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Short Communication

Total oxidation of selected mono-carbon VOCs over hydrotalcite originated metal oxide catalysts

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ABSTRACT

Hydrotalcite originated Cu–Mg–Al, Co–Mg–Al and Cu–Co–Mg–Al oxide systems were tested as catalysts for the total oxidation of mono-carbon VOCs (methane, methanol, and formic acid). Both calcination temperature of the hydrotalcite precursors as well as doping of the catalysts with potassium promoter influenced their catalytic activity. Increased calcination temperature, which resulted in a decrease of the surface area of the samples and formation of the spinel phases, activated the Co–Mg–Al catalyst, while the opposite effect was observed for the Cu–Mg–Al and Cu–Co–Mg–Al catalysts. On the other hand doping of the catalysts with potassium promoter significantly activated the Cu–Mg–Al and Cu–Co–Mg–Al catalysts in the processes of methanol and formic acid conversion, while only slightly influenced the catalytic performance of the Co–Mg–Al sample.

1. Introduction

Hydrotalcite-like material, called also layered double hydroxides (LDHs), were reported to be precursors of active catalysts for various processes, including among other DeNOx [1], ammonia oxidation [2] and N_2O decomposition [3]. Recently, there is an increased interest in application of hydrotalcite-like materials as precursors of the catalysts for total oxidation for volatile organic compounds (VOCs). Much attention was paid for the cobalt containing oxide systems. Gennequin et al. [4,5] used Mg–Al hydrotalcites, calcined at various temperatures, as supports for the deposition of cobalt. Such catalysts were tested in the process of toluene incineration. The best effectiveness in this process was obtained for cobalt supported on hydrotalcite calcined at 700 °C. Calcination of Mg–Al hydrotalcite at lower and higher temperatures resulted in the lower activity of the catalysts. These authors [5] showed also that the significantly more active catalysts for the total toluene oxidation can be obtained from the Co–Mg–Al hydrotalcite-like precursors calcined at 500 °C [6]. They related the increased activity of the second group of the catalysts to better dispersion of cobalt species. Pérez et al. [7] reported that the ultrasound assisted synthesis of the Co–Mg–Al hydrotalcite-like materials is much faster comparing to the traditional method and their calcination results in very active catalysts for the total oxidation of butanol. Authors related high activity of the catalysts to the increased surface area and porosity of the samples produced by the ultrasound assisted method. Kovanda at al. [8] reported the beneficial effect of using the Co–Mg–Mn–Al hydrotalcite precursors for the preparation of the catalysts for the ethanol incineration. The best results were obtained for the cobalt reach Co–Mn–Al oxide system, which as suggested authors, has an optimum content of the reducible components. Recently, the promoting effect of the potassium doping on activity of these catalysts in the total oxidation of toluene was reported [9]. There is also a lot of papers reporting successful application of the copper containing catalysts for VOCs oxidation [e.g. 10–13], however only limited number those related to using the hydrotalcite originated catalysts. Kovanda et al. [14] reported high catalytic activity of the hydrotalcite originated Cu–Mg–Al oxide systems (calcination at 450 °C) in the toluene combustion. The activity of the studied catalysts increased with an increase of the copper loading and, as it was suggested by the authors, is related to the contribution of the easy reducible copper species. Also the hydrotalcite-like materials containing apart from copper also other transition metal were reported to be precursors of the active catalysts for the VOCs combustion. Bahranowski et al. [15] showed the high catalytic activity of the Cu–Cr–Al hydrotalcite-like materials calcined at 600 °C in the complete oxidation of toluene and ethanol. Also the Cu–Mn–Al and Cu–Zn–Al oxide systems obtained from the hydrotalcite-like materials were found to be active and selective catalysts of the toluene combustion [16]. It was shown that the samples calcined at lower temperature (450 °C) were more active than those calcined at higher temperature (600 °C). Recently, Kovanda et al. [17], who studied a broad range of the hydrotalcite-like materials containing various transition metals as precursors of the metal oxide catalysts for

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the ethanol combustion, reported very high activity of the Cu–Co–Mn, Cu–Ni–Mn and Cu–Co–Al oxide systems.

The present paper reports the studies of the hydrotalcite originated Cu–Mg–Al, Co–Mg–Al and Cu–Co–Mg–Al metal oxide catalysts for the complete oxidation of methane, methanol and formic acid. An influence of the calcination temperature of the hydrotalcite precursors and doping of the samples with potassium promoter on their catalytic activity is discussed.

2. Experimental

Cu(II)Mg(II)Al(III), Co(II)Mg(II)Al(III) and Cu(II)Co(II)Mg(II)Al(III) hydrotalcite-like materials were prepared by the co-precipitation method using aqueous solutions of the following metal nitrates: $Mg(NO_3)_2 \cdot 6H_2O$ (Sigma), $Al(NO_3)_3 \cdot 9H_2O$ (Fluka), $Cu(NO_3)_2 \cdot 3H_2O$ (Merck) and $Co(NO_3)_2 \cdot 6H_2O$ (POCh). A solution of NaOH (POCh) was used as a precipitating agent. The mixture of metal nitrate solutions was slowly added to a vigorously stirred aqueous solution containing a slight excess of Na_2CO_3 (POCh). The pH was maintained constant at 10.0 ± 0.2 by dropwise addition of NaOH solution. Precipitates were aged in a suspension at 60 °C for 30 min under vigorous stirring. In the next step the suspension was filtered, washed with distilled water and dried overnight at 120 °C. Finally, the prepared hydrotalcite-like materials were calcined at 700 or 800 °C for 16 h. The hydrotalcites calcined at 800 °C were modified with potassium using the incipient wetness impregnation method. Aqueous solutions of KNO_3 (POCh) were used for the deposition of potassium (0.9 wt.%). The samples impregnated with potassium nitrate were calcined at 600 °C. A detailed description of the catalysts was presented in our previous paper [3].

The surface area of hydrotalcite-like materials calcined at different temperatures was determined by the BET method. The measurements were performed using ASAP 2010 (Micromeritics). Prior to the nitrogen adsorption at −196 °C the samples were outgassed under vacuum at 350 °C for 12 h. The X-ray diffraction (XRD) patterns of the fresh and calcined hydrotalcite-like materials were obtained with a Philips X'Pert APD diffractometer using CuK_∞ radiation ($\lambda = 1.54178$ Å). The TPRed (temperature-programmed reduction) of the samples (30 mg) was carried out from room temperature to 1100 °C with a linear heating rate of 5 °C/min. Measurements were performed in a fixed-bed flow microreactor. Prior to the TPRed experiment, the catalysts were outgassed at 600 °C for 12 h. The TPRed runs were carried out in a flow of 10 vol.% of H_2 diluted in Ar with a total flow rate of gas mixture of 6 mL/min. Evolving water was removed from effluent gas by means of a cold trap. The evolution of hydrogen was detected by microvolume TCD (Valco). More detailed characteristic of the samples was presented in our previous paper [3].

Calcined hydrotalites were tested as the catalysts of methane, methanol and formic acid incineration. The catalytic experiments have been performed under atmospheric pressure in a fixed-bed flow microreactor system. The reactant concentrations were continuously measured using a quadruple mass spectrometer RGA 200 (PREVAC) connected directly to the reactor outlet. Prior to the catalytic test each sample of the catalyst (100 mg) was outgassed in a flow of pure helium at 500 °C for 1 h. The isothermal saturator with a constant flow of helium was used for supply of methanol and formic acid into the reaction mixture. Methane was supplied from gas cylinder containing mixture of 1 vol.% of CH_4 diluted in pure helium. The composition of gas mixture at the reactor inlet was $[CH_4] = 0.5$ vol.% (or alternatively methanol or formic acid), $[O_2] = 4.5$ vol.% and $[He] = 95$ vol.%. The reaction was studied in the range from 100 to 450 °C (or 650 °C for methane incineration) with the linear temperature increase of 10 °C/min. The signal of the helium line served as an internal standard to compensate possible small fluctuations of the operating pressure. The sensitivity factors of analysed lines were calibrated using commercial mixtures of gases.

3. Results and discussion

The chemical composition and BET surface area of hydrotalcites calcined at 700 and 800 °C are presented in Table 1. In a series of hydrotalcites calcined at 700 °C, the samples containing only one type of transition metal (HT700-Co15 or HT-700-Cu15) have significantly higher surface area than the sample containing both copper and cobalt (HT700-CuCo15). An increase in the calcination temperature from 700 °C to 800 °C dramatically reduced surface area of the samples.

The XRD patterns of the as-prepared and calcined hydrotalcite-like materials are shown in Fig. 1. The reflections typical of the hydrotalcite structure (marked as *H* in Fig. 1, JCPDS 37-0630) were present in diffractograms of the non-calcined samples [18]. It should be noted that intensity of XRD reflections, which is related to crystallinity of hydrotalcite phases, is higher for the HT-Cu15 sample than for HT-Co15 and HT-Cu15Co15. Calcination of the samples at 700 °C resulted in a disappearance of diffraction lines typical of the hydrotalcite structure and formation of new broad reflections. Two of them, positioned at about 42° and 62°, are characteristic of the MgO phase (marked as *O* in Fig. 1, JCPDS 4–0829), whereas the band at about 37° could be attributed to the presence of the following spinel phases: $MgAl_2O_4$ (JCPDS 21-1152), $CuAl_2O_4$ (JCPDS-33-0448), $CoAl_2O_4$ (JCPDS 82-2246), $MgCo_2O_4$ (JCPDS 02-1073), Co_3O_4 (JCPDS 74-2120) and possible non-stoichiometric spinel phases containing Cu, Cu, Mg and Al cations. The spinel phases are marked as *S* in Fig. 1. Any intensive peaks related to the presence of CuO (JCPDS 41-0254) were not found [18,19]. The low-intensive reflections at about 19°, 31°, 59° and 65° are related to formation of the above-mentioned spinel phases. An increase in the calcination temperature to 800 °C resulted in an increase of the intensity of these reflections, suggesting a significant increase of the crystallinity of the spinel phases. Therefore, it could be concluded that calcination of the hydrotalite-like samples results in their thermal decomposition to the spinel and metal oxide phases. An increase in the calcination temperature favours formation of the low-surface area spinel phases. The detailed studies of thermal decomposition hydrotalcite-like materials into metal oxide systems were presented in our previous paper [3].

Fig. 2 presents the results of TPRed studies of HT800-Cu15 and HT800-Co15 and their modifications with potassium promoter. The reduction of copper oxide species [14] present in the HT800-Cu15 sample took place in the range of 120–305 °C with a sharp maximum located at 223 °C (Fig. 2A). The promotion of that catalyst with potassium (HT-800-Cu15/K) shifted the reduction maximum into 217 °C. Additionally, low-intensive and broad peak of hydrogen consumption, centred at about 620 °C, was detected for the samples promoted and non-promoted with potassium. According to the literature reports [e.g. 20–22] the reduction of CuO to Cu^0 occurs at 200–300 °C depending on the size and nature of CuO crystals.

$$CuO + H_2 = Cu^0 + H_2O. \quad (1)$$

The results of TPRed are not supported by XRD studies, in which there were not found any intensive peaks related to the presence of

Table 1
Composition, calcination temperature and surface area of the hydrotalcite based samples.

Sample code	Composition	Atomic ratio	Calcination temperature [°C]	S_{BET} of calcined hydrotalcite [m^2/g]
HT700-Cu15	Cu/Mg/Al	15/56/29	700	193
HT800-Cu15	Cu/Mg/Al	15/56/29	800	88
HT700-Co15	Co/Mg/Al	15/56/29	700	217
HT800-Co15	Co/Mg/Al	15/56/29	800	61
HT700-CuCo15	Cu/Co/Mg/Al	15/15/41/29	700	107
HT800-CuCo15	Cu/Co/Mg/Al	15/15/41/29	800	60