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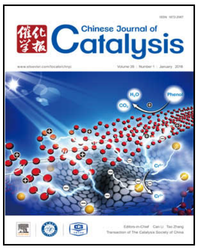

Article

In_2O_3-modified Cu/SiO_2 as an active and stable catalyst for the hydrogenation of methyl acetate to ethanol

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ABSTRACT

A series of indium oxide-modified Cu/SiO_2 catalysts were synthesized and used to produce ethanol via methyl acetate hydrogenation. In-Cu/SiO_2 catalyst containing 1.0 wt% In_2O_3 exhibited the best catalytic activity and stability. The physicochemical properties of the synthesized catalysts were investigated using several characterization methods and the results showed that introducing suitable indium to Cu/SiO_2 increased the copper dispersion, diminished the copper crystallite size, and enriched the surface Cu^+ concentration. Furthermore, the Cu/SiO_2 catalyst gradually deactivated during the stability test, which was mainly attributed to copper sintering and the valence change in surface copper species. In contrast, indium addition can inhibit the thermal transmigration and accumulation of copper nanoparticles to stabilize the catalyst.

1. Introduction

Owing to its environmental and sustainable economic advantages, ethanol has received much attention as a promising alternative to fossil fuels. In particular, ethanol is the second-most used fuel oxygenate for preventing groundwater pollution caused by methyl *tert*-butyl ether [1–3]. Although the ethanol-from-corn industry has traditionally played an important role in ethanol production, it has many issues, such as the dilemma of whether to use corn crops for food or fuel [2]. Therefore, finding new methods to produce ethanol is of great importance. As the hydrogenation of methyl acetate (MA) to ethanol is highly active and selective, it is a promising alternative method for ethanol production [4]. Traditionally, MA is mainly produced from coal and natural gas [5]. Increasing interest in shale gas and considerable coal reserves makes the hydrogenation of methyl acetate a promising ethanol production process.

Copper-based chromium oxide-supported catalysts are traditional catalysts for ester hydrogenation. However, the potential harm caused by Cr to health and the environment limits its application [6,7]. Therefore, the exploration of chromium-free catalysts has attracted much attention. Much research has focused on SiO_2-supported Cu catalysts, mainly due to their safety and low cost, which meet the needs of industrial catalysts [8]. However, problems such as short lifetime and poor stability will severely restrict the industrial application of Cu/SiO_2 catalysts. There has been much research into improving the stability and performance of Cu/SiO_2 catalysts, mainly focused on support modifications, different catalyst synthesis methods, and doping additives. Qin et al. [9] synthesized $Cu/MgO\text{-}SiO_2$ containing different MgO/SiO_2 mass ratios and found that catalysts with a MgO/SiO_2 mass ratio of 9 showed the best catalytic performance for MA hydrogenation. Yin et al. [10] studied Cu/SiO_2, Cu/TiO_2, and $Cu/SiO_2\text{-}TiO_2$ catalysts in the hydrogenation of dimethyl oxalate, and found that $Cu/SiO_2\text{-}TiO_2$ catalyst displayed high catalytic activity and long stability, which could be attributed to highly dispersed copper species and intimate

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interaction between copper species and the support. Dong et al. [11] reported a comparative study of different silica-supported copper catalyst preparation methods and found that Cu/SiO_2 catalysts synthesized using an ammonia-evaporation method exhibited the best activity in MA hydrogenation. As for doping additives, introducing noble metal additives, such as Au [12] and Pt [13], to synthesize bimetallic catalysts has been widely used to promote catalytic performance. However, the rising costs of noble metals limit further industrial use. Some noble-metal-free Cu/SiO_2 catalysts have been reported. He et al. [14] introduced B into Cu/SiO_2 catalysts, which showed greatly enhanced catalytic performance with a Cu/B atomic ratio of 6.6. Furthermore, Yin et al. [15] added an appropriate amount of Ni to increase the activity of Cu/SiO_2 catalysts, while Zheng et al. [16] synthesized lanthanum oxide-modified Cu/SiO_2 catalysts that showed better catalytic performance than Cu/SiO_2. Therefore, modifying Cu/SiO_2 with noble-metal-free additives is an efficient and low-cost approach to improving catalyst life and performance.

In the hydrogenation of biomass and steam reforming of methanol to produce H_2, the addition of indium has been shown to significantly enhance the catalytic performance of copper-based catalysts and stabilize copper surface activity [17,18]. Onyestyák et al. [19] also studied zeolite-supported Cu and Cu_2In nanoparticles for the hydrogenation of carboxylic acids to alcohols, finding that the conversion and selectivity of the catalysts was increased by In_2O_3 doping. When doped with In_2O_3, Cu-based catalysts exhibit excellent performance in some hydrogenation reactions. However, copper-based catalysts modified with In_2O_3 have not been reported in MA hydrogenation. Furthermore, changes to the structure and chemical state of copper species after In_2O_3 doping must be investigated.

Herein, xIn-Cu/SiO_2 catalysts doped with different indium oxide loadings were synthesized using the ammonia-evaporation (AE) method. The catalytic activity and stability were evaluated in the vapor-phase hydrogenation of MA. Furthermore, a series of catalyst characterization techniques were used to investigate the promotional influence of In_2O_3 on the Cu/SiO_2 catalyst.

2. Experimental

2.1. Catalyst preparation

xIn-Cu/SiO_2 catalysts with a Cu loading of 30 wt% were synthesized using the AE method, where x represents the In_2O_3 mass loading.

$In(NO_3)_3 \cdot xH_2O$ was purchased from Aladdin, China. Other reagents used were purchased from Tianjin Yuanli Chemical Institute, China. All reagents were of analytical grade and used directly without purification.

Firstly, certain amounts of $In(NO_3)_3 \cdot xH_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$ were dissolved in distilled water in a beaker. Aqueous ammonia (25 wt%) was added dropwise until the mixture reached an initial pH of around 11, and then an appropriate amount of silica sol with 25% mass content was added. All operations above were carried out at room temperature. The beaker was immersed in a water bath at 303 K and stirred for 4 h. The water bath temperature was then increased to 363 K to evaporate the ammonia. During ammonia evaporation, the pH of the mixture gradually decreased. Evaporation was terminated when the mixture pH decreased to 6–7. The resulting suspension was dried for 12 h at 393 K and the obtained powder was calcinated for 4 h at 723 K.

For comparison, $1In_2O_3/SiO_2$ samples, containing an In_2O_3 mass loading of 1%, and Cu/SiO_2 catalyst with a Cu mass loading of 30% were also prepared using the AE method.

2.2. Catalyst characterization

N_2 physisorption was performed using a Quantachrome autosorbiQ2 device. After degassing the sample for 3 h under vacuum at 573 K, N_2 adsorption-desorption isotherms were measured at 77 K. Specific surface areas ($A_{\rm BET}$) were calculated using the Brunauer-Emmett-Teller (BET) method. The total pore volume ($V_{\rm pore}$) and pore size ($D_{\rm pore}$) derived from the desorption branches of the N_2 isotherm distribution were estimated using the Barrett-Joyner-Halenda (BJH) method.

Copper dispersion is a vital index related to catalytic performance. N_2O chemisorption was performed on a Quantachrome Instrument AMI-90 apparatus to determine the copper dispersion according to a literature procedure [20].

The X-ray powder diffraction (XRD) profiles were collected on a D/MAX-2500 diffractometer with a Cu K_α radiation source under measuring conditions of 40 kV and 40 mA. The catalysts were reduced under pure hydrogen (250 mL/min) at 623 K for 4 h, and then the gas was switched to pure nitrogen under the same flow rate. After cooling to room temperature, the catalysts were collected and stored under a nitrogen atmosphere before conducting XRD measurements. The scanning angle was from 20° to 90° with a scanning rate of 5°/min. The Cu crystallite size was obtained using the Scherrer equation.

Fourier transform infrared spectroscopy (FT-IR) patterns of xIn-Cu/SiO_2 catalysts were obtained using a Nicolet iZ10 spectrometer to detect characteristics vibration bonds. Catalysts were mixed with KBr using an agate mortar and compressed into pellets for FT-IR measurement in a wavenumber range of 2200–400 cm^{-1}.

Inductively coupled plasma optical emission spectroscopy (ICP-OES), performed using an Agilent 7700ce spectrometer, was used to determine the copper and indium loadings in all catalysts. All samples were dissolved in a mixture of H_3BO_3, HF, and HNO_3, and diluted with distilled water before testing.

H_2-temperature programmed reduction (H_2-TPR) was conducted on a Quantachrome Instrument AMI-90. Prior to analysis, xIn-Cu/SiO_2 catalysts were pretreated under Ar (30 mL/min) at 373 K for 30 min. The catalysts were then reduced under 10 vol% H_2/Ar (30 mL/min) from 373 to 1073 K with a heating rate of 10 K/min.

Transmission electron microscopy (TEM) images were obtained using a JEM-2100F JEOL microscope with a voltage of 200 kV.

X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (XAES) were obtained using a Thermo ESCALAB