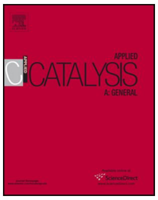
Applied Catalysis A: General 510 (2016) 244–259

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata



Synthesis and characterization of supported copper phyllosilicate catalysts for acetic ester hydrogenation to ethanol

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ARTICLE INFO

Article history:
Received 23 July 2015
Received in revised form 14 October 2015
Accepted 18 October 2015
Available online 23 October 2015

Keywords:
Cu/SiO_2 Catalyst
Copper phyllosilicate
Co-precipitation
Phase evolution
Cu^0/Cu^+
Acetic Ester Hydrogenation
Ethanol Synthesis

ABSTRACT

Supported copper phyllosilicate (Cu/SiO_2) catalysts were prepared by a simple co-precipitation method (CP), and compared with the urea hydrolysis deposition–precipitation method (DP) in terms of phase evolution during synthesis, physicochemical properties, chemical states of copper species after reduction, and catalytic performance in ester hydrogenation to ethanol. Catalysts were characterized by N_2-physisorption, X-ray powder diffraction (XRD), IR spectroscopy, H_2 temperature programmed reduction (TPR), transmission electron microscopy (TEM), in situ X-ray photoelectron spectroscopy (XPS), and FTIR/CO spectroscopy. It was confirmed that copper phyllosilicates species existed in all catalysts but the exact form differed in the Cu-CP catalysts and the Cu-DP catalysts. While the Cu-DP catalyst favored the form of 1:1 copper phyllosilicate, the Cu-CP catalysts tended to have more species of 2:1 copper phyllosilicate which led to only small amount of active copper species on surface after reduction and thus low ester conversion. Addition of ammonium ion and zinc ion during the CP method synthesis promoted the copper silicate phase evolution from 2:1 copper phyllosilicate to 1:1 copper phyllosilicate, and the reactivity of ester hydrogenation was greatly enhanced. Conversion of 99.67%, selectivity of 99.07%, and space-time yield of 1.23 g_EtOH/(g_cat·h) were achieved at 250 °C using a Cu-Zn-NCP catalyst.

1. Introduction

Ethanol was an important industrial commodity and a potential alternative synthetic fuel to be used in automobiles. Currently, ethanol was produced by two major processes: (1) fermentation of sugars derived from corn or sugar cane, and (2) hydration of petroleum-based ethylene. Due to the diminishing crude oil resource and potential food crisis, gasification of coal or biomass to syngas ($CO + H_2$), followed by catalytic conversion of syngas to ethanol, became more promising for large ethanol production. However, due to the slow kinetics of the initial C—C bond formation and fast chain growth of C_2 intermediates, the direct conversion process suffered from low yield and poor selectivity [1]. Alternatively, several indirect, multi-step processes, such as via hydrogenation of C_2 intermediates such (acetic esters and oxalic esters) to ethanol, had attracted extensive attentions [2,3]. Among these key steps, ester hydrogenation to ethanol was the only step that was still under research and development, and thus was the technical bottleneck we needed to overcome for a viable coal-to-ethanol process. This work presented the recent development of hydrogenation catalysts for acetic ester to ethanol conversion.

Catalysts for ester hydrogenation had generally been prepared by mixing hydrogenating metals (e.g., Fe, Co, Ni, Cu, and Zn) with various oxides (e.g., SiO_2, ZrO_2, V_2O_5, Cr_2O_3, and WO_3) [4]. Typically, copper-based catalysts were considered to be suitable for selective ester hydrogenation, because they allowed for selective hydrogenation of C═O bonds but were relatively inactive in CC bond hydrogenolysis [5]. However, due to the low melting point (ca. 1083 °C) and thus low Thùttig (ca. 178 °C) and TTammann (ca. 405 °C) of copper, single copper nano particles were not sintering-resistant or mechanically stable for industrial applications [6]. Adkins and Folkers, firstly described the application of a copper-chromium catalyst for ethyl ester hydrogenation [7]. Later on, Cr-free catalysts had been developed due to strong environmental restrictions, among which Cu/SiO_2 catalysts stood out in hydrogenation of dimethyl oxalate to ethylene glycol and ethanol [2,3,8,9]. Research on silica supported copper catalysts indicated that both high dispersion of copper species and strong metal-support interaction were vital to high activity and stability in vapor-phase hydrogenation of ester to alcohols or glycol, which was similar to the Cu-Cr catalyst system [3,10,11]. In addition, because of the weak acidic and basic properties of SiO_2, Cu/SiO_2 catalysts

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http://dx.doi.org/10.1016/j.apcata.2015.10.026
0926-860X/

had demonstrated highest yield of desired products in hydrogenation of esters at mild conditions [12].

In order to obtain desired performance of Cu/SiO_2 catalysts, it was necessary to disperse fine particles onto the support. Conventional methods such as wet impregnation often led to broad size distribution of metal particles and large particle size when the loading was high. Ion-exchange approach could well disperse and stabilize copper species on silica support, but the metal loading was low due to limited amount of terminal —OH groups on the surface of silica [13]. As early as 1990, Van der Grift confirmed that Cu/SiO_2 catalysts prepared by urea hydrolysis deposition-precipitation method (DP) could offer good metal dispersion, even at high metal loading, partially due to the formation of "chrysocolla (copper phyllosilicates) -like" precursors [10]. Almost at the same time, copper phyllosilicates were reported in Cu/SiO_2 catalysts by ammonia evaporation (AE) methods [3,12,14] and hydrothermal precipitation techniques [5,10,15–18].

The chemical states of copper in both calcined and reduced copper phyllosilicates were also of great importance to the catalytic hydrogenolysis of esters. Takezaw et al. claimed that isolated cupric precursors were reduced to monovalent copper while small clusters of cupric oxide (CuO) were reduced to metallic copper in copper/silica catalysts prepared by ion-exchange approaches [19]. Van Der Grift suggested that calcination at 550 °C, as well as direct reduction at 277 °C, the "chrysocolla-like" catalyst precursors prepared by DP method led to the decomposition of copper hydrosilicate and reorganization of silica support, furthermore, calcination of the same sample at 427 °C caused the subsequent reduction to occur at a lower temperature, which indicated the presence of small copper oxide particles over silica support [17]. Gong obtained Cu/SiO_2 catalysts by ammonia evaporation hydrothermal (AEH) method, and found the coexistence of copper phyllosilicates and cupric oxide even after calcination at 400 °C. After reduction, Cu^0 and Cu^+ species co-existed and were primarily originated from well–dispersed copper oxide nanoparticles and copper phyllosilicates, respectively [3]. The synergetic effect between Cu^0 and Cu^+ was believed to play an excellent role for Cu/SiO_2 catalysts during the hydrogenolysis of dimethyl oxalate (DMO) to ethylene glycol or ethanol [3,12,15]. Since copper phyllosilicates contributed to the good dispersion of metal particles and provide active sites upon reduction, they were often considered a key component in Cu/SiO_2 catalysts.

Copper phyllosilicates were copper silicates with a lamellar structure that consists of layers of SiO_4 tetrahedra and layers of CuO_6 octahedra. The 1:1 copper phyllosilicate, which was often known as chrysocolla [$Cu_2Si_2O_5(OH)_2$], was a poorly ordered mineral containing Si/Cu≈1 and one of the typical copper phyllosilicates available in nature [10,20]. Another type of copper phyllosilicate was the 2:1 copper phyllosilicate, also called Cu-talc or Cu-smectie, which was less common and only forms when there is large excess amount of Si [20]. Several researchers revealed that silica may react with certain metal (Ni [21–23], Cu [5,10,15–18], Co [24]) precursors to form phyllosilicates during preparation, depending on the reactivity of silicic species with the metal complexes [21]. Formation of silica-supported copper phyllosilicates and nickel phyllosilicates was a well-known case during catalyst preparation by DP method [21–23] and selective adsorption of metal tetraammine complex [25,26]. Characterization studies had confirmed the formation of phyllosilicates by IR [3,10,15,21,26], EXAFS [20], and ESR [25,26]. Siffert et al. found that the prerequisites for the formation of phyllosilicates include: (1) silicic species in solution must be monomeric; (2) metal hydroxo complexes must be present in solution; and (3) The pH must be lower than that of the hydroxide precipitation. The mechanism proposed was based on the formation of two types of monomeric species in solution, i.e., monomer 1 [$(HO)_3Si$]-O-[$M(H_2O)_4(OH)$] and monomer 2 [$(HO)_3Si$]-O-[$M(H_2O)_4$]-O-[$Si(OH)_3$], whose polymerization would lead to the formation of 1:1 and 2:1 phyllosilicates, respectively [27]. In addition, in the case of Ni/SiO_2 and Cu/SiO_2 systems, it was shown that addition of NH_4^+ could inhibit the formation of phyllosilicates, which could be attributed to the formation of "competitor ion" or the decrease of the concentration of $[Cu(OH)_2(H_2O)_4]^0$ complex [26].

In the present work, silica supported copper catalysts were prepared by adding acidic copper nitrate solution to a basic sodium silicate solution to co-precipitate copper hydroxo complexes and monomeric silica. As a comparison, another kind of Cu/SiO_2 catalyst with the same composition was prepared by urea hydrolysis deposition-precipitation method (DP). These two types of catalysts were calcined at the same temperature, and the catalytic performance was evaluated by using gas phase hydrogenation of ethyl acetate as the probe reaction. Characterization of physicochemical properties of catalysts by N_2-physisorption, X-ray powder diffraction (XRD), IR spectra, H_2 temperature programmed reduction (TPR), transmission electron microscopy (TEM), in situ X-ray photoelectron spectroscopy (XPS), and FTIR/CO spectroscopy were performed to correlate with activity performance. Special attention was paid to the nature of copper precursors and the valence states of active sites on the surface of reduced catalysts.

2. Experimental Section

2.1. Catalyst preparation

The Cu/SiO_2 Catalysts studied were prepared by two different precipitation methods co-precipitation (CP) and urea hydrolysis deposition precipitation (DP). Copper nitrate $Cu(NO_3)_2{\cdot}3H_2O$ (A.R., Sinopharm Chemical Reagent, China) was used as copper source. Silica sol (JN-30, 30.62 wt% SiO_2, Qingdao Haiyang Chemical) and sodium silicate $Na_2SiO_3{\cdot}9H_2O$ (A.R., Sinopharm Chemical Reagent, China) were used as silicon source. After drying, the catalyst precursors were calcined in static air at 450 °C for 4 h. All catalysts were denoted as Cu-x, where x represents the preparation technique (CP, NCP, DP) respectively.

a) Co-precipitation of copper hydroxo complexes and monomeric silica. The Cu-CP sample was prepared as following description: 31.2 g of $Na_2SiO_3.9H_2O$ was dissolved in 200 mL deionized water to form Solution A. According to stoichiometric ratio, 13.0 g of Cu $(NO_3)_2.3H_2O$ and nitric acid [$n_{HNO3} = 2(n_{Si} - n_M)$, M represents bivalent metal cation] were dissolved in 150 mL deionized water to form Solution B. Solution A was transferred to an oil bath preheated at 90 °C, then Solution B was added drop-wise into Solution A and stirred to form a suspension, with the pH of the solution changing from 14 to 7. After the precipitation, the suspension was aged at 90 °C with stirring for 5 h. The mixture was filtrated and washed with 500 mL of deionized water five times, and then was dried at 110 °C overnight. When ammonium nitrate was added to the solution B with a Cu^{2+}:NH_4^+ molar ratio of 1:5, the precipitated sample was denoted as Cu-NCP; The Cu–Zn-NCP sample was prepared by adding zinc nitrate and ammonium nitrate to Solution B with a Cu^{2+}:Zn^{2+}:NH_4^+ molar ratio of 1:0.1:5.

b) Urea hydrolysis deposition precipitation (DP) method. 13 g of Cu $(NO_3)_2.3H_2O$ and urea (per equivalent of copper three equivalents of urea) were dissolved in 150 mL deionized water. According to the desired formula, 22.5 g of acidulated silica sol was added into the mixed solution and the pH was adjusted to 2–3 by adding nitric acid at room temperature. Then the suspension was stirred and kept at 90 °C in an oil bath for 24 h, allowing for urea hydrolysis. The pH of the suspension solution increased gradually, and when it reached 6–7, the heating process was terminated. The mixture was