Performance of Pt catalysts dispersed on modified TiO_2 supports for the water-gas shift reaction

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The water-gas shift (WGS) reaction ($CO + H_2O \leftrightarrow CO_2 + H_2$, $\Delta H = -41{,}1$ kJ mol^{-1}), is one of the most studied reactions due to its applicability in various industrial chemical processes such as ammonia synthesis and petroleum hydro-processing [1]. The WGS reaction can be also used for the purification of PEM fuel cell feeds in order to reduce the CO content of the H_2-rich gas streams resulting from hydrocarbons reforming processes [1,2]. Well established industrial processes typically implement two WGS reactors in sequence, with the first operating at 350 – 450 ^oC (high-temperature shift, HTS) and the second at 180 – 250 ^oC (low-temperature shift, LTS) [3]. The HTS accelerates CO conversion, which is favored at elevated temperatures, whereas the LTS reduces the CO content at the desired levels exploiting the endothermic nature of the equilibrium limited WGS reaction [3]. Previous studies in our laboratory showed that Pt exhibits the highest activity toward WGS reaction among a series of noble metals investigated, including Pd, Rh and Ru, whereas the activity is maximized when it is supported on “reducible” supports, such as TiO_2 [4]. It has been also found that the promotion of TiO_2 with alkali and alkaline earth metals [5] as well as the combination of TiO_2 with a second oxide [6] can further improve the WGS activity of dispersed Pt crystallites. The aim of the present work is to study a series of Pt catalysts supported on modified TiO_2 based on the results of our previous studies [1-6]. Specifically, the effects of the combined promotion with alkali (Na, Cs) or alkaline earth metals (Ca, Sr), the addition of CeO_2 in the support, and the use of a second metal (Fe, Cu, Cr, Ru) on the WGS activity of the Pt/TiO_2 catalyst was investigated in detail. Catalytic performance tests were carried out employing an apparatus consisting of a fixed bed microreactor, an HPLC pump and an evaporator to control the H_2O content and a set of mass flow controllers to adjust the flow of the feed gasses (He, CO, CO_2, H_2). Analysis of the reactants and products of the WGS reaction was performed employing gas chromatography. The results showed that the $0.5wt.\%Pt/2wt.\%CaO/TiO_2$ catalytic system exhibited the highest activity for both HTS and LTS reactions. The performance of the optimized catalysts in the form of pellets or coatings on ceramic monoliths was further investigated under realistic reaction conditions and was compared with that of commercial catalysts (SUDCHEMIE and Johnson-Matthey). It was found that the optimized catalyst exhibited activity similar to that of the SUDCHEMIE catalyst under HTS conditions and to the Johnson-Matthey catalyst under LTS conditions.

References

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