Deep Oxidation of Ethanol over Co-Mn-Al Mixed Oxides Supported on Pelletized Magnesia-Alumina: Role of Acid-base Properties.

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Deep oxidation of ethanol over Co-Mn-Al mixed oxides supported on pelletized magnesia-alumina: role of acid-base properties

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Volatile organic compounds (VOC) emitted in industrial gases can be eliminated applying the catalytic total oxidation. Previously we found high catalytic activity of the Co-Mn-Al mixed oxides, obtained by heating of the coprecipitated layered double hydroxide (LDH) precursor, in the ethanol total oxidation. Activity of this catalyst was remarkably increased by addition of small amount of the potassium promoter. However, the catalysts prepared by pelletizing the powdered material contained high amounts of expensive cobalt, which was not fully utilized in the catalytic reaction. Therefore, we focused on preparation of supported catalysts with lower concentration of active components placed exclusively in the outer shell of the support pellets. In the present study, we applied the method of impregnation using acidic solution of metal salts in combination with a support having basic properties that could limit penetration of active components into the support pellets.

The catalysts were prepared by impregnation of magnesia-alumina pellets (5x5 mm, Sasol) with aqueous solutions containing Co, Mn and Al nitrates (molar ratio of Co:Mn:Al=4:1:1) and subsequent heating at 500 °C in air. The prepared samples were characterized by chemical analysis, powder XRD, measurement of nitrogen adsorption at -196°C, NH_3-TPD, CO_2-TPD, and TPR. Distribution of active metals in the catalyst pellets was determined by SEM. Catalytic activity in the total oxidation of ethanol, which was chosen as a model VOC, was measured under unsteady-state conditions with heating rate of 2.27 °C min^{-1} (100–400 °C), at ethanol concentration in air of 1.5 g m^{-3} and GHSV 20 l g_{cat}^{-1} h^{-1}. Temperatures T_{50}, at which 50% conversion of ethanol was observed, were chosen as a measure of the catalysts activity. In addition, specific activities of all catalysts, valid for 200 °C, were also determined. Apart from the studied catalysts, the pellets (5x5 mm) of commercial Co-Mn-Al mixed oxide catalyst (ASTIN 2-100) were also examined for comparison.

It was found out that magnesia-alumina support contained, apart from 30 wt. % of Al_2O_3, about 1 wt. % of Na. The SEM imaging of the catalysts confirmed limited penetration of active metals into the support pellets. Commercial catalyst with about 55 wt. % of (Co+Mn) exhibited uniform distribution. Sum of (Co+Mn) in the supported catalysts varied from 4 to 15 wt. %.Powder XRD patterns of all samples showed diffraction lines corresponding to spinel-like phases. Basic properties of the support as well as surface area of the samples were decreasing with gradual adding the active metal oxides, while acidity of the catalysts was increasing. Ethanol conversion over the studied catalysts showed that the most active sample, even more active than the commercial Co-Mn-Al mixed oxide catalyst with almost 55 wt.% of (Co+Mn), was the catalyst with much lower content (only about 12 wt.%) and non-uniform distribution of Co and Mn in the pellets. The main reaction byproduct, acetaldehyde, was completely transformed into CO_2 at temperatures lower than 300 °C. Formation of the other

reaction byproduct, CO, was not detected.

In conclusion, impregnation of the magnesia-alumina pellets having basic properties with acidic solution of Co, Mn and Al nitrates led to limited penetration of metal cations into the support and formation of catalysts with non-uniform distribution and reduced content of active components. The formed active layer in the support resisted to attrition during the catalytic reaction. The activity of the supported catalysts slightly differed from that of the commercial catalyst with uniform distribution of Co and Mn and (Co+Mn) about 55 %. Supported catalyst with optimum active metals concentration (ca. 12 wt. %) showed better catalytic properties than the commercial one.