



Research paper

Direct production of ethanol from glycerol over Ni-substituted stichtite derived catalysts



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ABSTRACT

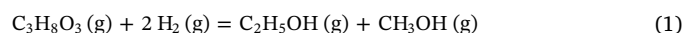
Ethanol is a widely used chemical and its primary source is via the fermentation of crops (such as corn, sorghum, rice and barley) or biomass (such as sugarcane). Direct production of ethanol from over-supplying glycerol is of great significance. In this research, we want to report a synthesis route of ethanol from glycerol over a series of Ni-substituted stichtite derived Ni/MgCr₂O₄ catalysts. The best yield of ethanol reached 0.50 g-ethanol/g-cat/h at 250 °C over Ni_{2.4}/Mg_{3.7}Cr_{2.0}O_{6.7}. The transformation process from Ni-substituted stichtite to Ni/MgCr₂O₄ catalysts was characterized by TG-DSC, XRD, XPS and TEM. Characterization results inferred that the formation of MgCrO₄ in calcined precursor played a crucial role for Ni dispersion and catalytic performance in the production of ethanol. Reaction mechanism for the formation of ethanol from glycerol was proposed.

1. Introduction

Ethanol (CH₃CH₂OH) is popularly used in medical, fuel additive, solvent, feedstock, drinks, food additive, and etc. The global production of ethanol reached 92 million cubic-meters in 2016 (Guo et al., 2016). Ethanol could be produced via the fermentation of sugar (Karimi et al., 2014; Tehrani et al., 2015), grain crops (such as corn, sorghum, rice and barley) (García et al., 2017), and waste biomass (such as sugarcane) under the help of yeasts (Tang et al., 2008; Silva et al., 2016) or through the hydration of ethylene over solid acid catalyst (Chu et al., 2004; Katada et al., 2008). And now, most ethanol is produced via fermentation process because of the growing price of crude oil. However, the toxicity of ethanol to yeast limits the concentration of ethanol in fermentation broth (Lam et al., 2014; Takagi et al., 2016), and further distillation is needed in order to get high concentrated ethanol. Thus, direct catalytic synthesis of high concentrated ethanol from renewable feedstock is of great importance (Luo et al., 2001; Yin et al., 2003a; Yin et al., 2003b; Pan et al., 2007; Chen et al., 2011; Pei et al., 2015).

Glycerol is an ideal renewable feedstock since it is formed in large quantities as a byproduct of biodiesel, and catalytic conversion of glycerol to commodity chemicals is a hot topic in the past decade (Zhou et al., 2008; Bozell, 2010; Okoye and Hameed, 2016; Sun et al., 2016). Among of which, selective dehydration of glycerol to acrolein (Chai et al., 2007; Atia et al., 2008), hydrogenolysis of glycerol to 1,2-propanediols (1,2-PDO) and 1,3-propanediols (1,3-PDO) (Nakagawa et al., 2010; Xia et al., 2014; Zhou et al., 2016; Yun et al., 2017; Zheng et al., 2017) and selective oxidation of glycerol to acids (Zope et al., 2010;

Brett et al., 2011; Nie et al., 2012; Miranda et al., 2014; Sharninghausen et al., 2014; Li et al., 2015) have attracted the attentions all over the world. In 2015, Hutchings et al. (Haider et al., 2015) disclosed that methanol could be produced directly from glycerol over MgO. Besides methanol, other products, such as ethanol, were also detected in their experiments. Furthermore, Perosa and Tundo (Perosa and Tundo, 2005) once found that ethanol was a byproduct during the liquid phase hydrogenolysis of glycerol over Ni catalyst due to the cleavage of C–C bond at high temperature and prolonged time. In a continuous flow reactor, Ryneveld et al. (van Ryneveld et al., 2011) found that the selectivity of propanol, ethanol and methanol over Ni/SiO₂ and Ni/Al₂O₃ catalysts increased gradually with the improving reaction temperature. And ethanol was also detected during hydrogenolysis of glycerol in several works (Shinmi et al., 2010; Nakagawa and Tomishige, 2011; Yun et al., 2014; Chen et al., 2016; Shozhi et al., 2016; Rajkhowa et al., 2017). These pioneering achievements inspired us that the selective formation of ethanol as the main product during catalytic transformation of glycerol is possible. Thermodynamic calculations also confirmed that the selective formation of ethanol and methanol from glycerol is favorable in thermodynamics (see Eq. (1)).



$$\Delta G = -71.8 \text{ kJ/mol at } 300^\circ\text{C}$$

In this work, a series of Ni_x/Mg_yCr_zO_{y + 1.5z} catalysts with different content of Ni and Cr were prepared via controlled calcination and reduction of Ni-substituted stichtite, and used in the selective production

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of ethanol from glycerol.

2. Experimental

2.1. Catalyst synthesis

$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (12–48 mmol), $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (48–12 mmol) and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (15–30 mmol) were mixed together in a mortar and grinded into powder, followed by the addition of NaOH (160 mmol) and Na_2CO_3 (50 mmol), and continued to grind for 15 min. The mixture was sealed and heated to 120 °C for 24 h. After that, the resulting powder was washed thoroughly with deionized water until the pH of filtrate reached 7.0, then dried at 80 °C overnight to form $\text{Ni}_x\text{Mg}_y\text{Cr}_z(\text{OH})_{2(x+y)+3z} - 2\text{CO}_3 \cdot 4\text{H}_2\text{O}$, where x, y and z represented the relative mole of Ni, Mg and Cr in final products. After calcination at 500 °C for 4 h, $\text{Ni}_x\text{Mg}_y\text{Cr}_z(\text{OH})_{2(x+y)+3z} - 2\text{CO}_3 \cdot 4\text{H}_2\text{O}$ changed into $\text{Ni}_x\text{Mg}_y\text{Cr}_z\text{O}_{x+y+1.5z}$ because water and CO_3^{2-} were removed during calcination. The composition of prepared $\text{Ni}_x\text{Mg}_y\text{Cr}_z\text{O}_{x+y+1.5z}$ was determined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and summarized in Table S1. Before catalytic reaction, $\text{Ni}_x\text{Mg}_y\text{Cr}_z\text{O}_{x+y+1.5z}$ was reduced in hydrogen flow (80 mL/min) at 650 °C for 1 h, and the reduced catalyst was denoted as $\text{Ni}_x/\text{Mg}_y\text{Cr}_z\text{O}_{y+1.5z}$ because Ni^{2+} species was reduced to Ni^0 .

2.2. Catalyst characterization

N_2 adsorption was measured at its normal boiling point using an ASAP 2010 analyzer (Micromeritics) after pretreated at 250 °C for 4 h in vacuum. Power X-ray diffraction (XRD) patterns of fresh and calcined stichtites were detected at room temperature on a Rigaku D/WAX-2500 diffractometer using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) with a 2θ step of 0.02°. X-ray photoelectron spectroscopy (XPS) measurements were performed on a KratosAxis Ultra DLD system with a base pressure of 10^{-9} Torr. Thermogravimetric and differential scanning calorimeter (TG-DSC) analysis was carried out on a Netzsch STA 409 thermo-balance. Analysis was done from 50 to 600 °C at a heating rate of 10 °C/min in air flow (30 mL/min). Transmission electron microscope (TEM) images were obtained using an accelerating voltage of 200 kV (JEOL-2020F). The sample was suspended in ethanol with an ultrasonic dispersion for 0.5 h. Drops of the suspension were deposited on copper grid coated with amorphous carbon film. Scanning electron microscope (SEM) images were detected on Leo Evo Series SEM (VP 1430, Germany). Samples were coated with platinum using sputter coating to avoid charging.

Temperature-programmed reduction (H_2 -TPR) of calcined $\text{Ni}_x\text{Mg}_y\text{Cr}_z\text{O}_{x+y+1.5z}$ was performed in the following procedures: samples (50 mg) were pretreated at 500 °C for 1 h in Ar flow (30 mL/min) and cooled to room temperature. A reduction gas (10% H_2/N_2 mixture, 30 mL/min) was shifted and the reactor was heated to 650 °C at a ramp of 10 °C/min. Effluent gas was dried by powder KOH and the consumption of hydrogen was recorded by thermal conductivity detector (TCD). The amount of surface metallic Ni was determined by pulse adsorption of H_2 using the procedure described by Wang (Wang et al., 2010). Samples were first reduced at 650 °C in a H_2 flow for 1 h and then cooled to room temperature in Ar. After that, H_2 was pulsed until no obvious chemisorption could be observed.

H_2 activation of reduced catalysts were carried out via temperature-programmed desorption of H_2 (H_2 -TPD). Sample was first reduced at 650 °C in H_2 flow of 30 mL/min for 1 h, purged by purified Ar for 0.5 h. And then the reactor was cooled to 50 °C in Ar, exposed to 10% H_2/Ar for 30 min, purged by Ar for 5 h at 50 °C in order to eliminate the physical adsorbed H_2 . Temperature-programmed desorption was conducted by ramping to 400 °C at 10 °C/min and H_2 ($m/e = 2$) in effluent was detected and recorded as a function of temperature by a quadrupole mass spectrometer (OmniStarTM, GSD301, Switzerland).

2.3. Catalytic reactions

Hydrogenolysis of glycerol was carried out in a vertical fixed-bed reactor with a back pressure regulator to control the system pressure. The reactor was a stainless steel tube with an internal diameter of 6 mm and a length of 540 mm. In a typical run, 0.25 g catalyst (40–60 mesh) was loaded in the constant temperature zone of the reactor, with quartz sand packed in both ends. Before reaction, catalyst was in situ reduced in pure H_2 flow (80 mL/min) at 650 °C for 1 h. After reduction, the reactor was cooled to reaction temperature and pressured to 2.0 MPa. An aqueous solution of glycerol (40 wt% glycerol) was continuously fed into the reactor with a flow rate of 0.02 mL/min using a HPLC pump. The reaction products were cooled in a condenser (remained at $-5 \text{ }^\circ\text{C}$) and collected in a gas-liquid separator. All products in gas phase were analyzed on-line using a gas chromatograph (HP5890, series II, equipped with a TDX-01 (4 mm \times 2 m) column and a TCD detector). The liquid products and unreacted glycerol were collected in a catch pot and analyzed on a gas chromatograph (Shimadzu, 14B) equipped with an FID and a 30-m capillary column (DB-WAX 52 CB, USA). All products detected in the liquid were verified by a gas chromatography–mass spectrometry system (GC–MS, Agilent 6890) and quantified via an external calibration method. And the product selectivity was calculated on carbon basis in all experiments.

3. Results and discussion

3.1. Properties of NiMgCr-stichtite

XRD analysis disclosed that all prepared $\text{Ni}_x\text{Mg}_y\text{Cr}_z(\text{OH})_{2(x+y)+3z} - 2\text{CO}_3 \cdot 4\text{H}_2\text{O}$ had the primary structure of stichtite (Fig. 1). The classical diffraction reflections of (003) and (006) planes ascribing to typical stichtite (JCPDS 00-045-1475) were observed in all synthesized samples (Mills et al., 2010; Theiss et al., 2013) (with different Ni/Mg mole ratio), which indicated the homogenous dispersion of Ni in stichtite. The calculated cell parameter a in Ni-free $\text{Mg}_6\text{Cr}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$ stichtite was 3.105 Å (Ashwal and Cairncross, 1997), and it decreased slightly when Ni^{2+} was added. The interlayer distance (parameter c) also decreased slightly when Ni^{2+} was added in stichtite (Table S2). The slight decrease of a and c when Ni^{2+} was added in stichtite might be attributed to the shrinkage crystal cell of nickel hydroxide hydrate ($a = 3.080 \text{ \AA}$, $c = 23.410 \text{ \AA}$). SEM images showed that the synthesized Ni-substituted stichtite consisted of

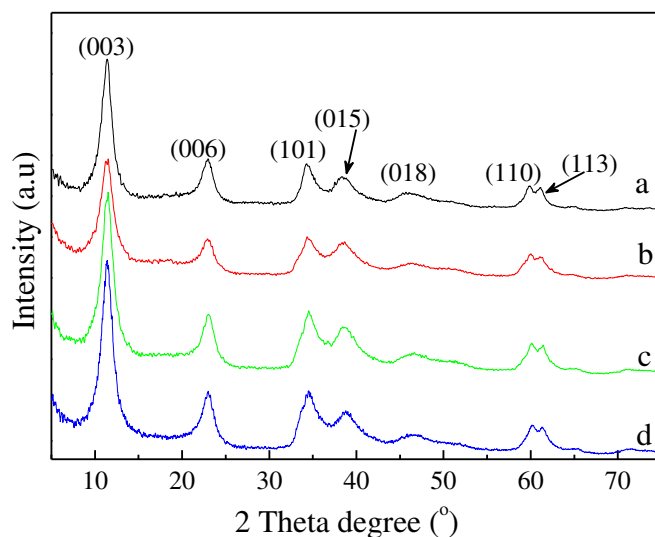


Fig. 1. XRD patterns of synthesized Ni-substituted stichtites.

(a) $\text{Ni}_{0.9}\text{Mg}_{4.5}\text{Cr}_{2.6}(\text{OH})_{16.6}\text{CO}_3 \cdot 4\text{H}_2\text{O}$, (b) $\text{Ni}_{2.4}\text{Mg}_{3.7}\text{Cr}_{2.0}(\text{OH})_{16.2}\text{CO}_3 \cdot 4\text{H}_2\text{O}$, (c) $\text{Ni}_{3.9}\text{Mg}_{2.5}\text{Cr}_{1.6}(\text{OH})_{15.6}\text{CO}_3 \cdot 4\text{H}_2\text{O}$, (d) $\text{Ni}_{4.5}\text{Mg}_{2.1}\text{Cr}_{1.4}(\text{OH})_{15.4}\text{CO}_3 \cdot 4\text{H}_2\text{O}$.

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