Selective hydrogenation of CO_2 into CO on a highly dispersed nickel catalyst: effect of pre-treatment and ageing

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Currently, the use of CO_2 is limited to a few industrial processes: synthesis of urea and its derivatives, salicylic acid and carbonates. There are other technologies currently under research to convert CO_2 into polymers, oxalates, formates, dimethyl ether, ethylene and propylene. However, even if all the polymers and chemicals (made from oil) consumed globally were synthesized from CO_2, emissions would not decrease by more than 5%. Saying that, CO_2 emissions will continue to be higher than CO_2 consumption unless hydrocarbon transportation fuels are produced from CO_2 (closed cycle) or they are no longer required. Reverse water gas shift (RWGS) is the first step to convert CO_2 to CO and then into fuels. However, RWGS is an equilibrium-limited endothermic reaction that is favored at high temperatures. In some cases, the products must be removed to shift the equilibrium toward the RWGS rather than the forward WGS. In addition, methane is commonly formed as an undesired side product. At low temperatures (<600∘C) methane is the thermodynamic product. Recently, we described that a nickel nanoparticles (NPs) catalyst, prepared via a magnetron sputtering deposition method, is highly selective for the RWGS reaction, showing a conversion close to the thermodynamic equilibrium at high temperature and stability for a long time on stream.[1] Moreover, the Ni catalyst produces less and less amounts of methane with time, which suggests that the methanation reaction was blocked due to changes that may have occurred on the catalyst surface after ageing.

The behavior of the Ni catalyst under reaction conditions and after ageing was studied in more detail here. Ni catalysts with different metal loading were prepared and were submitted to different pre-treatment with H_2, CO_2 and CO before the RWGS reaction. The pre-treatments and the RWGS reaction was performed in a Hiden CATLAB apparatus equipped with a calibrated mass spectrometer. The gas composition for RWGS was 2.5 mL/min of CO_2 : 7.5 mL/min of H_2, with Ar balance (total flow 100 mL/min). A mass of 20 mg of catalyst was loaded in the quartz tubular reactor and submitted to a pre-treatment with 10% H_2/Ar (500 ℃, 1h), or 5% CO_2/Ar (500 ℃, 1h), or 5% CO/Ar (500 ℃, 1h). Afterwards, the sample was cooled down to room temperature and heated up to 800 ℃, at a 10℃/min rate, with data acquisition under reaction atmosphere (CO_2/H_2). The production of methane was not afftected after treatment with H2 and CO_2, but was significantly suppressed after the pre-treatment under CO. This behavior suggests that the high selectivity of the Ni catalyst is developed during an ageing process by the product of the RWGS reaction, and not only by thermal or sintering processes. The local atomic structure properties of the freshly prepared Ni catalyst and under reaction conditions (in situ) were probed by EXAFS and XANES.

References

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