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ARTICLE

Effect of Metal Additives on Structure and Properties of a Co/SiO_2 Hydrogenation Catalyst

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Abstract: The effects of metal additives (Zn, Fe, Cu, and Sn) on the properties and catalytic performance of a Co/SiO_2 catalyst (prepared by a co-precipitation method) in the liquid-phase hydrogenation of ethyl lactate were investigated. The electronic properties and surface distribution of Co in the catalyst were significantly changed by incorporation of the additives. The particle size of the cobalt species was reduced, which strengthened the interaction between the cobalt particles and the silica support and decreased the reducibility of the catalyst. As a consequence, both ethyl lactate conversion and 1,2-propanediol selectivity decreased upon incorporation of the additives. Ethyl lactate conversion was related less to the size and surface area of the catalyst particles than to the distribution of the cobalt species and the reducibility of the catalyst.

Key words: cobalt; metal additive; structure; ethyl lactate; hydrogenation

Lactic acid, an important biomass-derived platform molecule, has been commercially produced by fermentation of renewable resources, such as sugars, starches, and xylose [1]. Much effort has been directed toward transforming lactic acid into high-value chemicals [1–9]. In particular, the selective hydrogenolysis of lactic acid to 1,2-propanediol (1,2-PDO), an important feedstock for the manufacture of polymers and pharmaceuticals, is a promising and environmentally benign alternative to the traditional petroleum-based process for the production of 1,2-PDO [2–7]. Previous reports on the hydrogenation of lactic acid have indicated that Ru- and Cu-based catalysts are significantly more active, however, severe reaction conditions (e.g., high temperature and pressure) are generally required with these catalysts [2,6]. Pd-based catalysts have also been evaluated for this important reaction, but they require a relatively high temperature (>300 °C) for reasonable activity [10].

In view of the severe reaction conditions required for the direct hydrogenolysis of lactic acid, as well as the lower reactivity of lactic acid relative to that of lactate, producing 1,2-PDO by hydrogenolysis of lactate is advisable. From the standpoint of molecular structure with a reactive hydroxyl group, high reaction temperature is undesirable for the hydrogenolysis of lactate because of the potential for side reactions such as polymerization, dehydration, and transesterification, which decrease the 1,2-PDO selectivity [2,6]. Therefore, it is of great importance to develop active catalysts with the research of the influence of the support, the preparation methods, the nature of the active phases, and the use of metal additives.

Bimetallic catalysts are of particular interest because they exhibit better selectivity, higher stability, fewer side reactions, and greater potential for reactivation than monometallic catalysts. Luo et al. [4,5,11] have extensively studied Ru-based catalysts with various metal additives prepared by a chemical reduction method for the hydrogenation of lactate. These investigators found that various RuM/B (M = metal) bimetallic catalysts exhibit different activities and selectivities owing to differences in electron transfer between B and metallic Ru and differences in H_2 adsorption behavior resulting from incorporation of the additives. Luo et al. proposed a catalytic mecha-

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nism based on the synergy between metallic Ru and oxidic additives during the hydrogenolysis.

Cobalt-based catalysts with various supports and metal additives are the most used catalysts for hydrogenation reactions in a variety of systems. Copper, zinc, tin, iron, and noble metals have already been studied as promoters for cobalt-based catalysts [12,13,17,28,35]. The addition of relatively small amounts of noble metals greatly enhances the performance of cobalt-based catalysts by increasing their reducibility [12,13]. Recently, vapor-phase hydrogenolysis of a lactate ester to 1,2-PDO over a Co/SiO_2 catalyst prepared by impregnation was systematically investigated [14], and a linear relationship between hydrogenolysis activity and the percentage of the bulk-like Co_3O_4 in the catalyst was observed. In our previous work, we found that the method used to prepare the Co/SiO_2 catalyst significantly affects the liquid-phase hydrogenolysis of lactate to 1,2-PDO, owing to variations in the cobalt species formed [15]. The significant catalytic activities were in correlation with different cobalt species based on the inherent different chemical phenomena during contrary preparation procedures from the Co–OH–Co olation and Si–O–Co oxolation molecular mechanisms.

In the present work, we investigated the effect of metal additives on Co-based catalysts for the hydrogenation of ethyl lactate. A series of CoM/SiO_2 bimetallic catalysts were prepared by a co-precipitation method. The catalyst structures were characterized by means of various chemical and physical techniques, including N_2 adsorption, X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS), temperature-programmed reduction (TPR), and transmission electron microscopy (TEM), and the resulting information was used to correlate the microstructures of the solid catalysts with their performance in the catalytic hydrogenolysis of ethyl lactate.

1 Experimental

1.1 Catalyst preparation

The monometallic Co/SiO_2 catalyst was prepared by a precipitation-gel method as follows. An aqueous solution of NaOH (4 mol/L) was added dropwise to a solution of $Co(NO_3)_2$ (0.55 mol/L) at a constant rate under vigorous stirring. A calculated amount of colloidal aqueous silica solution (SiO_2, 40.0 wt%, pH = 9.0–9.5, Guangzhou Renmin Chemical Plant, Guangzhou, China) was added dropwise to the resulting precipitate to form a gel, which was allowed to age at 80 °C for 4 h. The resulting slurry of the gel was filtered, and the gel was thoroughly washed with hot distilled water, dried at 120 °C overnight, and calcined at 450 °C under air for 3 h.

The bimetallic catalysts CoM/SiO_2 (M = Zn, Fe, Cu, or Sn) were prepared in a manner similar to that described for the monometallic catalyst except that solutions containing the desired concentrations of $Co(NO_3)_2$ and the corresponding metal salt of the metal additive used. The precursors for the Zn, Fe, Cu, and Sn metal additives were $Zn(NO_3)_2\cdot 6H_2O$, $Fe(NO_3)_3\cdot 9H_2O$, $Cu(NO_3)_2\cdot 3H_2O$, and $SnCl_2\cdot 2H_2O$ (analytical purity), respectively.

The metallic cobalt loadings, determined by X-ray fluorescence spectroscopy (XFS, PANalytical Magix PW 2403), were 19.6 wt%, 17.6 wt%, 18.0 wt%, 18.5 wt%, and 16.9 wt% for Co/SiO_2, $CoZn/SiO_2$, $CoFe/SiO_2$, $CoCu/SiO_2$, and $CoSn/SiO_2$, respectively. The metal additive content was determined to be 3 wt% for all the CoM/SiO_2 catalysts.

1.2 Catalyst characterization

The XRD patterns of the catalysts were obtained on a PANalytical X'pert Pro diffractometer using Ni-filtered Cu K_α radiation with a scanning angle (2θ) of 15°–80°, a scanning speed of 2°/min, and a voltage and current of 40 kV and 30 mA, respectively. The average Co_3O_4 particle sizes were calculated from the most intense Co_3O_4 line (2θ = 36.8°), using the Scherrer formula.

XPS spectra were obtained with a VG ESCALAB 210 spectrometer equipped with a Mg K_α X-ray radiation source ($h\nu$ = 1253.6 eV) and a hemispherical electron analyzer. The spectra were recorded in the constant pass energy mode with a value of 20 eV, and all binding energies (BEs) were calibrated using the Si 2p peak at 103.4 eV as the reference.

Brunauer-Emmett-Teller (BET) surface areas of the catalysts were measured on a Micromeritics Tristar II 3020 instrument at liquid nitrogen temperature. Both the nitrogen adsorption-desorption isotherms and pore size distributions of the samples were measured.

TPR experiments were conducted with an instrument constructed in our laboratory. A sample of catalyst precursor (20 mg) was pretreated in a He flow (50 ml/min) at 200 °C for 1 h and then cooled to room temperature. Then a reducing gas composed of 5% H_2/Ar was introduced at a flow rate of 50 ml/min, with a heating rate of 10 °C/min from ambient temperature to 850 °C. H_2 consumption was continuously monitored with a thermal conductivity detector.

TEM images were obtained with a JEM2010 electron microscope at 200 kV. Catalyst powders were suspended in alcohol with ultrasonic dispersion for 30 min, and then the resulting solution was dropped on a carbon film on a copper grid.

1.3 Catalytic hydrogenolysis

Discontinuous hydrogenolysis of ethyl lactate was carried out in a 100 ml stainless steel autoclave at a stirring speed of 400 r/min. Unless otherwise stated, Co/SiO_2 and CoM/SiO_2 prereduced in a H_2 stream at 350 °C for 3 h were used. The hydrogenolysis reaction was carried out under the following standard conditions: 160 °C, 6.0 MPa of initial H_2 pressure, 2 g of ethyl lactate, 18 g of ethanol solvent, 1 g of reduced catalyst,