Kinetics and mechanistic studies of CO-rich hydrogen production by CH_4/CO_2 reforming over Praseodymia supported cobalt catalysts

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ABSTRACT

The production of hydrogen and syngas by catalytic methane dry reforming is often accompanied by carbon deposition. In order to mitigate the effect of carbon deposition, it is important to have a full understanding of the elementary steps involve in the methane dry reforming over a given catalyst. This will enable the proper design and optimization of such catalyst to minimize catalyst deactivation by carbon deposition. In this study, the kinetic and mechanistic features of 20 wt%Co/Pr_2O_3 catalyst in the methane dry reforming reaction has been investigated as a function of CH_4 and CO_2 partial pressures and reaction temperature. The 20 wt%Co/Pr_2O_3 catalyst was synthesized by wet impregnation method and characterized for its physicochemical properties by TGA, XRD, N_2-physisorption analysis, TEM, FESEM, EDX, H_2-TPR, NH_3 and CO_2. The excellent physicochemical properties of the 20 wt%Co/Pr_2O_3 catalysts resulted in a high rate of CH_4 (r_{CH_4}) and CO_2 (r_{CO_2})consumption. The highest values of 3.6 mmol gcat^{-1} min^{-1} and 3.2 mmol gcat^{-1} min^{-1} were obtained for r_{CH_4} and r_{CO_2}, respectively at 50 kPa and 1023 K. The kinetic behavior of the as-synthesized 20 wt%Co/Pr_2O_3 catalyst in the methane dry reforming reaction was measured in a fixed bed stainless steel reactor at CH_4/CO_2 partial pressure range of 5—50 kPa and temperature range of 923—1023 K. The data obtained from the kinetic measurement were fitted into seven Langmuir-Hinshelwood (LH) Models. The Model were statistically discriminated using root mean square deviation (rmsd) and coefficient of determination (R^2). The statistical analysis revealed that LH kinetic Model 7 (2-step dual site rate determining steps (RDS) involving CH_4 activation by metal Co and C gasification by adsorbed CO_2 on support site) fits very well the experimental data. The R^2 values of 0.962, 0.982, and 0.989 as well as, rmsd values of 0.095 0.038, and 0.035 were obtained at 923, 973, and 1023 K respectively. Activation energies of 61.67 and 32.52 kJ/mol were obtained for the rate of consumptions of CH_4 and CO_2, an indication that lower energy barrier is required for the activation of CO_2 compared to CH_4. Based on Model 7, the mechanism of the methane dry reforming reaction over the 20 wt%Co/Pr_2O_3 catalyst can best be described by 2-step dual site rate determining steps whereby the activation of CH_4 by the metal Co resulted in hydrogen and carbon formation. The carbon formed was subsequently gasified by the lattice oxygen released from the activation of the CO_2 by the support site.