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ScienceDirect
Journal of Natural Gas Chemistry 21(2012)563–570
Journal of Natural Gas Chemistry
www.elsevier.com/locate/jngc

Effect of copper loading on texture, structure and catalytic performance of Cu/SiO_2 catalyst for hydrogenation of dimethyl oxalate to ethylene glycol

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[Manuscript received November 28, 2011; revised December 21, 2011]

Abstract

Cu/SiO_2 catalysts prepared by a convenient and efficient method using the urea hydrolysis deposition-precipitation (UHDP) technique have been proposed focusing on the effect of copper loading. The texture, structure and composition are systematically characterized by ICP, FT-IR, N_2-physisorption, N_2O chemisorption, TPR, XRD and XPS. The formation of copper phyllosilicate is observed in Cu/SiO_2 catalyst by adopting UHDP method, and the amount of copper phyllosilicate is related to copper loading. It is found the structure properties and catalytic performance is profoundly affected by the amount of copper phyllosilicate. The excellent catalytic activity is attributed to the synergetic effect between Cu^0 and Cu^+. DMO conversion and EG selectivity are determined by the amount of Cu^0 and Cu^+, respectively. The proper copper loading (30 wt%) provides with the highest ratio of Cu^+/Cu^0, giving rise to the highest EG yield of 95% under the reaction conditions of p = 2.0 MPa, T = 473 K, H_2/DMO = 80 and LHSV = 1.0 h^{-1}.

Key words

Cu/SiO_2; copper loading; dimethyl oxalate; ethylene glycol; copper phyllosilicate

1. Introduction

In recent years, synthesis of ethylene glycol (EG) from coal-derived syngas has attracted significant attention because it provided an alternative route to gain EG. EG is widely used as anti-freezer, polyester fibers, alkyd resin in polyester manufacture and solvents [1,2]. At present, direct hydration for the synthesis of EG from ethylene oxide (EO) is widely adopted in large-scale production plant.

It is well-known that catalytic hydrogenation of dimethyl oxalate (DMO) to EG is one of the most important parts in the coal-based EG synthesis process [3]. Catalysts for hydrogenation have drawn an increasing research interest since it is one of the key technologies during the coal-to-EG commercialization process. Copper-based catalysts were employed for hydrogenation of DMO to EG in heterogeneous phase. At the very beginning, copper-chromium catalyst has been used in hydrogenation process for its relatively high catalytic stability and long lifespan [4]. Nevertheless, the toxic chromium contained in copper-chromium catalyst constrains its practical applications due to the increasing environmental pressures. Silica-supported copper catalysts were then found widespread application in this area, which exhibited excellent activity in oxalates hydrogenation [5−7].

Generally, silica support is considered as inert, for instance, as a mere dispersant of the active phase. However, researchers revealed that silica may react with the metal precursors and form silicates during catalyst preparation. Silica-supported phyllosilicates are known to be formed during the preparations of Ni/SiO_2 [8−10], Co/SiO_2 [11,12], and Cu/SiO_2 [13−16] by cation exchange and/or deposition-precipitation. The advantages of high dispersion, poor crystallinity, and high thermal stability of the supported metal phyllosilicate, even at elevated metal loadings, make them promising materials for catalysts.

Recently, Cu/SiO_2 catalysts with different copper loadings synthesized by urea hydrolysis method have been investigated, but the effects of copper loading have not been discussed [17]. Lin et al. [18] prepared an array of Cu/SiO_2 catalysts by sol-gel method, but the actual copper loadings were inadequate to control, yet trace of copper phyllosilicate was observed. In addition, a series of hexagonal mesoporous silica (HMS) [19−21] and SBA-15 [22] supported copper

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doi:10.1016/S1003-9953(11)60405-2

catalysts were proposed with high catalytic activity, and they focused on incorporating copper or copper oxide into mesoporous materials. However, the preparation process of the mesoporous silica support is complicated and time consuming, which is beyond the scope of this paper.

Many researchers have been devoted to study the influence of preparation parameters on the formation of copper phyllosilicates in silica-supported copper catalysts. Toupance et al. [15] obtained copper phyllosilicate by cation exchange, and they found the amount of copper phyllosilicate depended on the pH value of the precursor solution and increased with the solution/silica contact time. Chen et al. [16] found ammonia evaporation temperature also affected the amount of copper phyllosilicate. However, the effects of copper loading on the formation of copper phyllosilicate have not been investigated and the roles of copper phyllosilicate played in catalytic performance are ambiguous.

In the present work, we report a convenient and efficient method via a urea hydrolysis deposition-precipitation (UHDP) technique for the preparation of silica-supported copper catalyst with copper phyllosilicate. The effects of copper loadings on the texture and structure of Cu/SiO_2 catalysts, especially on the formation of copper phyllosilicate, are systematically studied with a series of physico-chemical characterizations. To better understand the role of copper component, the evaluation of the catalytic performance of Cu/SiO_2 catalysts has been investigated. Furthermore, the assignments of active site are discussed and correlate with catalyst texture and catalytic performance.

2. Experimental

2.1. Catalyst synthesis

Cu/SiO_2 catalysts were prepared by urea hydrolysis deposition-precipitation (UHDP) method. $Cu(NO_3)_2{\cdot}3H_2O$ (A.R., Sinopharm Chemical Reagent Ltd.) was used as copper source, silica sol (JA-30, Qingdao Haiyang Chemical Ltd.) as silicon source, and urea (A.R., Sinopharm Chemical Reagent Ltd.) as precipitant. A requisite amount of $Cu(NO_3)_2{\cdot}3H_2O$ (depending on the desired copper loading of the catalyst) was dissolved in deionized water (200 mL). A stoichiometric amount of urea was added and stirred until the urea dissolved absolutely. Subsequently, silica sol mixed with 100 mL deionized water was added into the solution moderately, and the pH value of the mixture was adjusted to 2−4 by nitric acid. Then, the suspension was vigorously stirred at 363 K in an oil bath, to allow for the hydrolyzing of urea and the increase of pH and consequently the precipitation of silica and the deposition of copper species on silica. When the pH value of the suspension increased to 6−7, the heating process was terminated. The mixture was separated by vaccum filtration, then the filtrate was washed with deionized water three times, dried at 393 K for 12−14 h, and calcined in air at 723 K for 4 h. The calcined samples were crushed and sieved to 40−60 mesh. The catalyst samples were denoted as *x*-Cu, where *x* represents the copper content.

2.2. Catalyst characterization

The copper loadings were determined by the inductively coupled plasma method (ICP, thermo E. IRIS). FT-IR spectra were recorded on a Nicolet Protégé 460 spectrometer. The samples were finely ground, dispersed in KBr, and then pelletized. The spectral resolution was 4 cm^{-1}, and 32 scans were recorded for each spectrum.

Nitrogen adsorption-desorption isotherms at 77 K were measured with a Micromeritics ASAP 2020 instrument and the samples were outgassed at 423 K before each measurement. The specific surface areas were calculated following BET method. Pore size distribution were calculated by BJH method according to the desorption isotherm branch. The dispersion and metallic copper surface areas of the catalysts were determined by N_2O chemisorption at 333 K with a Micromeritics Autochem II 2920 equipped with a TCD.

The reducibility of the calcined sample was determined by H_2 temperature-programmed reduction (TPR) on a Micromeritics Autochem II 2920 instrument connected to a Hiden Qic-20 mass spectrometer (MS).

X-ray powder diffraction (XRD) patterns of catalysts were recorded using an X-ray diffractometer (Rigaku D/Max 2500VB/PC) operated at 40 kV and 100 mA, using Cu K_α (λ = 0.15056 nm) radiation to determine the crystal structure and crystallinity of the catalyst particles. For the reduced catalyst, pure Ar was used to protect the sample from oxidation.

The surface species were detected by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250). The spectrum was recorded with Al K_α line as the excitation source (h_ν = 1486.6 eV). The binding energy (B.E.) values were referenced to the C 1s peak of contaminant carbon at 284.6−285.2 eV.

2.3. Catalytic evaluation

The catalytic tests were carried out in a U-type stainless steel tubular reactor located in a salt bath with vigorously stirred. Typically, 4.0 mL (2.0 g) catalyst (40−60 mesh) was sandwiched with quartz sand and packed in the reactor with an inner diameter of 4 mm. The catalyst was reduced with pure H_2 atmosphere at 493 K for 18 h, with gas-phase space velocity (S.V.) = 1500 h^{-1}. After cooling to the reaction temperature of 463 K, 15 wt% DMO (purity >99.5%) in methanol and H_2 was preheated, then fed into the reactor at a H_2/DMO molar ratio of 80 and a system pressure of 2.0 MPa. The room-temperature liquid hour space velocity (LHSV) of DMO was 1.0 h^{-1}. The condensed products were analyzed off-line by an Agilent 6890GC equipped with a flame-ionization detector (FID).

3. Results and discussion

3.1. Formation of copper phyllosilicate

FT-IR spectra of SiO_2 and calcined catalyst samples are