Understanding Tri-Reforming of Methane Using Hydrotalcite-Derived Catalysts for Utilization of CO_2 of Flue Gases from Thermal Power Plants

Abstract

Tri-reforming of methane (TRM) is a synergic combination of dry reforming of methane, steam reforming of methane and partial oxidation of methane in a single reactor. Low activity and deactivation of transition metal catalysts are the major challenges to large-scale implementation of TRM process. The aim here is to develop a highly active and stable economic novel catalyst.

The first study evaluates various potential metal oxides (Al_2O_3, CeO_2-ZrO_2, MgO, TiO_2, SBA-15 and ZrO_2) as a Ni catalyst support. Under identical reaction conditions, Al_2O_3 supported Ni catalyst exhibited the highest CH_4, CO_2 and H_2O conversion. However, Ni/Al_2O_3 deactivated due to coking, sintering and Ni oxidation.

The second study investigates the role of metal-support interaction (MSI) in catalyst's performance in TRM reaction. The activity and stability of Ni/Al_2O_3 was found to improve as MSI strengthens. Moreover, the strength of MSI influenced the morphology of carbon deposits over Ni/Al_2O_3.

The third study employs hydrotalcite-derived Ni catalysts in TRM reaction. Despite high Ni dispersion, Ni-Mg-Al catalyst showed low CH_4, CO_2 and H_2O conversions due to low Ni^{2+} reducibility. Memory effect was applied to improve the Ni^{2+} reducibility, but, only at the cost of weaker MSI, making the catalyst susceptible to coking and sintering. Addition of Cu as a promoter resulted in a Ni-Cu nano alloy formation. Consequently, a higher CH_4, CO_2 and H_2O conversions were achieved. Moreover, the catalyst became stable against coking and sintering. However, Ni oxidation remained a problem. Addition of Zn as a promoter eliminated Ni oxidation issue owing to its oxophilic character. It also modified the catalyst electronically and geometrically, which resulted in enhanced activity and stability.

In the fourth study, the performance of Ni-Zn-Mg-Al catalyst was further enhanced by tuning divalent to trivalent metal molar ratio (M^{II}/M^{III}) and Ni loading. At M^{II}/M^{III} 3.0 and 5 wt.% Ni loading, the highest conversion rates of CH_4, CO_2 and H_2O was achieved. The catalyst with this particular composition demonstrated superior stability in 80 h long-term stability run.

The fifth study investigates the kinetic and mechanistic behavior of Ni-Zn-Mg-Al catalyst. A dual-site reaction mechanism has been proposed. Langmuir-Hinshelwood approach was used to derive kinetic rate expressions. Kinetic model assuming methane dissociation and carbon oxidation as RDSs predicts reaction rates closely to the experimental data.