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Copper-aluminum oxide catalysts for total oxidation of toluene synthesized by thermal decomposition of co-precipitated precursors

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ABSTRACT

Copper–aluminum containing precursors with various Cu/Al molar ratios (from 0.32–1.28) were prepared by co-precipitation in the presence of ammonium carbonate. The thermal stability of the obtained materials was investigated by thermal analysis, which revealed three crucial decomposition steps, finally resulting in the formation of mixed Cu–Al oxides. The changes in structure and texture of the samples at each decomposition step were examined by X-ray diffraction (XRD), diffuse reflectance UV–vis spectroscopy (UV–vis-DRS) and low temperature sorption of nitrogen. It was found that the entire removal of structural carbonates requires a calcination temperature as high as 900 °C. The samples after thermal treatment at this temperature varied in the phase composition of the bulk (determined by XRD) as well as of the surface (determined by X-ray photoelectron spectroscopy). All samples contained the $CuAl_2O_4$ phase. Furthermore, an increase in Cu content led to the appearance of an increasing amount of CuO. Copper oxide in the form of relatively small crystallites turned out to be the catalytically active phase in the total oxidation of toluene.

1. Introduction

Volatile Organic Compounds (VOCs), which are emitted during processes involving organic substances, are air pollutants that are harmful to the environment and organisms. VOCs deplete the stratospheric ozone layer, as well as take part in photochemical reactions resulting in the formation of tropospheric ozone. They also contribute to the greenhouse effect. Furthermore, some VOCs cause cancer and gene mutations, influence the functioning of the respiratory system and damage the central nervous system, liver and kidneys [1].

The most efficient method of VOCs removal from low emission sources is their catalytic total oxidation. In this process, noble metals as well as transition metal oxides are used as catalysts [2–5]. Although Pt or Pd supported on γ-Al_2O_3 are the most active systems, they are expensive and prone to poisoning. Therefore, transition metal oxides with mobile electrons and positive oxidation state have been widely investigated as catalysts in total oxidation. V, Cr, Mn, Fe, Co, Ni and Cu oxides have turned out to be the most promising catalysts for this process, which occurs by the strong adsorption of an organic molecule at an anionic oxygen site–chemisorbed or present in the oxide lattice, and its subsequent transformation to CO_2 and H_2O. When metal oxides are regarded as potential catalysts for VOCs' total oxidation, three factors are taken into consideration: their stability, the type of semiconductor which they belong to and oxygen mobility. It has been found that, generally, better catalytic properties are exhibited by unstable metal oxides, because metal remains reduced during oxidation reactions at relatively low temperatures and gas phase molecular oxygen may be the oxidant. These metal oxides, which are *p*-type semiconductors, can adsorb oxygen from the gas phase in the form of O^- active species–not too strongly bound to the surface and therefore highly mobile [2].

Toluene is a solvent and industrial feedstock, commonly used in various applications (e.g., the chemical industry, printing, and gasoline fuels) [6]. That is the reason why this toxic compound is often chosen as a model molecule of aromatic VOCs. Among supported oxide catalysts, copper oxide (about 5 wt.%) deposited on γ-Al_2O_3 – ensuring the best dispersion of the active phase – exhibited the highest activity in the total oxidation of toluene (almost 100% conversion at 350 °C) [7,8]. Such catalysts are usually thermally activated in

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the temperature range of 400–450 °C, which is high enough to obtain stable γ-Al_2O_3 (about 400 °C) [9] and to decompose copper nitrate, which is used as a common precursor of an active phase (about 350 °C) [10]. Another group of catalysts examined in the total oxidation of toluene involves mixed oxides (synthesized by reverse microemulsion [11] or coprecipitation [12,13]), which are characterized by high metal dispersion and good thermal stability as well as the presence of copper cations in the reduced state. To obtain a Cu-containing oxide phase free of impurities (e.g., structural carbonates), its precursor must be calcined at a temperature as high as 800 °C regardless of the applied precipitating agent – ammonium hydroxide [14] or ammonium carbonate [15].

The Cu-loaded mixed oxides prepared by reverse microemulsion turned out to be active catalysts in the combustion of toluene. The highest activity was found for the copper–manganese oxide material (with a Mn/Cu molar ratio equal to 2:1) calcined at 450 °C, which enabled achievement of above 98% conversion at a temperature as low as 220 °C [11]. Over hydrotalcite-derived copper–magnesium–aluminum oxides (a molar Cu/Mg/Al ratio equal to 0:4:2, 1:3:2, 2:2:2, 3:1:2 and 4:0:2), prepared by coprecipitation followed by thermal treatment at 450 °C, the total conversion of toluene was attained at 375 °C. The most efficient catalyst contained only copper and aluminum with a Cu/Al molar ratio 2:1. During calcination, copper oxide was formed as the only crystalline phase, and the catalyst was characterized by a specific surface area of 53 m^2/g [12]. Manganese–copper–aluminum (3:3:1) and zinc–copper–aluminum (1.5:1.5:1) oxides obtained by decomposition of hydrotalcite-like precursors (at 450 or 600 °C) were also studied by Palacio et al. [13]. The catalyst containing Mn crystallized as spinel, whereas the Zn–Cu–Al sample was an amorphous solid (after calcination at 450 °C) or a mixture of zinc and copper oxide crystallites (after calcination at 600 °C). The low crystalline manganese spinel was the most active in toluene oxidation. Among the Zn–Cu–Al catalysts, the sample containing mixed oxides was more efficient than the amorphous one.

The aim of this paper was to examine the thermal behavior of co-precipitated copper-aluminum precursors with different Cu/Al molar ratios (varying from 0.32–1.28). Co-precipitation was carried out without controlling pH using an aqueous solution of ammonium carbonate, which ensured alkaline conditions required for hydroxide precipitation and protected the prepared samples from contamination with alkali metals influencing their catalytic activity. The optimum conditions of thermal treatment resulting in the formation of carbonate-free mixed Cu–Al oxides were found. Such materials were tested as catalysts in the total oxidation of toluene. The catalytic activity was correlated with the bulk and surface structure of the examined samples, as determined by X-ray diffraction, diffuse reflectance UV–vis spectroscopy and X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. Synthesis of catalysts

Catalyst precursors were obtained by coprecipitation at a constant temperature of 50 °C. $Cu(NO_3)_2 \cdot 3H_2O$ and $Al(NO_3)_3 \cdot 9\,H_2O$ were sources of metal cations, whereas $(NH_4)_2CO_3$ was used as a precipitating agent. A total amount of metal nitrates equal to 0.25 M, at a Cu/Al molar ratio of 0.32, 0.64, 0.83, 0.96, 1.09 and 1.28, was dissolved together in 250 mL of deionized water. An aqueous solution (250 mL) containing the stoichiometric amount of ammonium carbonate with 20% excess was prepared. Both solutions were dosed simultaneously into a separate beaker at a constant rate of 4 mL/min under vigorous stirring. The obtained precipitate was aged at 50 °C for 1 h, then cooled to room temperature, isolated by filtration and washed with distilled water. The precursors were dried at room temperature for 12 h, and subsequently calcined at 400, 600 or 900 °C in air for 6 h with heating ramp time of 2 h. The obtained samples are denoted as Cu*x* where *x* expresses the intended Cu/Al molar ratio.

2.2. Characterization of catalysts

The metal content in the samples was measured by inductively coupled plasma optical emission spectrometry (ICP-OES) with a SPECTRO ARCOS SOP spectrometer (SPECTRO Analytical Instruments GmbH & Co., KG). The thermal stability of the synthesized materials was determined using thermogravimetric analysis (TGA). A sample (about 25 mg) was heated at a rate of 10°/min from 30 to 1000 °C in flowing air (80 mL/min). A Mettler Toledo TGA/SDA 851 thermogravimeter connected on-line with a Balzers Thermo Star quadrupole mass spectrometer (MS) was used for the analyses. The crystallographic structure of samples was examined using a Philips X'pert APD diffractometer with Cu radiation (λ = 1.540560 Å). Powder X-ray diffraction patterns were recorded in the 2θ range of 2–64° with a step of 0.02°. The molecular structure of samples was investigated by UV–vis-DR spectroscopy in the wavelength range of 190–900 nm with 2 nm resolution by means of a Nicolet Evolution 600 spectrophotometer equipped with an integrating sphere. Textural properties of the calcined materials were determined from results of low temperature sorption of nitrogen. N_2 adsorption–desorption isotherms were measured by means of an ASAP 2010 sorptometer (Micromeritics). Before measurements, the samples were outgassed at 350 °C under vacuum for 12 h.

X-ray photoelectron spectra were recorded with a Prevac photoelectron spectrometer equipped with a hemispherical VG SCIENTA R3000 analyzer. The examined samples were loaded through a load lock (where pressure lower than 3×10^{-7} mbar was achieved) into an ultrahigh vacuum analytical chamber with a base pressure of 5×10^{-9} mbar. XPS measurements were performed with a monochromatized aluminum source AlKα (E = 1486.6 eV) and a low energy electron flood gun (FS40A-PS) to

Table 1
Composition and textural parameters of the samples calcined at various temperatures.

Sample	Bulk Cu/Al atomic ratio	BET specific surface area [m^2/g]			Total pore volume [cm^3/g]		
		400 °C	600 °C	900 °C	400 °C	600 °C	900 °C
Cu0.32	0.30	68	60	46	0.16	0.13	0.09
Cu0.64	0.60	71	66	30	0.18	0.13	0.06
Cu0.83	0.81	137	129	21	0.50	0.46	0.07
Cu0.96	0.90	64	62	19	0.15	0.12	0.03
Cu1.09	1.05	107	101	16	0.27	0.29	0.03
Cu1.28	1.19	66	66	16	0.15	0.15	0.03