Sustainable Environment

Effect of Ternary Oxide Promotors (Al_2O_3,CeO_2) on CO_2 Hydrogenation to Methanol over CuO/ZnO Catalyst

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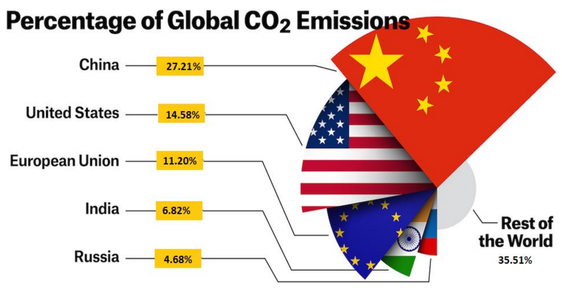
Abstract

Ternary metal oxides are known for providing thermal stability, avoiding sintering and enhancement of active sites for CuO/ZnO catalyst use for CO_2 hydrogenation to methanol. In this study CuO/ZnO/Al_2O_3 and CuO/ZnO/CeO_2 catalyst were synthesized by Co-precipitation and characterized by various characterization techniques XRD,BET,SEM,TEM and H_2-TPR. From the characterization results, it is demonstrated that Cu-ZnO/CeO_2 has high surface area, better dispersion and well-structured morphology. Variable oxidation states of CeO_2 might be responsible for these unique physiochemical properties of respective catalyst. Performance evaluation of this catalyst showed remarkable increment in methanol selectivity than Cu/ZnO/Al_2O_3 which is incoherence with structure of the catalyst.

Introduction

- India continued to increase its CO_2 emissions to 2.47 billion tonnes in 2017, which was 5.1% more than in 2016.
- India has agreed to reduce its CO_2 emissions to 25% from levels in 2005 by 2030 (COP 21 Paris agreement)

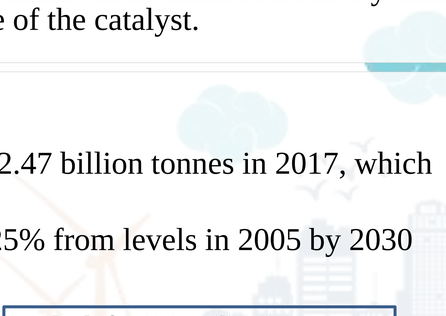


Methods for CO_2 utilization
- Thermo-catalytic
- Photochemical
- Biochemical

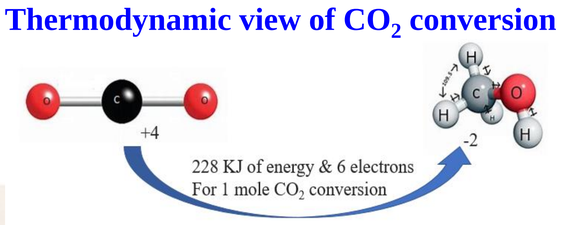
Possible products from CO_2
- Methane
- Formic Acid
- CO
- Methanol
- Dimethyl ether

Remedies to Reduce CO_2 Concentration
- Use of renewable energy sources.
- Hydrogen as a fuel.
- Carbon dioxide Utilization

Applications of Methanol



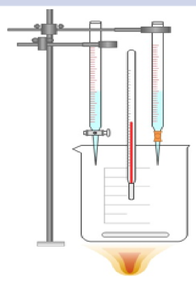
Thermodynamic view of CO_2 conversion



Materials and Methods

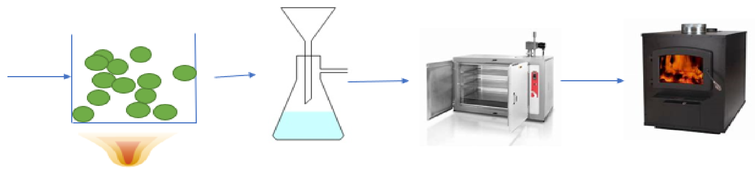
Catalyst Synthesis Procedure

Precipitation → Aging → Washing → Drying → Calcination

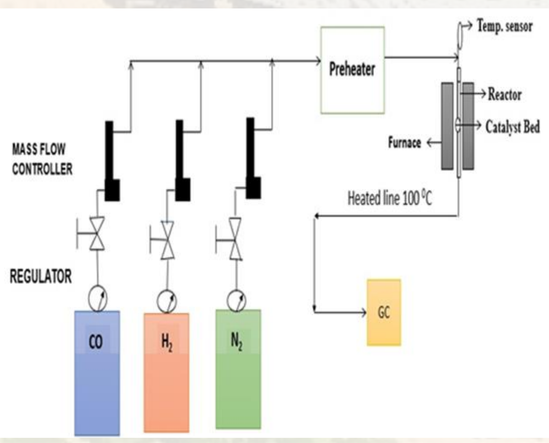


Copper, Zinc and Aluminium nitrate salts and Precipitant(Na_2CO_3)
Temperature 70 ^{0}C ± 5
pH 7 ± 0.5

Aging time 90 min
Drying at 100 ^{0}C over night
Calcination at 500 ^{0}C for 5 hours

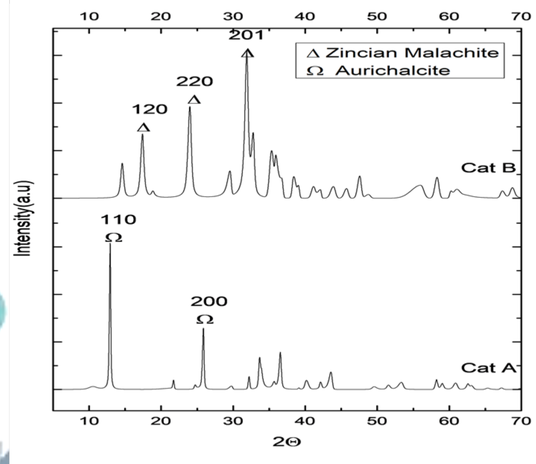


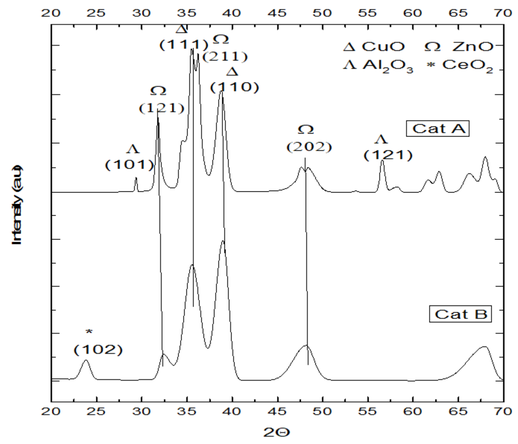
High Pressure Fixed Bed Reactor



Results

XRD





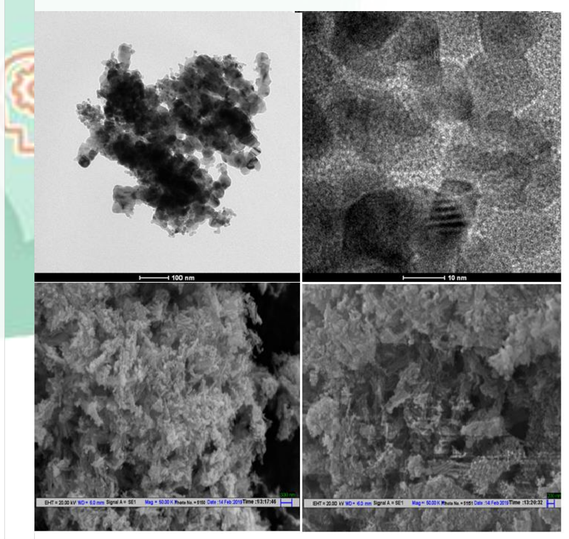
BET

Catalyst	BET surface area(m^2/g)	Pore volume (cm^3/g)	Pore Size(nm)
CuO/ZnO/Al_2O_3 (Cat A)	25.7	0.0076	9.8
CuO/ZnO/CeO_2 (Cat B)	29.8	0.0087	9.3

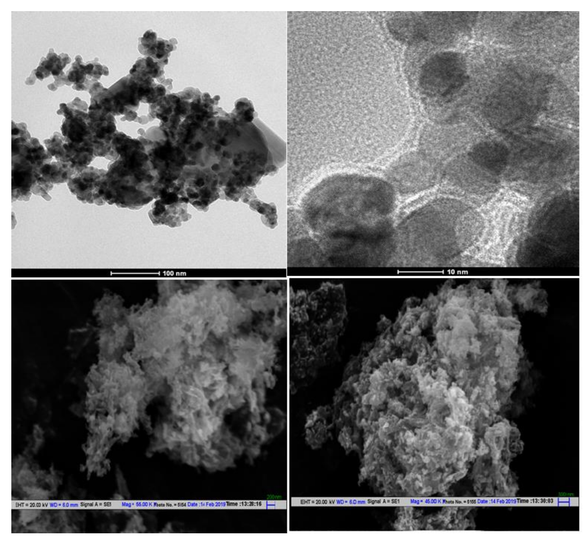
Zincian Malachite precursor phase is enhanced in Cat B, Whereas Aurichalcite if formed for Cat A. CuO of size (Scherrer Equation) 20 nm, and 15 nm are formed for Cat A and Cat B respectively.

BET surface area of Cat B is higher Compared to Cat A might be due to varible Oxidation states for Ce.

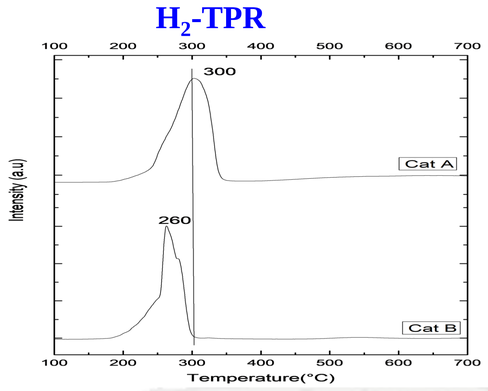
SEM



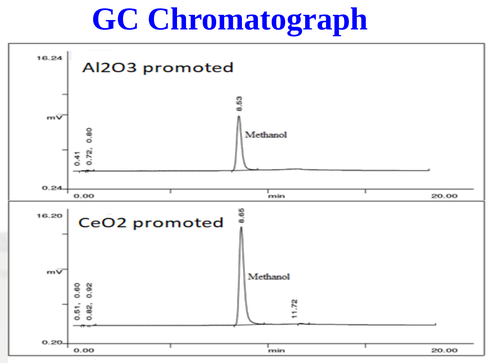
TEM



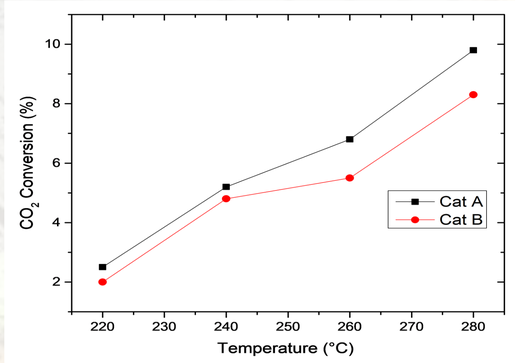
H_2-TPR

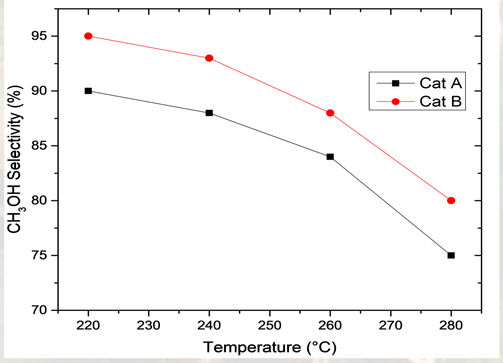


GC Chromatograph



Catalyst Performance Evaluation





- Average CuO size form TEM images is 16 nm and 22 nm for Cat A and Cat B respectively.
- Cat B is reducible at low temperature, signify that a synergetic effect between CeO_2 and CuO.
- Activity Evaluation of catalyst was done at 30 bar pressure, temperature range 220-280 and WHSV 3000 mL/gcat h^{-1} in a fixed bed reactor.
- At 220 °C methanol selectivity was 95% compared to 89% for Cat A, may be due to better dispersion of CuO crystals in presence of CeO_2.

Conclusions

- ❑Malachite phase is known to have the maximum activity for CO/CO_2 hydrogenation
- ❑ CeO_2 promoted catalyst prevents the active sites in the catalyst structure to collapse
- ❑ Side reactions forming higher alcohols and hydrocarbons with increasing temperature resulted in decreased methanol selectivity

Industrial Significance

- ❑Conversion of carbon oxides into value added chemicals helps in mitigation of green house gases in atmosphere
- ❑ Development of fossil fuel utilization and zero carbon emission technologies
- ❑Carbon oxides valorization technologies helps in reduced depletion of fossil fuels for industrial processes

References

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2. Chang, K., Wang, T. & Chen, J. G. (2017). Hydrogenation of CO_2 to methanol over CuCeTiO x catalysts. *Applied Catalysis B: Environmental* **206**, 704–711

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