



Synthesis of Fumed Silica-supported Catalysts for CO₂ Conversion

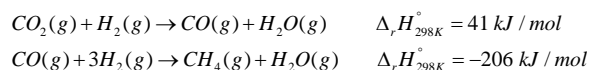
Anand Kumar^{1*}, Ahmed Aheed¹

¹ Department of Chemical Engineering, Qatar University, Doha, P O Box 2713, Qatar

*Corresponding author E-Mail: akumar@qu.edu.qa

1. Introduction

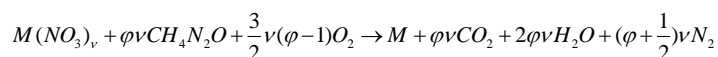
Carbon dioxide is considered as one of the major threats to the ecosystem, mainly by contributing to global warming. This has led major research initiatives in CO₂ capture, storage and conversion [1-4]. On such a track, CO₂ methanation has experienced intensive research due to its thermodynamic favorability under moderate temperature and pressure conditions to complete the so-called carbon cycle. CO₂ methanation is a consequence of two successive chemical reactions; reverse water gas shift (RWGS) and CO methanation [5]:



In this study we investigate the use of nickel and copper based catalysts supported on fumed silica to convert CO₂ to CH₄. Three different catalysts; 1%Ni/fumed-SiO₂, 1%Cu/fumed-SiO₂ & (0.5%Ni+0.5%Cu)/fumed-SiO₂ (weigh ratio basis) catalysts were synthesized through impregnation - followed by combustion method. Catalytic activity and selectivity were evaluated under wide range of temperatures (50°C – 650°C) and 1 atm using a flow reactor with GHSV = 4584.4 cc/g cat/h and feed consisting of exact stoichiometric ratio of H₂:CO₂ = 4:1. Thereafter, the catalyst stability performance was tested at 650°C and 1 atm for 2700 mins of TOS. Moreover, the as-synthesized and the spent catalysts were characterized using different techniques such as XRD, SEM/EDX, TEM, TPR and BET to study the structural properties and to investigate the influence of exposure to reaction conditions on active phases and the SiO₂ support.

2. Methods

First, a base of 3 grams of fumed silica (S.A. 350-420 m²/g) support was measured, then a desired amount of the active agent precursors (Ni(NO₃)₂·6H₂O, and Cu(NO₃)₂·3H₂O were taken and dissolved in water (2 ml for each 1 gram of support). Then, the required amount of fuel (Urea) calculated according to the following reaction was added.



Here M represents metal, and a φ value of 1 was used to calculate the amount of urea. Thereafter, the resultant solution was added to the support via impregnation method. The impregnated support was placed inside an oven under flowing stream of pure N₂ with 10 SCCM. The temperature was allowed to increase till 400°C with rate of 10°C / min, and dwell there for 3 hours. Then, all samples were cooled down, pelletized (600 μ m – 1mm) and tested in a tubular flow reactor (Autoclave Engineers BTRS-JR-PC with inner diameter = 0.8 cm) connected to a GC (Agilent Technologies 7890A with Carboxen 1010 PLOT column and TCD Detector with filament temperature of 150°C) for gas analysis purposes.

3. Results and discussion

1% Ni / fumed-SiO₂ exhibited good activity for CO₂ methanation up till 450°C, subsequently, CH₄ yield decreased and ended at zero at 650°C leaving behind CO as the only product. On the other hand, 1% Cu /

fumed-SiO₂ showed full selectivity towards CO with no CH₄ being detected. However, the bimetallic 0.5% Ni + 0.5% Cu / fumed-SiO₂ catalyst showed intermediate performance till 500°C, after which the synergistic catalytic behavior has been observed. All the three catalysts displayed excellent stability with no deactivation up to 2400 mins TOS. BET area and pore size analysis indicates 1% Cu / SiO₂ to have the largest surface area and pore volume among all synthesized catalysts; however, its catalytic activity was found to be the lowest.

4. Conclusions

Effect of nickel incorporation on Cu/fumed-SiO₂ catalyst for CO₂ hydrogenation reaction was investigated. The catalysts were synthesized (1wt.% Cu/fumed-SiO₂ and 1wt.% CuNi/fumed-SiO₂ (Cu=0.5wt.%, Ni=0.5wt.)) using a localized surface combustion synthesis technique, where a low concentration of metal precursors in presence of an active fuel ensures the combustion to take place on the surface of fumed-SiO₂ support. Both the catalysts were active and stable for CO₂ hydrogenation reaction, with CuNi/fumed-SiO₂ showing more activity than Cu/fumed-SiO₂. Both the catalysts showed selectivity for CO at lower temperature, and some CH₄ production was also observed in presence of nickel. The TPR results indicate a higher dispersion of the metals in presence of nickel. The metal dispersion increased almost four times when nickel was introduced leading to the availability of a large number of active sites, as well as a decrease in the activation energy for CO₂ hydrogenation reaction. DRIFTS studies indicate the formation of a formate and OH species on the surface that gradually decomposes and release CO and H₂O at elevated temperatures. The surface CO intermediate further reacts with the neighboring H intermediate successively to form methane in presence of nickel at temperature above 400°C.

References

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