



The quantitative description of the effects of cesium doping on the activity and properties of Cu/ZnO/Al₂O₃ catalyst in low-temperature water–gas shift

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ABSTRACT

The effects of cesium doping (in the concentration range up to 5 wt.% Cs₂O) introduced into a copper catalyst with the composition corresponding to that for the industrial catalysts used for low-temperature water–gas shift process (LT-WGS) have been investigated. Precursors and catalysts have been characterized by XRD, ICP-OS, TPD-EGA, N₂O chemisorption, TPR, N₂ physisorption and reaction rates for WGS and methanol synthesis under the pressure of 2.5 MPa have been determined. The results reveal that the cesium doping inhibits radically methanol synthesis, with the optimal Cs₂O content being <1 wt.%.

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Water–gas shift process (WGS) is an efficient method of hydrogen manufacturing and concurrent removal of carbon oxide. Depending on the desired product, partial or complete CO conversion is required according to Eq. (1):

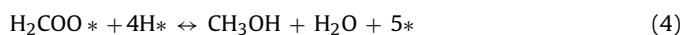


The WGS process is used for hydrogen generation and enrichment in hydrogen of gases for fuel cells and, most of all in high-capacity ammonia manufacturing plants as a correction element of raw syngas composition. Because of thermodynamic restrictions, the WGS process is performed in two stages in adiabatic reactors in the temperature range 340–450 °C (HT-WGS) in the presence of Fe–Cr–Cu catalysts and at 190–240 °C (LT-WGS) on Cu-based catalysts. Although a number of LT-WGS catalytic systems based on other formulas are known [1,2], in industrial practice the process is usually carried out in the presence of Cu/ZnO/Al₂O₃ and Cu/ZnO/Cr₂O₃ catalysts [3]. The formula of LT-WGS catalysts is similar to the one for methanol synthesis catalysts. Hence, despite the significant differences in process conditions for LT-WGS and methanol synthesis, a certain amount of methanol is generated on the LT-WGS Cu/ZnO/Al₂O₃-type catalyst as a result of a side reaction shown in Eq. (2). This reaction is undesirable because of the

hydrogen consumption and methanol formation, which is the cause of many technological problems [4,5].



The numerous literature data on the mechanisms and microkinetics of the WGS process on copper catalysts indicate that two process paths are possible: in a redox cycle [6,7] or through the formation of transient formate species [8,9]. Amadeo and Laborde [10] analyzed different kinetic models in terms of their adjustment to the results of measurements carried out at high pressure. The authors concluded that the reaction proceeded through the formate species. Analogous conclusions can be drawn from the comparative analysis by Ayastuy et al. [11]. Similarly, the results of Ovesen et al. [12] reveal that the major intermediate species in the WGS reaction is the surface formate species, which can undergo alternative transformations: decomposition to CO₂ and H₂ or hydrogenation to methanol in a series of reactions (* denotes for an active site):



A new type of the catalyst is a prerequisite for the LT-WGS process selectivity improvement by reduction of methanol formation. This is an impulse for the search for a new type of catalysts and further works on the modifications of standard Cu/ZnO/Al₂O₃ catalysts through doping [13,14], modification of catalyst preparation method and thermal treatment [15,16]. Many methods have been used in preparation of Cu/ZnO/Al₂O₃ catalysts [17], but the simplest way is to precipitate a precursor from the aqueous solutions of the

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