



Research paper

In-situ characterization of the thermal treatment of Zn-Al hydrotalcites with respect to the formation of Zn/Al mixed oxide active in aldol condensation of furfural

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ARTICLE INFO

Keywords:

Zn-Al mixed oxides
Hydrotalcites
Thermal treatment
Aldol condensation
In-situ XRD
In-situ DRS

ABSTRACT

Manuscript firstly describes the transformation of Zn-Al hydrotalcites into the appropriate Zn-Al mixed oxides during their thermal treatment up to 1000 °C. In detail, the structure, composition, morphology and growth of ZnO and ZnAl₂O₄ phases are analysed by using of TGA, *in-situ* XRD and *in-situ* diffuse reflectance UV–vis spectroscopy. Secondly, composition (XRF), structure (XRD), texture (N₂ adsorption) and acid-base properties (TPD-NH₃, TPD-CO₂) of Zn-Al mixed oxides prepared by thermal treatment of Zn-Al hydrotalcites at 400 °C are described. Zn-Al mixed oxides are studied with respect to their utilization in the aldol condensation of furfural with acetone. Manuscript defines the region of the ZnO phase formation and their role on textural, structural, acid-base and catalytic properties of Zn-Al mixed oxides formed by thermal treatment of hydrotalcites. High values of the conversion of furfural well correlated with the low values of ZnO crystallite size and high values of the specific surface area. The contribution of acid-base properties could not be discussed, as studied mixed oxides exhibited approximately the same amount and strength of basic sites.

1. Introduction

Zn-Al mixed oxides, prepared by thermal treatment of Zn-Al layered double hydroxides, possess high interest as catalysts (Centi and Perathoner, 2008; Xu et al., 2011) and photocatalysts (Seftel et al., 2008). Zn-Al mixed oxides are attractive in many organic reactions requiring the presence of solid base catalysts (e.g. transesterification (Bournay et al., 2005; Jiang et al., 2010)). Zn-Al mixed oxides are especially attractive in activation of methanol. Montanari et al. (2010) reported that methoxy groups terminally bonded to Zn²⁺ cations are those involved in transesterification and polyethoxylation reactions. Zn-Al mixed oxides were also patented as alkoxylation catalysts for compounds containing active H atoms or for fatty acid esters (Breuer and Rath, 1994). Zn aluminates also represent attractive supporting materials for industrial processes such as Cu containing Zn aluminates for methanol synthesis (Cavani et al., 1991). In order to prepare the Zn-Al mixed oxides effectively in all these applications, attention is focused on the preparation of Zn-Al mixed oxides with various textural, structural and acid-base properties. In general, final properties of Zn-Al

mixed oxides depend on Zn/Al molar ratio, the process of the preparation of hydrotalcites and the thermal treatment of hydrotalcites into the appropriate mixed oxides.

The understanding of the thermal treatment of layered double hydroxides allows to predict the properties of mixed oxides as well as their catalytic behaviour in the above mentioned catalytic reactions. Recently, the mechanism of thermal treatment of Zn-Al layered double hydroxides into the Zn-Al mixed oxides has been reported (Ahmed et al., 2012a; Zhao et al., 2010). Hydrotalcite layered structure is preserved up to 180 °C. Subsequently, dehydroxylation of the layered structure of hydrotalcite proceeds. ZnO nuclei doped with Al³⁺ forms between 200 and 400 °C as amorphous phase, following by formation of ZnO nanoparticles doped with Al³⁺ that are homogeneously dispersed throughout the amorphous phase. Above 500–600 °C, Al³⁺ ions are released from the ZnO structure resulting in the formation of ZnAl₂O₄ phase (Zhao et al., 2010). In spite of the intensive research, detailed understanding of the thermal treatment of hydrotalcites (particle morphology, phase composition and structure) into the Zn-Al mixed oxides with desired catalytic properties is still under progress. It is

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partially due to the limitation of characterization techniques, partially due to the presence of very complex system with a different morphologies, textural properties, phase composition, structure and acid-base properties of Zn-Al mixed oxides. Thus, a lot of effort is recently focused on the using of *in-situ* techniques. *In-situ* XRD (Inayat et al., 2014; Zhao et al., 2010) and *in-situ* EPR (Drouilly et al., 2013) were currently employed to investigate the structural changes during the thermal treatment of Zn-Al layered double hydroxides to appropriate Zn-Al mixed oxides.

Aldol condensation is a liquid phase reaction, typically homogeneously catalysed by calcium or sodium hydroxides (Salvapati et al., 1989), but this method generates significant wastewater stream that needs to be purified. Therefore, heterogeneous catalysis would replace the commonly used processes. For example, high potential of zeolites (Kikhtyanin et al., 2014), phosphates (Zeng et al., 2005) and mixed oxides (Hora et al., 2015; Liu et al., 2010; Smoláková et al., 2017a; Xu et al., 2011) has been reported. Aldol condensation of furfural represents attractive route of the biomass utilization. Furfural can be obtained, for example, by acid hydrolysis of sugar cane with subsequent extraction (Lavarack et al., 2002). FAc and F2Ac are useful products of aldol condensation of furfural. Followed by hydrogenation/deoxygenation, these products give C8 and C13 alkanes (Hora et al., 2014) that can be used as a fuel.

In this work, *in-situ* XRD and *in-situ* diffuse reflectance spectroscopy were applied to study phase composition, crystal size, crystal size distribution and lattice parameters during the thermal treatment of Zn-Al hydrotalcites. Both *in-situ* techniques represent powerful tools to study the process of thermal transformation of Zn-Al hydrotalcites into the appropriate Zn-Al mixed oxides. Secondly, we focused on the analysis of the optimal thermal treatment and the preparation of Zn-Al mixed oxides active in the aldol condensation of furfural. Zn-Al hydrotalcites with a Zn/Al molar ratio of 1.3, 1.9, 3.2, 4.2 and 4.9 were prepared by co-precipitation method. Main attention was focused on the analysis of the thermal treatment of hydrotalcites up to 1000 °C with respect to the systematic investigation of the structure (presence of ZnO and ZnAl₂O₄ phases) of formed material. This information was used to prepare Zn-Al mixed oxides (thermal treatment of Zn-Al hydrotalcites at 400 °C) studied in the aldol condensation.

2. Experimental

2.1. Preparation of Zn-Al hydrotalcites and mixed oxides

ZnO was purchased from Penta. ZnAl₂O₄ spinel was synthesized according to Cesteros et al. (2000) by precipitation of the stoichiometric mixture of zinc nitrate (Zn(NO₃)₂·6H₂O) and aluminium nitrate (Al(NO₃)₃·9H₂O) with ammonium hydroxide. Ammonium hydroxide was added at a constant rate until the pH of the reaction mixture had changed from pH value of 4 to 9. The precipitation was carried out at 25 °C under vigorous stirring. The prepared material was filtered, washed with redistilled water, dried overnight at 80 °C and calcined for 8 h at 1000 °C in a muffle furnace.

Zn-Al hydrotalcite-like precursors with theoretical Zn/Al molar ratios from 1 to 5 were prepared by co-precipitation method from solution of zinc nitrate and aluminium nitrate under constant pH (Jiang et al., 2010). The synthesis was carried out in 3000 ml batch glass reactor placed in a water bath. Appropriate amount of zinc nitrate and aluminium nitrate were dissolved in distilled water (total concentration metal ions was 1 mol.l⁻¹). This solution was added with flow rate of 7.5 ml.min⁻¹ into 200 ml distilled water and the reaction mixture was intensively stirred (1400 rpm). The base solution (sodium carbonate dissolved in distilled water) was simultaneously added to the solution of zinc and aluminium nitrates in order to keep the value of pH to 10 ± 0.1. The resulting suspension was aged for 18 h at 60 °C. The product was filtered off, washed thoroughly with distilled water and dried at 80 °C overnight. Synthesized materials were denoted as Zn-Al-

Table 1

Chemical composition, specific surface area, phase composition and the calculated unit cell parameters of Zn-Al hydrotalcites.

	Zn-Al-1.3	Zn-Al-1.9	Zn-Al-3.2	Zn-Al-4.2	Zn-Al-4.9
S _{BET} (m ² g ⁻¹)	21	39	29	30	19
Zn/Al molar ratio ^a	1.0/1.3	2.0/1.9	3.0/3.2	4.0/4.2	5.0/4.9
a (Å) ^b	3.06	3.07	3.08	3.08	3.08
c (Å) ^b	22.61	22.65	22.85	22.83	22.82
D (Å) ^b	189.70	231.40	166.10	184.90	180.90
Interlayer thickness ^c	2.74	2.75	2.82	2.81	2.81
ZnO phase (wt%)	0	0	3.5	21.8	33.9
a (Å) ^d	–	–	3.25	3.25	3.25
c (Å) ^d	–	–	5.20	5.20	5.20
D (Å) ^d	–	–	165.40	178.30	118.60

^a Zn/Al molar ratio (theoretical/experimental).

^b Layered double hydroxalcalites.

^c Interlayer thickness (Å) = c/3–4.8 Å (thickness of the brucite-like sheet).

^d ZnO phase in hydrotalcites.

x, where x refers to the Zn/Al molar ratio determined by XRF analysis. With exception of Zn-Al-1.3 hydrotalcite, experimentally determined Zn/Al molar ratios were close to the theoretical ones (calculated from the amount of zinc and aluminium nitrates) (Table 1), so the proportion of metal cations in the precursor was well controlled and regulated during the co-precipitation process.

Zn-Al mixed oxides were obtained by the thermal treatment of Zn-Al hydrotalcite-like precursors at 400 °C for 4 h in a muffle furnace.

2.2. Characterization

Thermogravimetric and differential thermal analysis (TG-DTA) were performed using TA Instruments TGA Discovery series equipment. The samples (20 mg) were heated in an open alumina crucible with a heating ramp of 10 °C.min⁻¹ from room temperature to 900 °C in the flow of nitrogen 3.0 (20 ml.min⁻¹).

Specific surface area of Zn-Al hydrotalcites and Zn-Al mixed oxides was measured by using of ASIQUO 000–5 (Quantachrome Instruments) instrument. Specific surface area was measured by using of nitrogen at the boiling point of the liquid nitrogen (77 K) and it was determined by the fitting of the experimental data to the BET isotherm.

Scanning electron microscopy (SEM) images were obtained on a JEOL JSM-7500F with cold cathode as source of electron beam. The microscope is equipped with “sem-in-lens” detector, which can distinguish signal between secondary and backscattered electron according its energy.

In-situ UV–vis spectra were recorded using Evolution 300 UV–vis spectrophotometer (Thermo Scientific) equipped with the Praying Mantis diffuse reflectance accessory. Praying Mantis reflectance diffuse accessory used two 6:1 90° off-axis ellipsoidal mirrors. Such an optical geometry permits to collect up to 20% of all diffused reflected radiation. The pellet of measured sample was placed into the reaction chamber. Diffuse-reflectance spectra were measured in a reaction cell at a helium flow from the laboratory temperature (30 °C) to 550 °C, the temperature was let to be constant for 20 min at 50 °C, and successively at every 50 °C to 550 °C (the limit of *in-situ* cell). The spectra were recorded in the range of 200–800 nm (lamp source changed at 350 nm). The setting parameters were slit width of 4 nm, scan speed of 60 nm.min⁻¹ and step size of 1 nm. The reflectance was recalculated to the Kubelka-Munk function based on the eq. $F(R_{\infty}) = (1 - R_{\infty})^2 / (2 \cdot R_{\infty})$, where R_{∞} is the diffuse reflectance from a semi-infinite layer. As ZnO is direct semiconductor, the obtained spectra were transformed to the dependencies $(F(R_{\infty}) \cdot h\nu)^2$ against $h\nu$ (photon energy) in order to obtain the values of the direct energy of absorption edge (E_g) (Smith, 1978).

In-situ X-ray diffraction analysis was performed on Zn-Al hydrotalcites in powder form on a Panalytical X'Pert Pro MPD diffractometer

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