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Total oxidation of ethanol over layered double hydroxide-related mixed oxide catalysts: Effect of cation composition

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ABSTRACT

Ethanol total oxidation over mixed oxide catalysts containing various transition metal cations was studied. The M^{II}–M^{III} layered double hydroxide (LDH) precursors with M^{II}/M^{III} molar ratio of 2 (M^{II} = Cu, Co, Ni, Cu–Ni, Cu–Co, and Co–Ni; M^{III} = Mn or Al) were prepared by coprecipitation of nitrate solutions. The ternary mixed oxides containing Mn were more active than the binary Cu–Mn, Co–Mn, and Ni–Mn ones as well as the ternary Al-containing catalysts; the Cu–Ni–Mn mixed oxide was the most active. The catalytic activity increased with increasing amount of easily reducible components and amount of oxygen desorbed from catalysts surface at lower temperatures (up to 500 °C). Main byproduct of the ethanol oxidation was acetaldehyde. Ethanol oxidation over Al-containing catalysts produced lower amounts of acetaldehyde than that over the catalysts comprising Mn; both the Cu–Ni–Mn and Co–Ni–Mn catalysts showed the lowest temperatures of acetaldehyde disappearance.

1. Introduction

Volatile organic compounds (VOCs) in industrial gases represent a serious environmental problem, as some of them exhibit toxic, narcotic, or carcinogenic properties. They can also react with nitrogen oxides and air oxygen to form harmful ozone: $VOC + NO_x + O_2 + h\nu \rightarrow O_3 +$ other products. Concentration of VOCs in air can be reduced applying the total oxidation to carbon dioxide and water as final products; catalytic process is markedly energy saving compared to elimination of VOCs by thermal combustion. The catalysts containing noble metals are currently used, as they are highly active and stable but expensive [1–3]. Platinum is more active in oxidation of saturated and aromatic hydrocarbons, while palladium is more efficient in oxidation of unsaturated hydrocarbons, carbon monoxide, methane, and in oxidation reactions in the presence of water vapor [4–6]. Oxides of transition metals (in particular Cu, Mn, Cr, Co, and Ni) are a cheaper alternative to the noble metal catalysts; they are highly active but more sensitive to deactivation [4]. For example, a mixture of Cu and Mn oxides was the first mixed oxide catalyst used for oxidation of VOC in submarines.

Mixed oxides of transition metals can be easily obtained by calcination of layered double hydroxide (LDH) precursors. Such mixed oxide catalysts show fine dispersion of active components, large surface area and good thermal stability. There is a question, whether a synergic effect of transition metal cations present in the multicomponent LDH-related mixed oxide catalysts could increase their activity in oxidation of VOCs. In this work the LDH precursors containing divalent and trivalent transition metal cations in various combinations were prepared and properties of the related mixed oxide catalysts as well as their activity in the ethanol deep oxidation were examined, with the aim to enhance the activity and selectivity of the mixed oxide catalysts. Optimization of the catalysts composition could also minimize undesirable reaction byproducts formed during VOCs oxidation. Ethanol was chosen as a model volatile organic compound because ethanol is often used as a fuel for buses and cars (e.g., in Scandinavian countries and especially in South America). Therefore, the total oxidation of ethanol including the reaction intermediates is interesting and worth studying.

2. Experimental

2.1. Catalysts preparation

The M^{II}–M^{III} LDH precursors (M^{II} = Cu–Ni, Cu–Co, or Co–Ni in molar ratio of 1:1, M^{III} = Mn or Al, M^{II}/M^{III} molar ratio of 2) were prepared by coprecipitation. An aqueous solution (450 ml) of appropriate nitrates, i.e., $Cu(NO_3)_2 \cdot 3H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2.6H_2O$, $Mn(NO_3)_2 \cdot 4H_2O$, and $Al(NO_3)_3 \cdot 9H_2O$ (total metal

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ion concentration of 1.0 mol l^{-1}) was added with flow rate of 7.5 ml min^{-1} into 1000 ml batch reactor containing 200 ml of distilled water. The flow rate of simultaneously added alkaline solution of 0.5 M Na_2CO_3 and 3 M NaOH was controlled to maintain reaction pH 10.0 ± 0.1. Coprecipitation was carried out under vigorous stirring at 25 °C. The resulting suspension was stirred 1 h at 25 °C, the product was then filtered off, washed thoroughly with distilled water and dried overnight at 60 °C in air. The dried and powdered product was formed into pellets and calcined at 500 °C for 4 h in air. After cooling to room temperature, the calcined pellets were crushed and sieved to obtain the fraction of particle size 0.160–0.315 mm, which was used in further experiments. The obtained catalysts were denoted by acronyms with cation composition in the form M^{II}–Mn or M^{II}–Al, for example Cu–Ni–Mn or Co–Cu–Al. In addition to the ternary mixed oxide catalysts, the binary analogs Cu–Mn, Co–Mn and Ni–Mn (M^{II}/Mn molar ratio of 2) were also prepared and examined for comparison.

2.2. *Characterization of samples*

The content of metal cations in the prepared catalysts was determined by atomic absorption spectroscopy (AAS) using a SpectrAA880 instrument (Varian) after samples dissolution in hydrochloric acid.

Powder X-ray diffraction (XRD) patterns were recorded using a Seifert XRD 3000P instrument with Co Kα radiation (λ = 0.179 nm, graphite monochromator, goniometer with the Bragg-Brentano geometry) in 2θ range 10–80°, step size 0.05°. The qualitative analysis was performed with a HighScore software package (PANanalytical, The Netherlands, version 1.0d)

Surface area and mesoporous structure of the catalysts were examined by adsorption/desorption of nitrogen at −196 °C using Micromeritics ASAP 2010 instrument. The BET and BJH (Barrett, Joyner, Halenda) methods were used for evaluation of surface area and pore size distribution, respectively. Presence of micropores and their volume was determined by the t-plot method.

Temperature programmed reduction (TPR) measurements were performed with 0.025 g of a calcined sample, stored in a closed bottle, with a H_2/N_2 mixture (10 mol. % H_2), flow rate 50 ml min^{-1} and linear temperature increase 20 °C min^{-1} up to 1000 °C. Changes in H_2 concentration were detected with a katharometer. Reduction of the grained CuO (0.160–0.315 mm) was repeatedly performed to calculate absolute values of the hydrogen consumed during reduction of the calcined samples.

Temperature-programmed desorption of NH_3 (NH_3-TPD) was carried out to examine acidic properties of the catalysts surface. The measurements were accomplished with 0.050 g of a sample in the temperature range 20–900 °C, with helium as a carrier gas and NH_3 as adsorbing gas. Before the NH_3-TPD measurements the samples were heated in helium from 25 to 500 °C with temperature ramp 20 °C min^{-1}, then was the sample cooled in He to 25 °C. The heating rate of 20 °C min^{-1} was applied. Composition of gases evolved during the experiments was determined by a mass spectrometer (Balzers). The following mass contributions m/z were collected: 2-H_2, 18-H_2O, and 16-NH_3. The spectrometer was calibrated by dosing an amount (840 μl) of NH_3 into the carrier gas (He) in every experiment.

In the same set-up, temperature-programmed desorption of oxygen (O_2-TPD) from the oxide catalysts into helium was carried out. The catalysts (50 mg) calcined in air at 500 °C for 4 h were cooled to 25 °C, placed in the reactor vessel and changed He stream of 30 ml min^{-1} was introduced. The catalyst was then ramped to 900 °C at a linear heating rate of 20 °C min^{-1}. The analysis of O_2 in the effluent gas was performed with a mass spectrometer (OmniStar QMS 200, Pfeiffer Vacuum) while monitoring the m/z signal 32-O_2. The desorption peak areas corresponding to the adsorbed species were calibrated in separate experiments using pulses of oxygen from a calibrated volume.

The TPR, NH_3-TPD and O_2-TPD experiments were evaluated using OriginPro 8.0 software with an accuracy of ±5%.

2.3. *Catalytic measurements*

The catalytic reaction was carried out in a laboratory fixed-bed glass reactor (5 mm i.d.) in the temperature range from 80 to 400 °C and the temperature ramp of 2 °C min^{-1}. The catalyst (0.1–0.4 g of the sieved grains with particle size of 0.16–0.315 mm) was examined at space velocity (GHSV) of 20 and 80 m^3 kg^{-1} h^{-1}. The inlet ethanol concentration in air was 1.2 g m^{-3} (equaled to 750 ppm). Reaction products were analyzed using a gas chromatograph Hewlett-Packard 6890 equipped with a FID detector and a capillary column (HP-5 19091 J-413, 30 m × 0.32 mm × 0.25 mm with 5% phenyl methyl silicone). Conversions of ethanol at two values of GHSV were calculated according to the equation $x_{EtOH} = (c_o - c)/c_o$, where $\underline{c_o}$ is inlet concentration of ethanol and $\underline{c}$ is ethanol outlet concentration at the actual reaction temperature. Temperatures T_{50} and T_{90} (the temperatures, at which 50% and 90% ethanol conversion were achieved) were chosen as a measure of the catalysts activity. Selectivity in ethanol conversion was evaluated as the amount of formed acetaldehyde (ppm) in the temperature range from 50 (or 100) to 400 °C. The accuracy of the conversion and selectivity determination was ±3%.

3. Results and discussion

3.1. *Chemical and phase composition*

Chemical analysis (AAS) of the prepared catalysts showed that molar ratios of cations in solids corresponded approximately to those in the nitrate solutions used for coprecipitation (Table 1). The ternary mixed oxide catalysts contained low amounts of residual sodium cations (<0.1 wt.%), which were not removed from the LDH precursors during washing. Higher Na contents (up to 1.3 wt.%) were found in the binary M^{II}–Mn samples.

Powder XRD patterns of the dried precursors showed diffraction peaks characteristic for hydrotalcite-like LDHs, no other phases were found (Fig. 1). The Al-containing LDHs exhibited a higher crystallinity compared to the samples containing Mn; the Cu–Co–Mn and Cu–Ni–Mn precursors were almost amorphous but the diffraction peaks characteristic for LDHs can be still distinguished. During the coprecipitation, the majority of Mn^{2+} was oxidized to Mn^{3+}, as it was determined from the mean valence of the metal cations in the coprecipitated LDHs containing manganese [8,9]. It is known that both Cu^{II} and Mn^{III} show distortions in octahedral coordination due to the Jahn–Teller effect, which could make the formation of brucite-type sheets more difficult. Among the binary M^{II}–Mn precursors, the hydrotalcite-like LDH was found only in the Ni–Mn sample, together with the trace amount of $MnCO_3$ (rhodochrosite). In the Co–Mn sample, a phase with d ~6.65 Å was detected, which was ascribed to an unidentified, probably hydroxide- and/or oxyhydroxide-type product [9]. The Cu–Mn precursor showed amorphous phase and only poorly crystalline CuO (tenorite) was detected in this sample (not shown here).

Formation of oxide phases during heating of the coprecipitated binary Ni–Mn, Co–Mn, and Cu–Mn precursors was described in our former reports [8–10]. In the calcination product obtained by heating of the Ni–Mn LDH at 500 °C in air the Mn^{IV}-containing mixed oxides were found, including Ni_6MnO_8 with a murdochite-type structure and $NiMnO_3$ isostructural with ilmenite [8]. Thermal decomposition of the Co–Mn precursor resulted in the formation

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