Catalytic and adsorption studies for the hydrogenation of CO_2 to methane

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Abstract

CO_2 methanation has been evaluated as a means of storing intermittent renewable energy in the form of synthetic natural gas. A range of process parameters suitable for the target application (4720 h^{-1} to 84 000 h^{-1} and from 160°C to 320°C) have been investigated at 1 bar and $H_2/CO_2 = 4$ over a 10 % Ru/γ-Al_2O_3 catalyst. Thermodynamic equilibrium was reached at $T \approx 280$°C at a GHSV of 4720 h^{-1}. Cyclic and thermal stability tests specific to a renewable energy storage application have also been conducted. The catalyst showed no sign of deactivation after 8 start-up/shut-down cycles (from 217°C to RT) and for total time on stream of 72 h, respectively. In addition, TGA-DSC was employed to investigate adsorption of reactants and suggest implications on the mechanism of reaction. Cyclic TGA-DSC studies at 260°C in CO_2 and H_2, being introduced consecutively, suggest a high degree of short term stability of the Ru catalyst, although it was found that CO_2 chemisorption and hydrogenation activity was lowered by a magnitude of 40 % after the first cycle. Stable performance was achieved for the following 19 cycles. The CO_2 uptake after the first cycle was mostly restored when using a H_2-pre-treatment at 320°C between each cycle, which indicated that the previous drop in performance was not linked to an irreversible form of deactivation (sintering, permanent poisoning, etc.). CO chemisorption on powder Ru/γ-Al_2O_3 was used to identify metal sintering as a mechanism of deactivation at temperatures higher than 320°C. A 10 % Ru/γ-Al_2O_3//monolith has been investigated as a model for the design of a catalytic heat exchanger. Excellent selectivity to methane and CO_2 conversions under low space-velocity conditions were achieved at low hydrogenation temperatures ($T = 240$°C). The use of monoliths demonstrates the possibility for new reactor designs using wash-coated heat exchangers to manage the exotherm and prevent deactivation due to high temperatures.

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