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Novel hierarchical Co_3O_4/ZnO mixtures by dry nanodispersion and their catalytic application in the carbonylation of glycerol

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ABSTRACT

Cobalt oxide nanoparticles (40–50 nm) were hierarchically dispersed on ZnO microparticles (0.2–1 μm) using a low-energy dry mixing method, resulting in a zinc–cobalt interaction that stabilizes Co^{2+} sites. Raman spectroscopy is used to evidence the nature of the interphase reaction between ZnO and Co_3O_4 particles. The system evolves toward the formation of the spinel phase, $ZnCo_2O_4$, with further temperature thermal treatment at 400 °C. The catalytic activity of these materials was tested in the transformation of renewable materials via the carbonylation of glycerol by urea. Room-temperature-prepared Co_3O_4/ZnO systems exhibit catalytic behavior in the production of glycerol carbonate reaching conversions up to 69% in 4 h with close to 100% selectivity.

1. Introduction

Glycerol is a renewable strategic raw chemical, which use depends on its efficient conversion to value-added products. However, glycerol exhibits a too versatile chemistry, resulting in a broad distribution of products that typically hampers its application [1–4]. The use of co-reactants to narrow product distribution is a particularly successful approach; for instance, the use of ammonia to make acrylonitrile, both in the vapor phase and in the liquid phase, results in yield values to acrylonitrile of 40% with nearly 90% selectivity [5–7]. Like acrylonitrile, glycerol carbonate is also a valuable chemical. Glycerol carbonate is one of the glycerol derivatives that attract more scientific and industrial interest due to its potential end uses. The search for successful routes to efficiently produce glycerol carbonate from renewable raw materials is a key subject for different manufacturing areas since these may compete and replace petroleum-derived materials [8–10]. CO_2 has been used as a carbonylating agent under supercritical conditions [11]; but its experimental conditions are highly demanding. Other carbonylating agents like dimethyl carbonate [12,13], dialkyl carbonates [14] or urea [15] allow for milder reaction conditions. Urea is a particularly attractive carbonylating agent; Mouloungui et al. [15] patented the synthesis of glycerol carbonate by carbonylation of glycerol with urea over heterogeneous zinc catalysts such as zinc sulfate, zinc organosulfate and zinc ion exchange resins. Calcined $ZnSO_4$ affords the best results by reaction with urea (glycerol carbonate yields 86% in 2 h) at 150 °C and 40 mbar; the ammonia formed is removed during reaction. However, $ZnSO_4$ salt is soluble in glycerol; thus, this is a homogeneous catalysis reaction, where the catalyst is partially recovered after reaction. There is a strong strategic and environmental benefit in developing a heterogeneous catalyst for this process. Heterogeneous catalysts are particularly efficient for cabonylation of glycerol with urea [16,17] affording good yield values under more moderate reaction conditions. Climent et al. [17] have recently reported the carbonylation of glycerol (glycerol carbonate yield 72% in 5 h) with urea at 145 °C over heterogeneous catalysts such as basic oxides (MgO and CaO) and mixed oxides (Al/Mg and Al/Li) derived from hydrotalcites with adequate acid–base pairs [17].

The reactions described above have a significant environmental and sustainable value; the development of environmental friendly catalytic process requires heterogeneous catalysts. The preparation stage is a key component in the environmental value of a catalyst. We have reported a residue-free and solvent-free preparation method to make hierarchical nanoscaled catalysts dispersed on microscaled particles [18,19]. This nanodispersion method opens up opportunities to obtain hierarchical nanoparticles–microparticles

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systems with unusual properties by mixing oxides of dissimilar materials. The interfaces created after the partial reaction of two oxides exhibits new and interesting properties due to proximity and diffusion phenomena [20,21], which become relevant at the nanoscale range. We have demonstrated that interface-related properties lead to the appearance of ferrimagnetism in mixtures of ZnO and Co_3O_4 despite the constituting oxides present diamagnetic and paramagnetic characters at room temperature, respectively [22,23].

The effects in the preparation procedure of Co_3O_4/ZnO mixtures obtained by dry nanodispersion is presented and discussed. In addition, the effects on the phase structure and morphology of Co_3O_4/ZnO mixtures are evaluated. It is shown that Co_3O_4/ZnO interface properties are modified producing changes in the catalytic properties of the mixtures as it was tested in the carbonylation reaction of glycerol with urea.

2. Experimental details

2.1. Nanodispersion procedure of Co_3O_4/ZnO mixtures

The compositions with 0.5, 1, 5 and 10 wt.% of Co_3O_4 nanoparticles (hereafter, named as ZCo0.5-Nps, ZCo1-Nps, ZCo5-Nps and ZCo10-Nps respectively) were prepared by incorporating the appropriate amounts of Co_3O_4 nanoparticles and ZnO microparticles by a previously described dry nanodispersion procedure [18]. The dry dispersion process consisted on shaking Co_3O_4/ZnO mixtures and 1 mm ZrO_2 balls in a 60 cm^3 nylon container for 5 min at 50 rpm using a tubular-type mixer. Pure ZnO and Co_3O_4 powders were also subject to the same mixing process to ensure that no structural disorder contributions were produced by the mixing process. The raw materials used in this study are cobalt oxide (Co_3O_4, 99.99%) and ZnO (99.99%). Analytical grade powders were dried at 110 °C for 2 h before dry mixing.

2.2. Morphology characterization

The particle size and morphology of the powders were evaluated using secondary electrons images of Field Emission-Scanning Electron Microscopy, FE-SEM (Hitachi S-4700) and Transmission Electron Microscopy (TEM, Hitachi H-7100 175) with an accelerating voltage of 120 kV. For TEM investigations, powders were suspended in isopropanol, and a drop of this suspension was deposited on a holey carbon-coated film supported on a 400 mesh copper grid.

2.3. Structural characterization

The crystalline structure was determined by X-ray diffraction analysis (XRD, Siemens D5000, Munich, Germany, Cu Kα radiation). The Raman spectra were measured in air atmosphere at room temperature, using the 514 nm excitation line from an Ar^+ laser operating at 10 mW. The signal was collected by a microscope Raman spectrometer (Renishaw Micro-Raman System 1000) in the 100 cm^{-1}–1100 cm^{-1} range.

2.4. Reaction procedure in the carbonylation of glycerol with urea

In a typical experiment, an equimolecular mixture of glycerol and urea were placed in a 10 mL round-bottom flask in a batch reactor for 5 min before the catalyst was added. The reaction was heated in an oil bath at 140–145 °C and stirred at 300 rpm. Reactions were run in the absence of a solvent at atmospheric pressure removing ammonia from the system by air passing through the reactor. The amount of catalyst used was 6% by weight of the initial amount of glycerol. After the reaction was completed, water was added and the catalyst was removed by filtration. The catalyst was washed with acetone several times and dried at room temperature for 24 h to be used in a new cycle of reaction. The reactions were followed by gas chromatography using a HP5890 gas chromatograph (GC) equipped with a 50-m-long Ultra2–5% Phenyl methyl siloxane capillary column and a flame ionization detector (FID) (Accuracy <5% relative).

3. Results and discussion

3.1. Morphology of the Co_3O_4/ZnO mixtures

Fig. 1a and b shows the morphology of pure ZnO and Co_3O_4 raw materials. The FE-SEM micrograph, Fig. 1a, shows the typical ZnO morphology, consisting mainly of elongated prismatic particles and nearly cubical particles, with sizes of 0.2–1.0 μm and an average particle size 0.5 μm. The morphology of Co_3O_4 particles is that of small spherical particles with sizes of 40–50 nm (see insert Fig. 1b) which form globular agglomerates ranged from 0.5 μm to 4 μm, Fig. 1b. On the other hand, the FE-SEM image of the mixture of ZnO with 10 wt.% of Co_3O_4 nanoparticles prepared by dry nanodispersion method is shown in Fig. 1c. The micrographs show that most of the Co_3O_4 agglomerates disappear and the individual nanoparticles are adhered to the ZnO surfaces Fig. 1d. The dispersion and great adherence of nanoparticles could indicate the appearance of Co_3O_4/ZnO interfaces at room temperature between these materials, due to the high initial reactivity of the Co_3O_4 and ZnO. All individual nanoparticles are dispersed below 10 wt.% Co_3O_4, but some agglomerates become apparent at higher Co_3O_4 loadings. This means that a dispersion limit of Co_3O_4 nanoparticles on ZnO microparticles has been reached. It is worth to mention that ZnO particles morphology is kept invariant, as a result of the low energy of the mixture process. The TEM micrograph in Fig. 1d confirms the presence of interfaces between ZnO–Co_3O_4 after the dry mixing process.

3.2. Structural characterization of Co_3O_4/ZnO system

The X-ray diffraction patterns of the raw materials and the Co_3O_4/ZnO mixtures, displayed in Fig. 2, can be indexed on the basis of a phase mixture constituted by a majority of ZnO and a minority of Co_3O_4. As expected, the intensity of the diffraction peaks of Co_3O_4 phase becomes increasingly stronger with Co_3O_4 loading.

In order to check the effect of the thermal treatment temperature on the phase structure, the mixtures were thermally treated at 500 °C for 36 h. No changes are observed in the XRD pattern after such thermal treatment, Fig. 2.

No evidence of metallic Co, CoO or any additional phases different than ZnO, Co_3O_4 were found in any sample, within the XRD resolution. The expected reaction between Co_3O_4 and ZnO is the formation of a $Zn_{1-x}Co_xO$ wurtzite-type solid solution, which possesses the same lattice parameters than ZnO. This would explain the fact that only the diffraction peaks of ZnO are observed at 500 °C. There is little difference between the ionic radii of Co^{2+} (0.058 nm) and Zn^{2+} (0.060 nm) and, therefore, small changes in the *c*-axis value due to Co substitution in ZnO can be expected. At higher temperatures, the formation of the spinel phase $ZnCo_2O_4$ is possible but this phase is isostructural with Co_3O_4 and X-ray diffraction patterns cannot determine whether the spinel forms.

The Co_3O_4/ZnO mixtures prepared by nanodispersion method and thermally treated at 500 °C have also been investigated by Raman spectroscopy, and the resulting spectra are depicted in Fig. 3a. ZnO has a wurtzite structure, with two formulae per primitive cell