Synthesis of nanostructured CuO/ZnO/Al$_2$O$_3$ low temperature water-gas shift catalyst

Soheil Saffary [a], Reza Roohollahi [a], Amin Mardanloo [a], Hassan Navaei [a]

[a] Kharazmi Technology Development Company, Alborz, 31648-83171, Iran, saffari@kharazmi-rt.com
[a] Kharazmi Technology Development Company, Alborz, 31648-83171, Iran, roohollahi@kharazmi-rt.com
[a] Kharazmi Technology Development Company, Alborz, 31648-83171, Iran, mardanloo@kharazmi-rt.com
[a] Kharazmi Technology Development Company, Alborz, 31648-83171, Iran, navaei@kharazmi-rt.com

Abstract:

Current low temperature water gas shift catalyst with the composition of mixed oxides of copper, zinc and aluminum is commonly being used in water gas shift (WGS) reactors in petrochemical and refinery plants in order to remove carbon monoxide from gas streams especially synthesis gas. In this contribution, LTS catalyst is prepared by co-precipitation of mixed nitrate solution of copper, zinc and aluminum under a strict control of pH and temperature thought the synthesis stage. The microstructure of the final prepared material was characterized using XRD, TEM and physisorption analysis. The activity of the prepared catalyst in WGS reaction was compared with the commercial LTS SiftMax-210 catalyst. The analysis showed that particle diameter of the synthesized catalyst is smaller than 50 nanometer and the average crystallite size of CuO phase as the potential active site was 9 nm. The Surface area of the sample and pore volume was relatively higher than the commercial sample while the pore size distribution was narrower. Ultimately, the activity of the synthesized sample was higher than that of the commercial sample.

Keywords: co-precipitation, water-gas shift catalyst

Introduction

Synthesis gas (mixture of hydrogen and carbon monoxide) is one of the main feedstocks in chemical industries. However, the H2/CO ratio or CO content in the synthesis gas should be prepared according to the process demand. In order to regulate the H2/CO ratio in the industrial units, CO should be converted to CO$_2$ via water-gas shift (WGS) reaction, Eq. 1.

CO $_{(g)}$ + H$_2$O $_{(g)}$ → CO$_2$ $_{(g)}$ + H$_2$ $_{(g)}$ (1)

ΔH= -9.84 kcal/mole at 298K
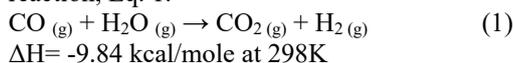
Common commercial low temperature shift (LTS) catalyst is comprised of CuO, ZnO and Al$_2$O$_3$. This catalyst is activated through the reduction of CuO to metallic Cu which is the catalyst active site for the WGS reaction [1-3].

Different synthesis methods for the preparation of CuO/ZnO/Al$_2$O$_3$ catalyst is reported in the literature such as co-precipitation of mixed aqueous salt solution (nitrate, sulphate, acetate …) of the metals by an alkali solution like sodium carbonate [3,4], sol-gel [5], mechanical milling [6] and impregnation of the active element in catalyst base [4]. Among these methods, co-precipitation is the most common and appropriate rout for preparation of CuO/ZnO/Al$_2$O$_3$ catalyst precursor [3,8]. With the advent of nanotechnology co-precipitation synthesis method has been of interest to researchers as a method for synthesis of nano sized powders [8].

The activity and stability of the catalysts prepared by co-precipitation method is highly dependent on even small variation on the synthesis parameters like pH, temperature, ageing time and etc. Therefore, optimization and precise control of the synthesis conditions during the precursor preparation is vital [9]. In this study, it was tried to strictly control the synthesis parameters with the aid of an automatic co-precipitation setup, Fig 1, equipped with pH and temperature controller in order to prepare a catalyst with superior activity.
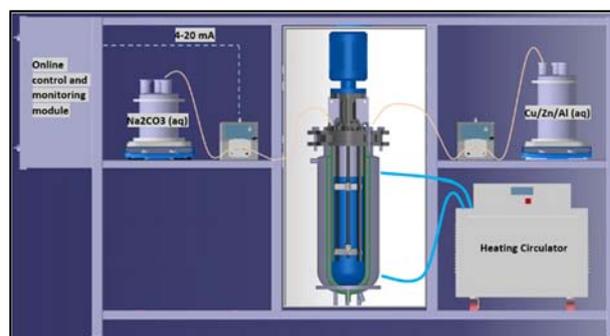

Fig 1. Schematic of the automatic co-precipitation setup equipped with pH and temperature controller.

Materials and method

Preparation of catalyst precursor:

Copper cathode bar, zinc bar and industrial Al(OH)$_3$ powder were dissolved in nitric acid (63%) to prepare Cu/Zn/Al mixed aqueous metal nitrate solution feed. This solution was named as solution A. The materials weight ratios were chosen in order to the composition of final product be 42.5% CuO, 47.5% ZnO and 10% Al$_2$O$_3$ which

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is the composition of the commercial LTS catalyst ShiftMax-210. On the other hand, a 1M solution of sodium carbonate was prepared as the precipitant. This solution was named as solution B. Solution A with the same temperature was added to reactor with the rate of 30 ml/min under vigorous stirring. At the same time, solution B simultaneously injected into the reactor using a slave peristaltic pump at a given rate specified by the pH controller so that the pH of precipitating media remain fixed at 7 thought the injection of the feed solutions. The maximum fluctuation of pH throughout the precipitation step was ±0.05. The slurry aged for 2 hours under vigorous stirring and similar temperature but without pH control. At the end, the slurry was filtrated and the obtained cake washed several times with warm distilled water to remove sodium content. The precipitate then dried at 100°C overnight. The resulted precursor calcined at 350°C for 2 hours. The obtained powder thereafter was shaped to tablets using Lab scale pressing machine to the sizes of 6*4 mm.

Characterization methods:

XRD data were collected on a PHILIPS PW1800 diffractometer using CuKα radiation. TEM images were taken on a Zeiss-EM10C microscope operated at 100 kV. Specific surface areas, pore volume and pore size of product were determined by nitrogen physisorption in a Micromeritics TriStar II Plus machine. The activity of the catalysts in the WGS reaction was obtained in a screening test in which at first catalysts were activated (CuO areas reduced to Cu) through passing a mixture of H_2/N_2 over the catalyst. Then feed gas which is an appropriate mixture $H_2O/CO/CO_2/H_2/N_2$ was passed over catalyst and the outlet gas was analysed by an Agilent 7890A gas chromatography equipped with 2 TCD to calculate the CO conversion.

Results and Discussion

Structure characterization:

Image and the XRD spectrum of the prepared LTS catalyst tablets are shown in Fig 2-a and Fig 2-b, respectively. Main peaks of the CuO structure can be seen in the XRD spectrum. Two of the main peaks of the ZnO structure at $2\theta = 34.4°$ and $36.5°$ overlap to the peak at $2\theta = 35.4°$ belonging to CuO structure and have made a pretty wide peak in the spectrum, but the weak peaks which can be distinguished at $2\theta = 31.8°$ and $2\theta = 47.8°$ confirm the presence of ZnO phase. Average crystallite diameter of CuO phase calculated by Debby-Scherrer [10] formula $(L=k\lambda/\beta Cos(\theta))$ is 9 nm. This calculation is based on the most intense peak at $2\theta = 38.74°$ which doesn't overlap with any of the ZnO peaks.

TEM image of the synthesized catalyst powder is shown in Fig 3. As indicated, the distinct grains with the size smaller than 50 nm can be seen in the image. High resolution TEM images prepared by Behrens [4] from a nano-structured $CuO/ZnO/Al_2O_3$ catalyst that he

synthesized by co-precipitation method revealed that the catalyst grains are in fact poly-crystals composed of distinct areas of copper, zinc an aluminium oxides.
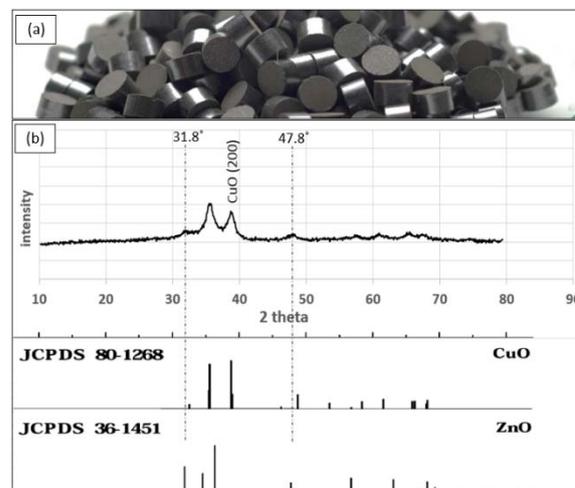

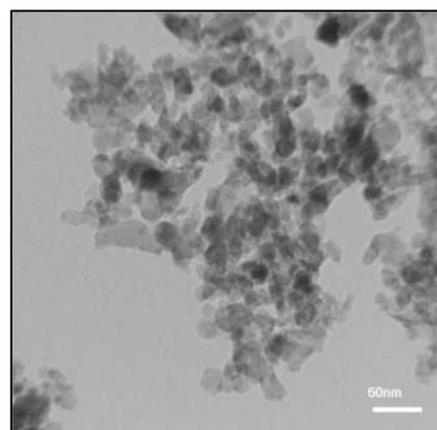Fig 2. Image of the prepared catalyst tablets (a) and the XRD spectrum of the synthesized catalyst powder (b).

Fig 3. TEM image of the synthesized catalyst powder.

Physisorption analysis:

As indicated in Table 1, the surface area of the synthesized sample is about 25% higher than that of the commercial sample. Also the pore volume of the synthesized sample is relatively higher. The relatively sharper pore size distribution and more uniform channel like pores of the synthesised sample in comparison with commercial ShiftMax-210 catalyst is distinguishable in Fig 4 and Fig 5, respectively.

Table 1: Pore Analysis for the synthesized sample and the reference commercial sample

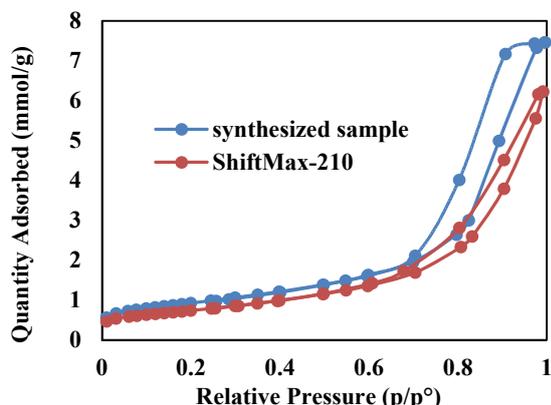| Sample name	BET (m^2/g)	Pore size (nm)	Pore volume (cm^3/g)
ShiftMax-210	59.4	11.2	0.216
Synthesized Sample	74.1	10.2	0.259

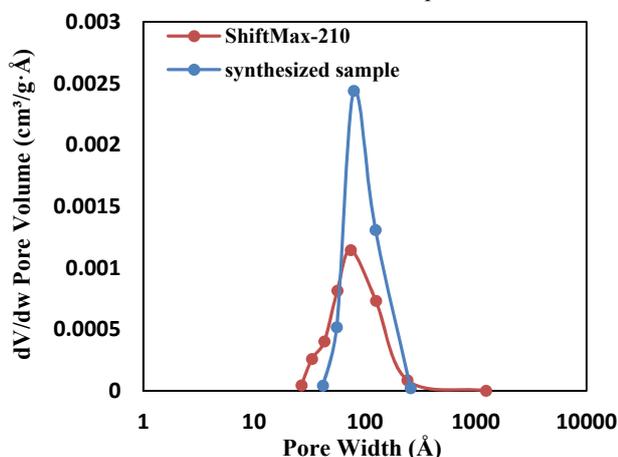Fig 4. Isotherm reference plot of the sythesized sample and the reference commercial sample

Fig 5. BJH Desorption dV/dw Pore Volume of the synthesized sample and the reference commercial sample.

Activity result:

The trend of catalyst performance for the synthesized and ShiftMax-210 in terms of CO conversion in WGS reaction is represented in Fig 6. As the figure shows the activity of the synthesized sample is higher than that of commercial ShiftMax-210 catalyst with a satisfactory stability.
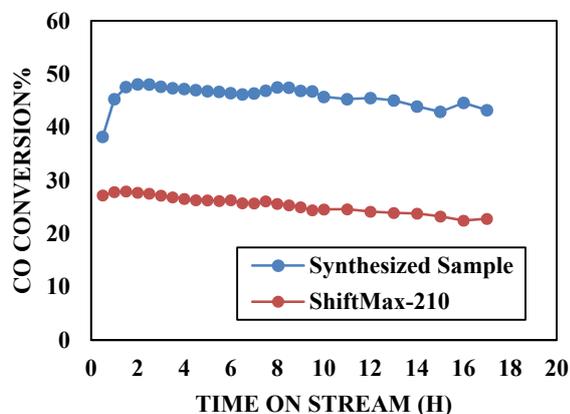

Fig 6. CO conversion activity of the synthesized catalyst and the reference ShiftMax-210 commercial catalyst.

Conclusion

LTS catalyst composed of $CuO/ZnO/Al_2O_3$ prepared via co-precipitation method under a strict control of pH and temperature. To summarize, the synthesized sample had a nano-metric microstructure with fine and uniform texture and appropriate pore distribution which resulted in superior operation compared with the commercial sample.

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