

CATALYTIC CONVERSION OF CO₂ TO METHANOL OVER SUPPORTED INTERMETALLIC CATALYST

ABSTRACT

The global warming and change in climatic conditions due to rising concentration of CO₂ in atmosphere are the most important challenges of the 21st century. Catalytic conversion of CO₂ to methanol will not only check global warming but will also provide an alternative source of fuel. In this thesis, a detailed experimental investigation into direct hydrogenation of CO₂ to methanol has been carried out. Herein, initially, a comprehensive and comparative thermodynamic analysis of various CO₂ hydrogenation processes including methanol synthesis was performed in a wide range of reaction conditions. The thermodynamic limitations of the reaction and favourable range of reaction-parameters were then found to be helpful in the experimental study. In the experimental work, a new class of intermetallic catalysts was prepared and tested for the CO₂ hydrogenation to methanol. The alloys of Ga with Pd and Ni over SiO₂ support were synthesized using different preparation methods to get the most desirable catalytic properties. The prepared catalysts were characterized by various techniques like XRD, TEM-EDX, SEM, BET, H₂-chemisorption, H₂-TPR, CO₂-TPD, ICP-MS, and FTIR. The activity test of the H₂-reduced catalysts was carried out in a differential plug flow fixed bed reactor. From the catalyst screening, the Ga₃Ni₅/SiO₂ catalyst prepared through co-precipitation method (Ga₃Ni₅-CP) was found to be most active for methanol synthesis among all the catalysts including Pd₂Ga/SiO₂. Further analysis like the influence of various reaction parameters on catalytic activity to get the best set of parameter values was performed over co-precipitated Ga₃Ni₅/SiO₂ catalyst. The co-precipitated Ga₃Ni₅/SiO₂ catalyst was found to be more active than the traditional Cu/ZnO/Al₂O₃ methanol catalyst under the same reaction conditions. A detailed kinetic analysis of methanol synthesis from CO₂/H₂ including RWGS reaction over Ga₃Ni₅ catalyst was performed in a continuous differential plug flow fixed bed reactor after identifying the mass transfer resistance-free regime. From the kinetic study, the hydrogenation of formate to give surface-bound H₂COO was found to be the rate-determining step. The kinetic model was found to follow a single site mechanism and was found consistent with literature reports. The Ga₃Ni₅-CP also showed better stability followed by Ga₃Ni₅-IWI and Ga₃Ni₅-CE respectively. From the deactivation analysis, the loss in catalytic activity is attributed to the loss of active surface area due to sintering and Carbon-deposition as evident from the spent catalyst characterizations. The higher activity was related to the highly accessible Ga₃Ni₅ surface during methanol synthesis. From the deactivation kinetics, the deactivation rate of Ga₃Ni₅ catalysts was found to fit the first order power-law model and the order of their deactivation constants followed, Ga₃Ni₅-CE > Ga₃Ni₅-IWI > Ga₃Ni₅-CP.