Steam reforming of methanol over cobalt catalysts: Effect of cobalt oxidation state

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ABSTRACT

Temperature-programmed reduction (TPR) employing hydrogen and methanol as reducing agents and in-situ X-ray diffraction have been employed to investigate the oxidation state of Co–Mn catalysts prepared by oxidative or pyrolytic treatment of fumarate precursors and correlate observations with catalyst activity in methanol reforming. Pyrolytic treatment leads to almost fully reduced catalysts, while catalysts prepared by oxidation are of the spinel structure and get reduced in a stepwise fashion. Both hydrogen and methanol are efficient reducing agents. Interaction of methanol with the catalyst surface occurs more readily with the reduced catalysts.

Introduction

Hydrogen is considered to be an important future energy carrier. Examples of sustainable production of hydrogen include water electrolysis powered by "green" electricity or biomass gasification. Steam reforming of natural gas is currently the most widespread process of hydrogen production. As storage and transportation of hydrogen pose certain technological and economic challenges, the use of liquid biofuels, such as biomethanol, as hydrogen carriers is an attractive option. In this context, hydrogen is produced from methanol via the steam reforming process and can be used as a fuel in fuel cells upon demand. Depending on the specific application requirements, a variety of fuels, including methanol, ethanol, diesel, gasoline, and others, have been investigated for H_2 generation by reforming technologies for fuel cell systems [1–6].

Supported cobalt catalysts are commonly employed in conversion of synthesis gas to hydrocarbons (Fischer–Tropsch process) but have been scarcely studied in methanol reforming. Catalysts which combine cobalt and manganese are typically prepared as spinel oxide phases via calcination. Reduction of the produced spinels results in materials containing metallic cobalt, MnO and a certain residual amount of mixed spinels [7]. On the contrary, pyrolytic treatment of cobalt–manganese catalysts prepared through fumarate salt precursors can lead to the reduced state of the catalyst in a single step due to the reductive action of gases (H_2, CO) and carbon produced during pyrolysis. In a similar manner, pyrolysis of iron fumarate or gluconate and cobalt gluconate

under inert atmosphere leads to the production of iron or cobalt nanoparticles in a carbonaceous matrix [8,9]. Use of fumarate salts has been reported in the literature for synthesis of simple or mixed transition metal oxides via oxidative treatment of such salts [10,11]. We have reported on the catalytic properties of mixed cobalt–manganese catalysts obtained from pyrolytic decomposition of the respective fumarate salts in steam reforming of methanol [12]. These catalysts are more active than Co–Mn spinel oxide catalysts and they do not need preactivation. In the present work, the oxidation state of CoMn catalysts prepared by calcination or pyrolysis of fumarate precursors has been investigated by temperature-programmed reduction and in-situ XRD.

Experimental

The precursor compounds for catalyst synthesis were mixed fumarate salts of cobalt and manganese with Co/Mn atomic ratio: 1/1, 1/2, 1/9. They were prepared by mixing aqueous solutions of cobalt and manganese acetate with an ethanolic solution of fumaric acid followed by drying at 120 °C (catalysts are named as CoMn1xAF with x = 1, 2 or 9). The fumarate salts were pyrolyzed under inert gas flow (50 cm^3 He min^{-1}) in the temperature range of 500–700 °C. Pyrolysis procedure was as follows: heating at 5 °C min^{-1} to the target temperature, soak for 10 min and cooling down to room temperature. The pyrolyzed catalysts are named as CoMn1xAFpTTT, with TTT the pyrolysis temperature. Samples were also prepared via oxidative treatment of the salts by calcination at 500 °C for 2 h (named as CoMn1xAFc500). Temperature-programmed reduction (TPR) measurements were carried out with 40 mg of catalyst samples under a flow of a 3%H$_2$/He mixture (50 cm^3 min^{-1}) using a linear heating rate of 10 °C min^{-1} up to 700 °C. A quadrupole mass spectrometer (Omnistar, Pfeiffer Vacuum) was used for on-line monitoring of effluent gases. Pyrolyzed samples were tested right after (in-situ) pyrolysis as well as after exposure to a 1.1%O$_2$/He mixture (50 cm^3 min^{-1}) at 50 °C until oxygen adsorption was complete. Calcined catalysts (CoMn1xAFc500) that had been reduced by the 3%H$_2$/He mixture at 600 °C for 30 min are named as CoMn11AFc500(TPR). Temperature-programmed reduction of the catalysts has been also studied by using methanol as the reductant. A 50 cm^3 min^{-1} flow of a 1500 ppm CH$_3$OH/He mixture was employed in these experiments. In-situ XRD measurements were carried out on a Bruker D8 Advance system equipped with CuKa radiation, Ni filter and a high temperature furnace. Nitrogen physisorption was conducted at 77 K after sample degassing for 1 h at 200 °C (Autosorb-1, Quantachrome Instruments). The specific surface area was elucidated using the standard BET method.

Results

Nitrogen physisorption isotherms of pyrolyzed samples were of type II, while those of calcined samples were of type III. In both cases, a H3 hysteresis loop between adsorption and desorption branches was found. The specific surface area of all pyrolyzed samples was in the range of 200–220 m^2 g^{-1},

while total pore volume was in the range 0.34–0.40 cm^3 g^{-1} regardless of the pyrolysis temperature. Calcined samples had considerably smaller surface area in the range of 21–35 m^2 g^{-1} and total pore volume in the range 0.01–0.09 cm^3 g^{-1}. It is evident that the presence of residual carbon in pyrolyzed catalysts leads to materials with a higher surface area by approximately one order of magnitude.

Produced water profiles during temperature-programmed reduction of calcined catalysts are presented in Fig. 1. Reduction of Co–Mn spinel oxides takes place in the form of two distinct steps as evidenced by the two water peaks. The first peak is at 380–400 °C and is attributed to reduction of spinel phases to MnO and CoO. The second peak appears above 500 °C and is attributed to reduction of Co^{2+} to metallic cobalt since its intensity increases with increase of catalyst cobalt content. These findings are in agreement with the works of Hosseini et al. [13,14], who synthesized CoMn$_2$O$_4$ spinel oxide by a sol–gel combustion method. Its TPR profile contained one peak at 410–420 °C and one above 600 °C. Bordeneuve et al. [15] performed structural studies applied to the whole range of the Mn$_{3-x}$Co$_x$O$_4$ system. They showed that Mn^{2+} ions on tetrahedral sites are progressively replaced by Co^{2+} for x varying from 0 to 1, then Mn^{3+} on octahedral sites are substituted by Co^{2+}, Co^{3+} and Mn^{4+} for 1 < x < 3.

In order to identify the structural transformations taking place during TPR, in-situ XRD measurements during heating of the CoMn11AFc500 sample under a 5% H$_2$/N$_2$ flow were taken and are presented in Fig. 2. Before heating, the XRD pattern corresponds to the CoMn$_2$O$_4$ phase (JCPDS 01-077-0471). Heating to 435 °C under a hydrogen-containing flow leads to decomposition of the spinel phase and peaks corresponding to MnO (JCPDS 00-002-1158) and traces of CoO (JCPDS 00-043-1004) are detected. At 533 °C and 600 °C the intensity of MnO peaks increases while the CoO peak disappears. At 650 °C, a new peak corresponding to metallic cobalt appears (JCPDS 00-0152-0806). At the same time, the MnO peaks shift to lower theta values, which agree to those reported in JCPDS 01-075-1090. Combination of the TPR and in-situ XRD results leads to the conclusion that the first TPR
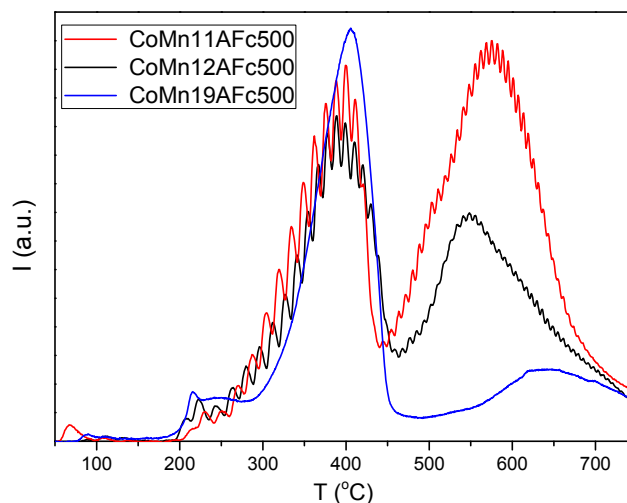

Fig. 1 – TPR profiles of water production during H$_2$-TPR of CoMn1xAFc500 catalysts (x = 1,2,9).