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METHANE COMBUSTION OVER HIGHLY EFFECTIVE COBALT-PROMOTED COPPER-CERIUM-BASED LDH-DERIVED MIXED OXIDES CATALYSTS

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Introduction

The most effective and commonly used method for the elimination of volatile organic compounds (VOC) from the low-concentration gas streams is their catalytic complete oxidation. However, three-fourths of the catalysts used are based on noble metals that, in spite of their high activity, have some disadvantages such as sintering and volatility at elevated temperatures, high sensitivity to poisoning and high price. Therefore, much effort is done to find highly active oxide-based catalysts to replace the noble metals in this process, which are cheaper and easier to prepare and have higher thermal stability and resistance to poisoning. In this work, the promoting effect of cobalt on the catalytic performance of a series of Co(x)CuCeMgAlO mixed oxides obtained from layered double hydroxide (LDH) precursors in the complete oxidation of methane, a test reaction for VOC abatement, was studied.

Materials and methods

The Co-promoted mixed oxide catalysts were obtained by the calcination at 750 °C of their corresponding Co(x)CuCeMgAl-LDH precursors prepared by coprecipitation, with $x = 1, 3, 6$ and 9 % Co, 15 % Cu, 10 % Ce (at. % with respect to cations) and with Mg/Al atomic ratio of 3. The catalysts were characterized using a battery of techniques, such as XRD, TG-DTG-DTA, TEM, SEM-EDX, XPS, DR-UV-Vis, N_2 adsorption/desorption and H_2-TPR. Then, they were tested in the complete oxidation of methane in a fixed bed quartz tube down-flow reactor at atmospheric pressure using a feed gas of 1 % CH_4 in air with a gas hourly space velocity of 16,000 h^{-1} in the temperature range from 300 to 650 °C. The reactants and product gases were analyzed on-line by gas chromatography. The carbon balance was satisfactory in all runs to within ±2 %.

Results and conclusions

The catalyst precursors consisted of well-crystallized LDH phase together with poorly crystallized boehmite AlOOH side phase, while the calcined oxides consisted of periclase-like Mg (Al, Co, Cu) O mixed oxide, CeO_2 fluorite, and CuO tenorite phases, the segregation of the latter phase going increasingly with the Co content. The mixed oxide catalysts were mesoporous materials with surface areas lower than that of the parent CuCeMgAlO mixed oxide (120 m^2 g^{-1}), in the range from 66 to 70 m^2 g^{-1}. Unexpectedly, the hydrogen consumption in the TPR experiments did not increase with increasing the Co content, following the order: Co(1)CuCeMgAlO < Co(9) ≤ Co(6) < Co(3). This suggests that the transition-metal species were decorated with non-reducible Mg(Al)O mixed oxide, which diminished the accessibility of hydrogen, in line with both the XRD analysis and the UV-VIS spectroscopy data showing that the cobalt cations were homogeneously dispersed in the Mg(Al)O periclase-like phase.

The cobalt content strongly influenced, in a complex manner, the catalytic activity of the Co(x)CuCeMgAlO catalysts (Figure 1), which, in terms of both T_{50} and T_{90} and specific and intrinsic rates, followed the order: CuCeMgAlO < Co(1)CuCeMgAlO < Co(9) < Co(6) < Co(3). Notably, for the most active Co(3)CuCeMgAlO catalyst the T_{50} value was 25 °C lower than that of the unpromoted CuCeMgAlO system and only 19 °C higher than that of a reference Pd/Al_2O_3 catalyst tested in similar conditions. Moreover, this Co-promoted catalytic system was shown to have a good stability at 520 °C for 60 h on stream (Figure 2).

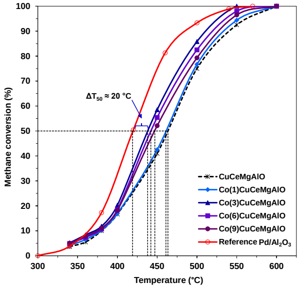

Fig. 1. The light-off curves.

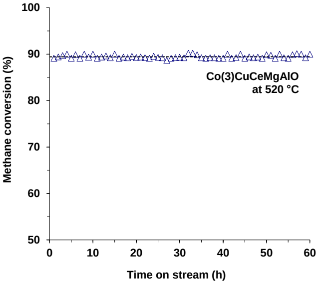

Fig. 2. The stability test.

The catalytic activity in this series was shown to increase with increasing of both the Co^{3+}, Cu^{2+}, and Ce^{4+} surface concentrations and the catalyst reducibility. This demonstrates that a synergistic interaction between these species is a key factor controlling their catalytic behavior in the complete oxidation of methane. Thus, the enhanced catalytic activity of the Co(3)CuCeMgAlO system was attributed to an excellent Cu-Co-Ce synergistic interaction.