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Effect of reaction conditions on the activity of novel carbon nanofiber-based Cu/ZrO$_2$ catalysts for CO$_2$ hydrogenation to methanol

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Abstract. The increasing concentrations of CO$_2$ in the environment result in catastrophic phenomena like global warming. Hydrogenation of emitted CO$_2$ to methanol is one of the economically viable strategies to tackle the problem. In the current work, methanol synthesis by CO$_2$ hydrogenation was studied over carbon nanofiber-based Cu/ZrO$_2$ catalysts. The effect on rate of reaction by varying reaction temperature, reaction pressure, and feed gas ratio were investigated. Rate of reaction increased with increasing temperature and 220 °C was found as an optimum reaction temperature. The study revealed a linear relationship between the rate of reaction and applied pressure of the feed gases. The rate of reaction was accelerated by increasing feed gas ratio and the highest activity was recorded for $H_2/CO_2 = 3$.

Keywords. CO$_2$ conversion, Effect of reaction conditions, Temperature effect, Feed gas ratio, Pressure effect.

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1. Introduction

Global warming, due to emissions of greenhouse gases such as CO$_2$, is one of the catastrophic phenomena faced by the world today. Many strategies have been devised for the reduction of CO$_2$ emissions; however, CO$_2$ conversion to methanol provides a vital route as it diminishes CO$_2$ concentration on the one hand and produces valuable fuel like methanol on the other [1–4].

Methanol synthesis is generally carried out by using a mixture of CO$_2$ and syngas at the indus-

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trial level [5]. However, pure CO_2 hydrogenation to methanol is more preferable than traditional syngas gas route from the environmental point of view. Methanol synthesis by syngas route has been extensively investigated; however, literature on the former route is very limited [6]. The performance of catalysts for pure CO_2 conversion to methanol has been affected by various reaction parameters like reaction pressure, temperature, and composition of feed gases. In general, rate of reaction is directly proportional to the reaction temperature. Nevertheless, reaction temperature for CO_2 reduction to methanol has not been univocal in the literature. Rate of methanol synthesis by CO_2 hydrogenation was increased by increasing reaction temperature and 220 °C was recorded as an optimum reaction temperature [7]. Likewise, according to An *et al.* [8], 250 °C was reported as the maximum reaction temperature for best methanol selectivity and CO_2 conversion. Similarly, both methanol production and CO_2 conversion were enhanced by increasing temperature up to 250 °C [9].

Thermodynamically, according to Le Chatelier's principle, high reaction pressure is favorable for CO_2 hydrogenation to methanol. Liu *et al.* [10] claimed that CO_2 hydrogenation to methanol could be synthesized at a low reaction pressure of 20 bar. Another study carried out by Liaw *et al.* [11] summarized that at 210 °C methanol yield was higher when increasing the total reaction pressure.

CO_2 reduction to methanol is also affected by variation of feed gas ratio. From the thermodynamic point of view, $H_2/CO_2 = 3$ is considered favorable for the process. Nevertheless, this factor has also been quite debatable in the literature. Methanol synthesis by CO_2 hydrogenation at various feed gas ratios and constant reaction temperature 260 °C and pressure 360 bar over $Cu/ZnO/Al_2O_3$ catalyst was investigated by Bansode and Urakwa [12]. They observed remarkable increase in the rate of methanol synthesis as well as CO_2 conversion by increasing feed gas H_2/CO_2 ratio from 3 to 10. Such results were also documented by Kim *et al.* [13] for CO_2 hydrogenation to methanol carried out in a slurry phase reactor. In summary, CO_2 reduction to methanol is affected by the magnitude of reaction conditions and hence performance of the catalysts is determined by the reaction medium.

The current work describes CO_2 reduction to methanol over Cu/ZrO_2 catalysts supported by CNFs. Furthermore, the effect of reaction parameters such as pressure, temperature, and feed gas composition on the performance of the catalysts were also studied.

2. Experimental section

2.1. *Catalysts synthesis*

Deposition precipitation method was adopted to synthesize CNF-based Cu/ZrO_2 catalysts. The detailed procedure for catalysts synthesis has been documented elsewhere [14–16]. Catalysts $Cu{\cdot}ZrO_2/CNFs$ with 15 wt% each of Cu and ZrO_2 with CNFs as a support were synthesized. The prepared catalysts were cooled, filtered and dried overnight at 100 °C. The dried catalysts were calcined under N_2 flow at 450 °C for 3 h. A 0.5 g of pre-reduced catalysts (reduced in H_2 for 6 h with 2000 $cm^3\ h^{-1}$ flow rate at 380 °C) was used for reaction studies.

2.2. *Variation of reaction parameters*

Parr autoclave slurry reactor model, Parr 4593, was employed for the activity studies of the catalysts. The detailed procedure is reported elsewhere [17,18]. Methanol synthesis via CO_2 hydrogenation was first optimized in terms of reaction temperature. Hence, a range of reaction temperatures: 180, 200, 220, and 240 °C, was selected at constant reaction pressure of 30 bar. After an optimized reaction temperature was identified, methanol synthesis was tested at different reaction pressures of 20, 30, 40, and 50 bar at a constant reaction temperature of 220 °C. Similarly, the effect of feed gas ratio was also studied by carrying out methanol synthesis at different H_2/CO_2 ratios of 0.8, 1.5, and 3 at 220 °C and 30 bar reaction temperature and pressure respectively. Methanol content was evaluated by using flame ionization detector (FID). Gas chromatography GC Agilent 6890 was employed for the current study.

Methanol synthesis rate was calculated by the following equation:

$$\text{Rate of methanol yield} = g \text{ of methanol produced}/\text{kg of catalyst} \times h$$

3. Results and discussions

3.1. *Effect of reaction temperature*

The rate of methanol synthesis was studied in a slurry reactor at fixed pressure of 30 bar in a range of 180–240 °C. The correlation of reaction temperature and methanol synthesis rate is displayed in Figure 1.

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$$
$$\Delta H^0{}_{298\ K} = -49.5\ kJ/mol \qquad \text{(reaction 1)}$$

As shown by (reaction 1), reduction of CO_2 to methanol is exothermic in nature so that low temperature is thermodynamically favorable. However, keeping in mind the higher stability of CO_2, some adequate energy is required for breaking such a stable molecule. Moreover, methanol synthesis rate increases kinetically with the increasing reaction temperature. Therefore, the methanol productivity is controlled by kinetics as well as thermodynamics. A maximum methanol synthesis rate is obtained at the critical point where the reaction transitions from kinetics to thermodynamics. This critical point of reaction depends on a number of reactivity factors like the nature of the catalyst, the number of active sites and the exposure of such catalyst sites to the approaching reactant molecules. Therefore, literature regarding the critical point is not univocal and different degrees of temperature are reported by different catalysts and operating systems. Similarly, reverse water gas shift reaction (RWGS) is also associated with the main CO_2 hydrogenation to methanol (reaction 2).

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$
$$\Delta H^0{}_{298\ K} = +41.2\ kJ/mol \qquad \text{(reaction 2)}$$

As RWGS is endothermic in nature, an increase in reaction temperature facilitates this reaction. Likewise, an increase in reaction temperature can also bring about the decomposition of methanol to CO, according to (reaction 3).

$$CH_3OH \rightleftharpoons CO + 2H_2$$
$$\Delta H^0{}_{298\ K} = +90.64\ kJ/mol \qquad \text{(reaction 3)}$$

In the current case, methanol synthesis rate was increased by increasing reaction temperature. The optimum rate was observed at 220 °C before it declined at the highest reaction temperature of 240 °C. A similar trend of methanol synthesis rate as a function of reaction temperature was documented by Xin *et al.* [8] over Cu/Zn/Al/Zr fibrous catalyst. Similarly, methanol yield as a function of reaction temperature also revealed a similar dependency of methanol synthesis by CO_2 reduction route [19]. The decline of methanol synthesis rate at the highest reaction temperature could be due to the selectivity of RWGS reactions. This can also be further justified by the fact that RWGS reaction has higher apparent activation energy as compared to the methanol formation [20,21]. Therefore, the CO formation rate was faster as compared to methanol formation at higher reaction temperature. Likewise, the decomposition of methanol to CO at higher reaction temperature could also be one of the reasons of decreasing methanol synthesis rate.

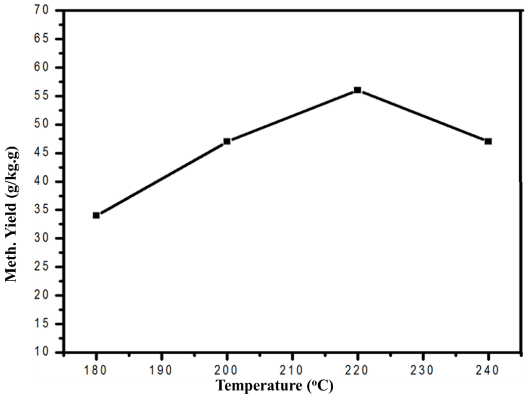

Figure 1. Correlation of reaction temperature and methanol synthesis rate.

3.2. *Effect of pressure*

Methanol synthesis by CO_2 hydrogenation was also studied at different pressures like 20, 30, and 40 bar. Figure 2 shows the correlation of reaction pressure and methanol synthesis rate. As observed, CO_2 reduction to methanol is a molecule decreasing reaction so that it is thermodynamically facilitated at higher pressure. In the current study, a linear relationship was observed between pressure and methanol synthesis rate. Rate of methanol synthesis was increased from 45 to 57 g/kg·h when pressure was increased from 20 to 30 bar. A similar trend of increasing rate was continued with further increase in

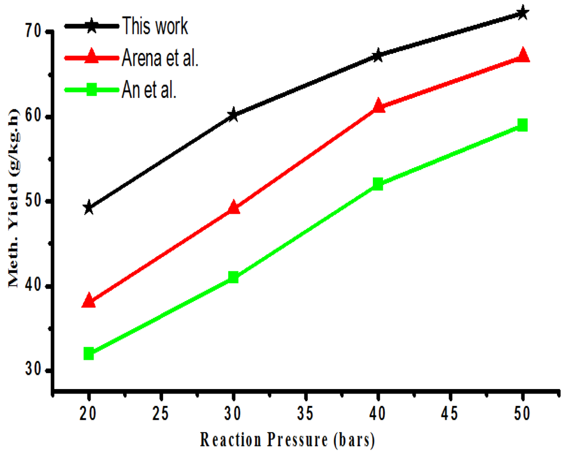

Figure 2. Correlation of reaction pressure and methanol synthesis rate.

pressure and maximum rate was obtained with the highest reaction pressure.

The obtained observations were in good agreement with the work of An *et al.* [8] and Arena *et al.* [22]. Although the process is favorable at high reaction pressure, too high pressure demands higher requirement of materials strength, high cost of operation and it is associated with safety problems.

3.3. *Effect of feed gas composition*

Rate of methanol synthesis by CO_2 hydrogenation was also studied by varying feed gas composition. Figure 3 displays the rate of methanol synthesis as a function of increasing H_2/CO_2 ratio. The methanol synthesis rate was increased from 32 to 41 g/kg·h when the H_2/CO_2 ratio was increased from 0.8 to 1.5. A similar trend was observed with further increase in H_2/CO_2 ratio. This trend is quite understandable keeping in mind the stoichiometric chemistry of CO_2 hydrogenation reaction.

Even though H_2/CO_2 ratio of unity has been favorable for formation of CO as the main product, the rate of methanol synthesis was enhanced by increasing H_2/CO_2 ratio. Equation (reaction 1) rightly justifies this trend, where higher H_2/CO_2 ratio was desirable for better methanol yield. This could be one of the reasons of lower activity of catalyst to methanol synthesis with H_2/CO_2 ratio <3.0. In addition, Shen *et al.* [23], reported similar observations for methanol synthesis via CO_2 hydrogenation over $Cu/Zr/Al_2O_3$ catalyst.

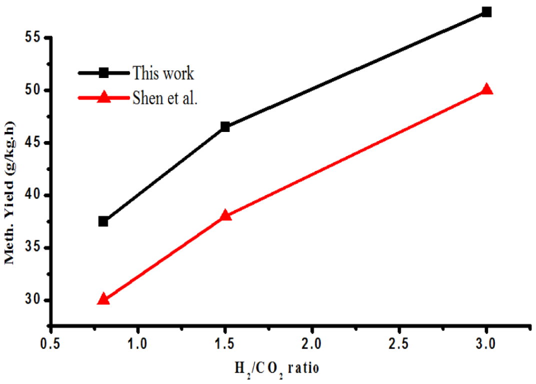

Figure 3. Correlation of H_2/CO_2 ratio and methanol synthesis rate.

4. Conclusion

The current work documented the effect of reaction variables on the CO_2 reduction to methanol. Rate of methanol synthesis was significantly altered with variation in reaction temperature. It was initially raised with increasing temperature and the highest rate was observed at 220 °C before it declined with further increase in temperature. Likewise, the influence of reaction pressure was investigated by conducting the methanol synthesis at different magnitudes of total pressure. It was concluded from the pressure variation study that the rate of methanol synthesis progressively enhanced as a function of increasing total pressure. Finally, rate of methanol synthesis was also optimized in terms of feed gas ratio. The study concluded that a linear relationship existed between the rate of methanol synthesis and the increasing H_2/CO_2 ratio.

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