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Coprecipitated Co–Al and Cu–Al oxide catalysts for toluene total oxidation

Anna Bialas[a], Paula Niebrzydowska[a], Barbara Dudek[a], Zofia Piwowarska[a], Lucjan Chmielarz[a], Marek Michalik[b], Marek Kozak[c], Piotr Kuśtrowski[a,*]

[a] *Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Kraków, Poland*
[b] *Institute of Geological Sciences, Jagiellonian University, Oleandry 2a, 30-063 Kraków, Poland*
[c] *Division of Petroleum Processing, Oil and Gas Institute, Łukasiewicza 1, 31-429 Kraków, Poland*

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ABSTRACT

Highly crystalline mixed cobalt– and copper–aluminium oxides were obtained from coprecipitated precursors. These Co–Al and Cu–Al oxide systems appeared to be active catalysts of the total oxidation of toluene in the temperature range of 250–450 °C. The study on chemical and phase composition, thermal stability, texture and reducibility of the synthesized samples allowed to identify their active phases in toluene combustion.

1. Introduction

Among transition metal-containing catalysts for the total oxidation of volatile organic compounds (VOCs), copper and cobalt oxides are considered as the most active [1]. Usually, they are supported on alumina in order to expose their active phases. The highly dispersed, easily reducible metal ions play the role of active sites in the oxidation of organic compounds [2]. On the other hand, coprecipitated mixed oxides exhibit high catalytic activity in this reaction as well [3,4]. Mesoporous Cu–Mg–Al mixed oxides with a high specific surface area catalyse the total oxidation of methane at about 500 °C. The most efficient of them contain, besides CuO, the spinel phase—$CuAl_2O_4$, but their activity depends on the presence of surface CuO species [3]. In the case of copper–manganese oxides their activity in toluene combustion increases with the increasing Mn ions' content in surface layers. Although, the only crystalline phase is copper oxide, a surface spinel phase is supposed to be active in the hydrocarbon oxidation [4]. Bulk spinel catalysts containing cobalt and copper also turn out active in the VOCs' oxidation [5].

The aim of this work was the synthesis of crystalline Co–Al and Cu–Al oxide catalysts from coprecipitated precursors. Changes in a Me/Al ratio resulted in the different distributions of the transition metal oxides' forms, which allowed to determine the influence of the chemical vicinity on their activity in the total oxidation of toluene.

2. Experimental

2.1. Catalyst preparation

Mixed metal oxide catalysts with various Co:Al and Cu:Al molar ratios were synthesized by the coprecipitation method. Metal nitrates $Co(NO_3)_2{\cdot}6H_2O$ or $Cu(NO_3)_2{\cdot}3H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$ were dissolved in 250 ml of water, in the same volume the precipitating agent $(NH_4)_2CO_3$ was dissolved separately. The molar concentrations of the cations in solutions were equal Co^{2+}(Cu^{2+}): 0.24, 0.45, 0.56; Al^{3+}: 0.76, 0.55, 0.44 and NH_4^+: 3.31, 3.06 and 2.93 mol/dm^3, for Co0.32, Co0.83 or Co1.28 and Cu0.32, Cu0.83 or Cu1.28 samples, respectively. The coprecipitation reaction was carried out at a constant temperature 50 °C. The metal containing solution and ammonium carbonate (with 20% excess) were dosed at a constant rate to a beaker and vigorously stirred. After mixing the substrates, the obtained precipitate was stirred for 1 h, and then cooled to room temperature. The filtered and washed, with distilled water, preparations were dried at 30 °C and calcined at 900 °C for 6 h in air.

2.2. Catalyst characterisation

The metal content was determined by ICP-OES with a SPECTRO ARCOS SOP (Spectro Analytical Instruments). Thermogravimetric measurements were performed using a Mettler Toledo TGA/SDA 851 thermogravimeter on line with a Balzers Thermo Star mass spectrometer. Samples (25 mg) were heated at a rate of 10°/min from 30 to 1000 °C in flowing air (80 ml/min). Specific surface

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[*] Corresponding author. Tel.: +48 12 6632006; fax: +48 12 6340515.
E-mail address: kustrows@chemia.uj.edu.pl (P. Kuśtrowski).

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Table 1
Composition and textural parameters of Co- and Cu-containing catalysts.

Catalyst	*Co*0.32	*Co*0.83	*Co*1.28	*Cu*0.32	*Cu*0.83	*Cu*1.28
Measured transition metal/aluminium atomic ratio	0.26	0.85	1.32	0.26	0.94	1.34
BET specific surface area (m^2/g)	81	19	14	46	21	16
Pore volume (cm^3/g)	0.21	0.05	0.02	0.09	0.07	0.03

area and total pore volume were measured by means of an ASAP 2010 sorptometer (Micromeritics). Before measurements samples were outgassed at 350 °C under vacuum for 12 h. XRD patterns were recorded using a Philips X'pert APD with Cu radiation ($\lambda = 1.540560$ Å) for $2\theta = 2$–$64°$, with a step of 0.02°. H_2-TPR experiments were carried out in a quartz microreactor with a reduction mixture of 2 vol.% H_2 in Ar flowing at a rate of 20 ml/min. A 20 mg sample was placed on quartz wool and reduced in the temperature range 100–1000 °C, at a constant heating rate 15 °C/min. The amount of the consumed hydrogen was determined using a TCD detector.

2.3. Toluene total oxidation

A 0.05 g sample of a catalyst was placed on quartz wool in a quartz flow microreactor. Temperature in the catalyst bed was controlled by a thermocouple placed inside the catalyst bed. Before catalytic tests samples were outgassed at 400 °C in flowing air, and then cooled to 200 °C. Toluene was dosed using a syringe pump (Cole-Palmer 74900) at a rate of 100 μl/h into flowing air—50 ml/min (GHSV = 60,000 h^{-1}). At 200 °C three 15 min analyses were conducted. Subsequently, the temperature was raised to 250 °C and the analysis was repeated, such a procedure was continued to 550 °C, with a 50 °C step. Reaction products were analysed in a gas chromatograph Varian Chrompack CP 3800 equipped with a capillary column DB-1 (J&W Scientific, internal diameter—0.32 mm, length—30 m, thickness of stationary phase—5 μm) and a TCD detector. Conversion of toluene was calculated as an average from three analyses carried out at one temperature on the basis of hydrogen balance from the following equation:

$$C_{C_7H_8} = \frac{1/4 n_{H_2O,\text{outlet}}}{n_{C_7H_8,\text{inlet}}} \times 100\%$$

Selectivity to CO_x was calculated based on the amount of formed water, while the selectivity to carbon dioxide was determined by the comparison of the amounts of produced water and carbon dioxide.

3. Results and discussion

The composition of the investigated catalysts is shown in Table 1. Transition metal loading in the 0.83 and 1.28 samples was slightly higher than intended in the synthesis, while for the samples with the lowest Co and Cu concentration, the metal loading was 19% lower.

TG analysis of catalyst precursors showed that the cobalt preparations attained their thermal stability at about 400 °C, after decomposition of hydroxyl groups resulting in water evolving. The presence of nitrogen oxides and CO_2 among the evolved gases, attributed to nitrates' and carbonates' decomposition, was detected at 200–250 °C. The decomposition mechanism of the Cu-containing samples was quite similar. However, stabilization of carbonates by Cu^{2+} cations was so strong that decomposition of carbonates was completed at a temperature as high as 850 °C. Taking into account this observation and expecting the formation of spinel phases, a temperature of 900 °C was chosen to obtain stable cobalt and copper oxide catalysts by calcination in air.

The obtained oxide-type samples exhibited the BET specific surface area (S_{BET}) decreasing with the increasing transition metal

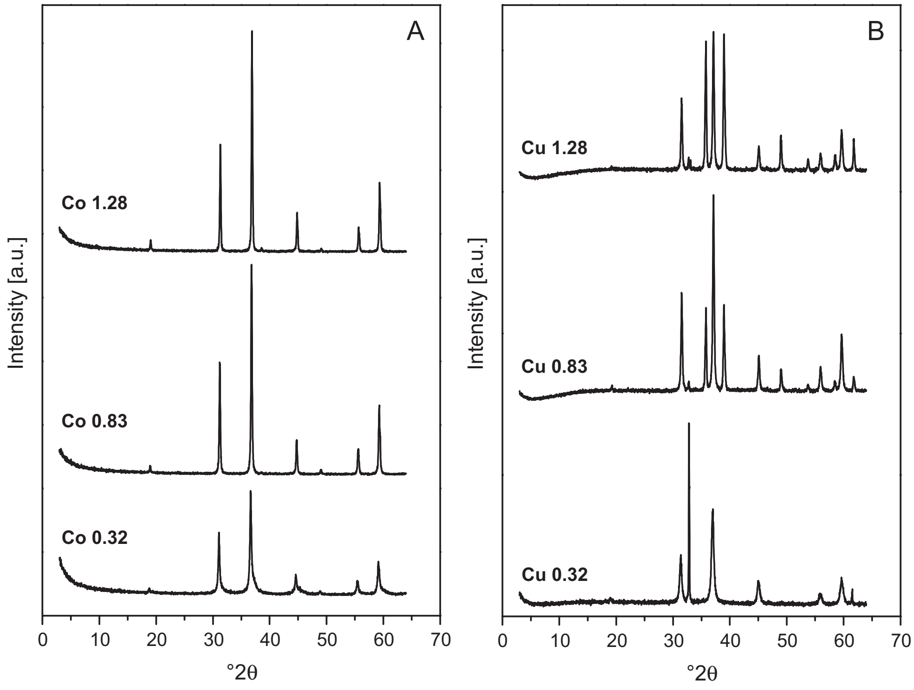

Fig. 1. X-ray diffraction patterns of Co- (A) and Cu-containing (B) catalysts.

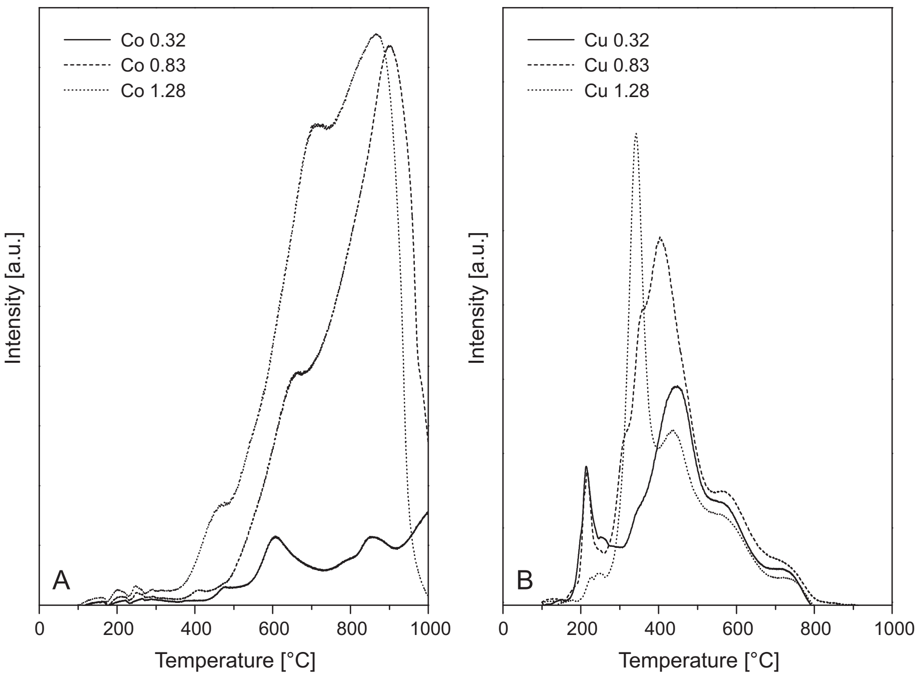

Fig. 2. Temperature-programmed reduction profiles of Co- (A) and Cu-containing (B) catalysts.

content (Table 1). The same tendency was observed for total pore volume. The Co0.32 preparation exhibited the biggest surface area and pore volume. The shape of N_2 adsorption–desorption isotherms (not shown) revealed that the samples with the lowest transition metal loading were mesoporous solids. An increase in the Cu and Co content resulted in sintering of catalyst particles and the materials showed only wide interparticle porosity.

The catalysts crystallised mainly in the spinel structure. For the preparations containing cobalt two spinels—Co_3O_4 and $CoAl_2O_4$ with very similar interplanar distances, appeared. The only XRD peak characteristic of the cobalt aluminate (3 3 1) plane [AMCSD 99-100-5469], which is absent in the diffraction pattern of Co_3O_4 [AMCSD 99-100-6234], is seen in Fig. 1A at 2θ ca 49.0°. Its relative intensity lowers with increasing cobalt loading suggesting the biggest share of the Co_3O_4 phase in the Co1.28 sample. This finding was confirmed by the observation of sample colours, the Co0.32 preparation was blue like Thénard blue, the Co0.83 and Co1.28 samples were green, whereas Co_3O_4 is black. In the XRD patterns of the copper aluminium oxide samples, shown in Fig. 1B, one can see that the sample with the lowest Cu loading crystallised as copper aluminate with the peaks at $2\theta = 18.9$, 31.3, 36.9, 45.0, 55.8 and 59.6° from the (1 1 1), (2 2 0), (3 1 1), (4 0 0), (4 2 2) and (5 1 1) planes, respectively [PDF-2 33-448]. The increase in the copper content resulted in the formation of CuO beside $CuAl_2O_4$. The intensities of the peaks at $2\theta = 32.7°$, 35.7°, 38.9°, 49.0°, 53.7°, 58.5° and 61.8° originating from the copper oxide (1 1 0), (0 0 2) or (−1 1 1), (2 0 0), (−2 0 2), (0 2 0), (2 0 2), and (−1 1 3) planes [PDF-2 41-254], respectively, were the highest for the Cu1.28 sample.

Fig. 2 presents reducibility of the transition metal containing catalysts. For the sample with the lowest Co loading at least three peaks in the H_2-TPR profile (Fig. 2A) can be distinguished at ca 480, 600 and 850 °C, their resolution is not good and worsens for the preparations with the higher cobalt contents. It should be however assumed that the catalysts containing cobalt underwent reduction in three essential steps, in two first probably Co^{3+} and Co^{2+} ions occurring in the Co_3O_4 structure were reduced and in the third—cobalt ions built into the aluminate spinel structure. The

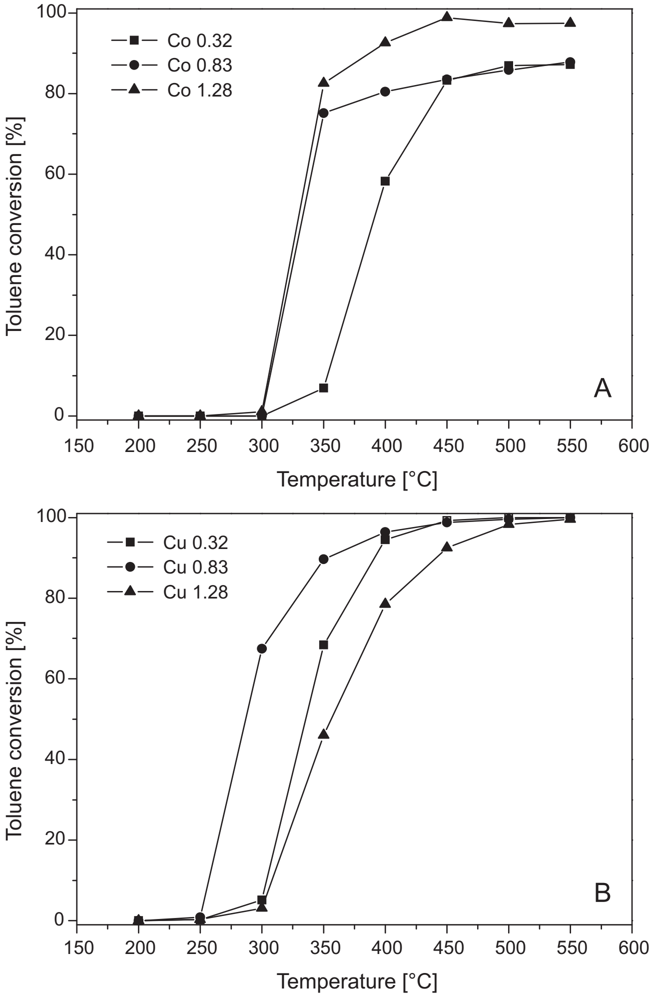

Fig. 3. Toluene conversion over Co- (A) and Cu-containing (B) catalysts.

high temperature of $CoAl_2O_4$ reduction reveals a strong stabilization of Co^{2+} ions surrounded by Al^{3+} in the spinel phase [6]. With the increase in the cobalt content the beginning of samples' reduction was observed at lower temperatures (about 430, 360 and 340 °C for Co0.32, Co0.83 and Co1.28, respectively). In the case of the copper catalysts (Fig. 2B) the multi-step reduction took place as well. For the samples Cu0.32 and Cu0.83 the first reduction peak is observed at 215 °C. The main stage of the reduction for all samples started at about 260 °C and occurred in a few steps, which shoulders confirm. The low temperature reduction—to 400 °C, can be ascribed to reducing CuO, at ca 215 °C highly dispersed copper oxide undergoes reduction and at ca 310 °C its clustered form [2]. The high dispersion of CuO in the Cu0.32 sample is confirmed by the absence of this phase in the XRD pattern (Fig. 1B). The TPR peak at ca 340 °C in the Cu1.28 sample plot can be attributed to crystalline copper oxide, because this phase was dominant as seen in Fig. 1B. At 440 °C copper ions in the $CuAl_2O_4$ structure were reduced in the Cu0.32 preparation containing only the copper aluminate phase according to XRD. Raising the Cu content caused the shift of the reduction temperature of the copper ions in the spinel structure to lower values. Comparing the cobalt and copper oxide catalysts one can state that the copper containing samples were more easily reducible.

The obtained samples were tested as catalysts in the total oxidation of toluene. The only detected carbon-containing product of this reaction was carbon dioxide. Over the cobalt-doped samples toluene oxidation started at about 300 °C (Fig. 3A). The toluene conversion increased with the Co loading and achieved the maximum at about 450 °C for the Co1.28 sample. The correlation between the catalytic activity and the phase composition can be found. The samples containing a relatively high amount of easily reducible Co_3O_4 were significantly more catalytically active compared to the materials with a dominant share of $CoAl_2O_4$. It seems that the porosity of the cobalt containing samples did not influence their catalytic activity. In the case of the Cu-doped samples (Fig. 3B), the reaction began at 250 °C and the least active catalyst contained the biggest amount of copper. This Cu1.28 sample, containing the highest amount of crystalline CuO (Fig. 1B), underwent low temperature H_2 reduction to the lowest extent (Fig. 2B). The sample Cu0.83 exhibited the highest catalytic activity. Since the samples Cu0.32 and Cu0.83 contained the comparable amounts of copper oxide undergoing the low temperature reduction at ca 215 °C, it seems that besides this phase copper aluminate strongly influences the catalytic oxidation of toluene. The Cu0.83 catalyst was characterised by lower pore volume compared to Cu0.32, therefore the observed catalytic activity cannot be attributed to its textural properties. It is most likely that the good catalytic performance of the Cu0.83 sample could arise from clustered copper oxide covering the spinel phase, an evidence of its presence can be the shoulder at 310 °C in the TPR profile (Fig. 2B).

4. Conclusions

Cobalt–aluminium and copper–aluminium hydroxide precursors were prepared by the coprecipitation method. Cobalt containing preparations attained their thermal stability above 400 °C, whereas copper containing samples were thermally stable at ca 900 °C. At this temperature the highly crystalline catalysts composed of the mixture of Co_3O_4 and $CoAl_2O_4$ spinels or CuO and $CuAl_2O_4$, respectively, were obtained. The cobalt-containing samples underwent three step H_2 reduction beginning at ca 400 °C, while the Cu–Al–O catalysts were reduced in a few steps, with the first distinct peak at ca 215 °C. The catalysts containing copper turned out more active in the low-temperature total oxidation of toluene. It was found that Co_3O_4 and clustered CuO deposited on $CuAl_2O_4$ were the phases responsible for the high catalytic activity of the studied oxide systems.

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