to the fact that methane is more than the required amount of stoichiometry; thus, it reactes completely with sulfur dioxide.

3.3. Effects of feed gas composition

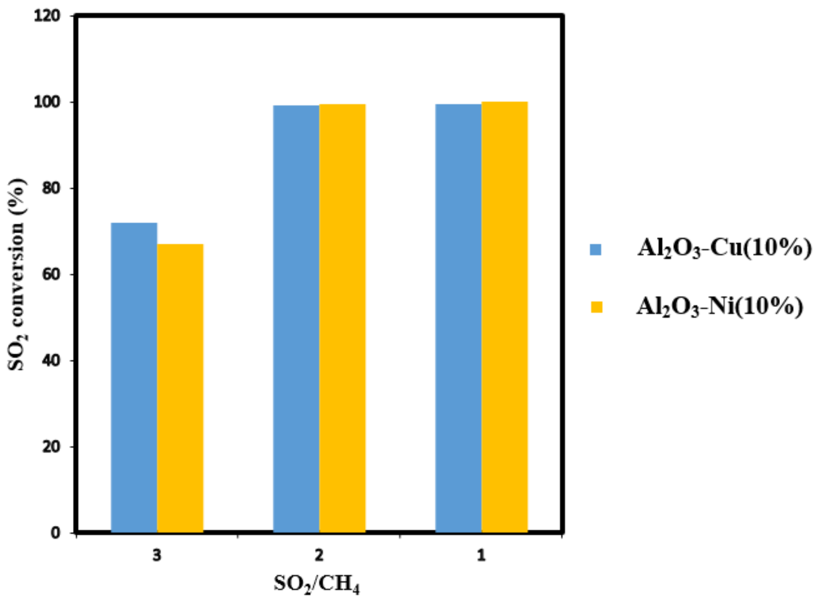

Figure 7. Effects of feed gas composition on SO_2 conversion for Al_2O_3-Cu (10 %) and Al_2O_3-Ni (10 %) catalysts (S.V. = 3000 mL/h^{-1}).

Fig. 8(a) shows that, at stoichiometric feed ratio, the lowest amount of H2S is produced (both catalysts). At SO_2/CH_4 feed ratios of 3 and 1, the amount of produced H2S is increased. For SO_2/CH_4 ratio of 1, this increase is much higher. In addition, COS production in the stoichiometric feed ratio is minimum for Al_2O_3-Cu (10 %) catalyst. While, for Al_2O_3-Ni (10 %) catalyst, at SO_2/CH_4 feed ratios of 3 and 2, the amount of produced COS is low, this amount is increased with decreasing SO_2/CH_4 ratio to 1.

The great increases in productions of H_2S and COS at SO_2/CH_4 ratio of 1 (excess methane) indicate that when methane is in excess of stoichiometric molar ratio, secondary reactions between SO_2 and methane can take place to produce H_2S byproduct according to reaction (2).

Moreover, the excess methane was decomposed according to reaction (3), produced H_2. Then, H_2 reacted with SO_2 and formed H_2S according to reaction (4).

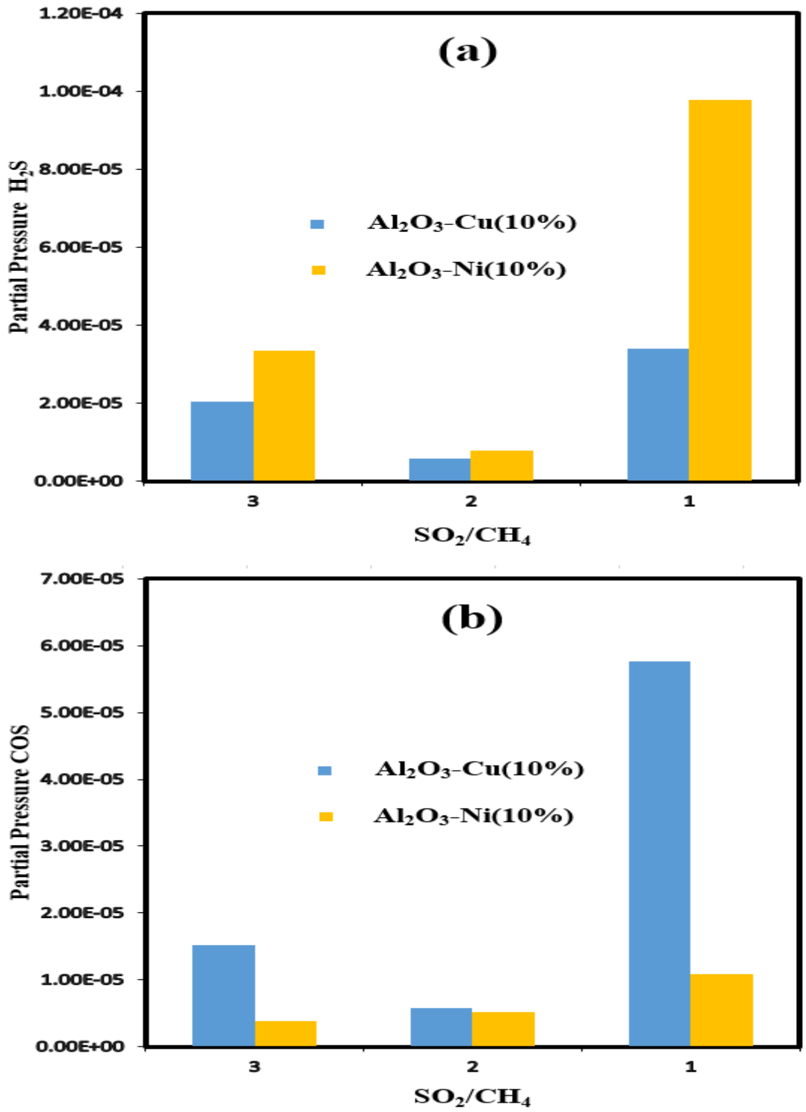

Figure 8. Effects of feed gas composition on the production of (a) H_2S and (b) COS for Al_2O_3-Cu (10 %) and Al_2O_3-Ni (10 %) catalysts (S.V. = 3000 mL/h^{-1}).

On the other hand, the excess methane reacted with elemental sulfur and produced CS_2 according the following reaction:

$$CH_4 + 2S \rightarrow CS_2 + 2H_2 \quad (7)$$

Then, the generated CS_2 produced COS according to reaction (6). Therefore, the amount of COS greatly increased with decreasing SO_2/CH_4 ratio.

It should be noted that, for Al_2O_3-Ni (10 %) catalyst in all feed ratios, the amount of produced H_2S is more than Al_2O_3-Cu (10 %) catalyst.

It probably may be due to the fact that nickel is a good catalyst for methane reforming, and it produces more hydrogen. This hydrogen increases the amount of H_2S produced (reaction 4).

Given that, at a stoichiometry feed ratio, SO_2 and CH_4 are consumed completely, there is no excess methane and sulfur dioxide, and the least side products are produced. Therefore, the stoichiometric feed ratio is the best choice for this system.

3.4. Stability of catalyst

Considering that Al_2O_3-Cu (10 %) and Al_2O_3-Ni (10 %) showed the best performance among all the catalysts, their stability as the best catalysts was tested at 750 °C for 5 h. The results are presented in Fig. 9.

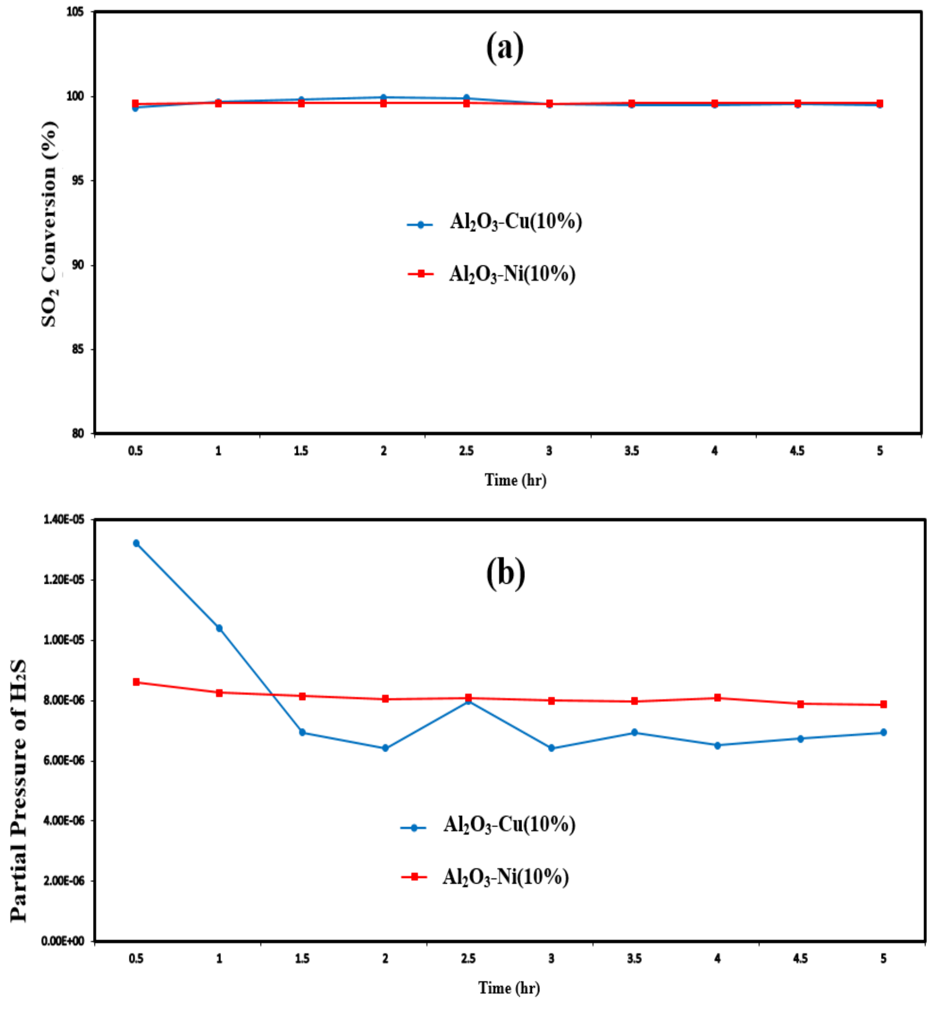

Figure 9. Effect of reaction time on (a) SO_2 conversion and (b) H_2S production over Al_2O_3-Cu (10 %) and Al_2O_3-Ni (10 %)(2 % SO_2–1 % CH_4–Ar; S.V. = 3000 mL/h^{-1}).

As illustrated in Fig. 9(a), both catalysts exhibited good stability during 5 hours, and the conversion rate was almost constant. Fig. 9(b) shows the amount of H_2S production in the stability test.

For Al_2O_3-Cu (10 %) catalyst, at the beginning of stability test, the amount of H_2S was slightly high. However, it was diminished quickly. H_2S production for Al_2O_3-Ni (10 %) catalyst shows almost the same trend at all times.

In general, it is worth mentioning that the amount of H_2S production for both catalysts is negligible, and they show very good selectivity during the stability test.

Coke production can be the main cause of catalyst deactivation. Coke can be produced by decomposition of methane according to reaction (3).

However, a very important advantage of the process is the production of water vapor since it is a very functional agent for coke removal. In the main reaction, per each mole of sulfur dioxide, two moles of water vapor are produced, and this vapor can consume the deposited coke as follows:

$$C + H_2O \rightarrow CO + H_2 \quad (8)$$

Consequently, using coke by produced steam from the main reaction can prevent the catalyst against deactivation. As regards, the catalysts showed good stability for SO_2 reduction with methane.

4. Conclusions

In this study, SO_2 reduction by CH_4 over alumina, Cu-alumina, and Ni-alumina was examined and compared. Both kinds of modified alumina (with 5 and 10 weight percent of loading metal) were prepared by the wet impregnation technique. Performances of all the catalysts were tested at the temperature range of 550–800 °C in a fixed-bed pilot reactor.

The reactor tests showed that the reaction was strongly temperature dependent. The catalysts with copper and nickel showed a much better performance than pure alumina. At temperatures lower than 700 °C, Al_2O_3-Cu (10 %) catalyst showed the best performance. However, at 700, 750, and 800 °C, Al_2O_3-Cu (10 %) and Al_2O_3-Ni (10 %) catalysts showed similar performances.

For Cu (10 %) and Al_2O_3-Ni (10 %) catalysts, about 100 % SO_2 conversion and more than 99.5 % selectivity was obtained at 750 and 800 °C. After studying the effect of molar feed ratio of SO_2/CH_4 between 1 to 3, it was found that the best feed ratio for this reaction was the stoichiometric molar feed ratio, since the highest conversion and the least amounts of H_2S and COS were produced in this molar feed ratio and the side-reactions were well controlled. In addition, long-term stability of the catalysts was tested during 5 hours, and the catalysts showed a good long-term lifetime for SO_2 reduction.

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