



Promotional effect of transition metal doping on the basicity and activity of calcined hydrotalcite catalysts for glycerol carbonate synthesis



Peng Liu^{a,*}, Margherita Derchi^b, Emiel J.M. Hensen^{a,*}

^a Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, P.O. Box 513, Eindhoven, The Netherlands

^b Dipartimento di Ingegneria Chimica, Civile e Ambientale, Università degli Studi di Genova, I-16145 Genova, Italy

ARTICLE INFO

Article history:

Received 11 April 2013

Received in revised form 30 June 2013

Accepted 2 July 2013

Available online 12 July 2013

Keywords:

Heterogeneous catalysis

Transesterification

Hydrotalcite

Reconstruction

Glycerol carbonate

ABSTRACT

A series of transition metal doped hydrotalcites (HT-M) were prepared by using the “memory effect” of hydrotalcites (HT). Further calcination yields mixed oxides with more open structure and tunable basicity. The basicity of the calcined hydrotalcites (HTC-M) strongly depends on the type of transition metal and calcination temperature. The resulting HTC-M materials were used as solid base catalysts and evaluated in the transesterification between glycerol and dimethyl carbonate without using organic solvent. The correlation between the basic properties of the solid catalysts and the catalytic performance was investigated. The activity of HTC-M catalysts was demonstrated to be proportional to the surface density of basic sites. The HTC-Ni calcined at 500 °C exhibited maximum activity, which is about 10 times higher than uncalcined HT precursor for the transesterification reaction. The promotional effect of Ni²⁺ doping could be attributed to the enhancement of the base strength of all three types of basic sites of the calcined hydrotalcite. The HTC-Ni catalyst can be readily recycled while maintaining high catalytic activity and selectivity of glycerol carbonate.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Heterogeneous base catalysis is an important field of growing interest in both academic and industrial research [1,2]. In practice, the substitution of homogeneous base catalysts (such as metal hydroxides or amines) with solid base catalysts is very attractive in view of the reduction of waste formation, as well as for safety and corrosion aspects [3].

Among various solid bases, hydrotalcite (Mg₆Al₂(OH)₁₆CO₃·nH₂O) type layered double hydroxides find much industrial interest [4,5] and are the subject of considerable academic investigation [6]. Due to their unique properties such as cation- and anion-exchangeability of the Brucite layer and interlayer, respectively, their tunable surface basicity and the “memory effect” of the layered structure [4,7], hydrotalcite-like compounds have been demonstrated to be effective redox catalysts, solid base catalysts, catalyst precursors and catalyst supports [8]. Being basic in nature hydrotalcites have been widely studied for various base catalyzed or assisted reactions such as alkylation, Michael addition, Claisen–Schmidt condensation, Knoevenagel condensation, aldol

condensation, transesterification, hydrogenation, olefin epoxidation and alcohol oxidation [8–15]. Through controlled thermal decomposition, hydrotalcites are converted to mixed oxides with high specific surface areas, homogeneous dispersion of metal cations and strong Lewis basic sites [16,17]. The basic properties of these mixed oxides depend on the composition of metal cations in the precursor hydrotalcite. Interestingly, the catalytic activity of calcined hydrotalcites can also be enhanced by rehydration in an inert atmosphere, which results in reconstruction of the original layered structure, with Brønsted basic sites OH⁻ as the charge compensating anions in the interlayer [18,19]. Consequently, the facile adjustment of the type of basic sites and surface base strength makes hydrotalcite versatile precursors for optimal solid base catalysts for a wide range of base-catalyzed reactions.

Recently, the utilization of surplus glycerol has received much attention because of the growing biodiesel production [20–22]. Glycerol carbonate (GLC), due to its low toxicity, low flammability, biodegradability and high boiling point, is one of the most important glycerol derivatives and is widely used as protic solvent, chemical intermediate and precursor in the synthesis of polycarbonates, polyurethanes, glycidol-based polymers and surfactants [23,24]. Hydrotalcite-based solid base catalysts have, in particular, shown promise for transformation of glycerol to value-added GLC [25–33]. Zinc-containing hydrotalcite was reported to be effective catalyst for GLC synthesis by carbonylation of glycerol with

* Corresponding authors. Tel.: +31 40 247 2833; fax: +31 40 245 5054.

E-mail addresses: pliu503@hotmail.com, p.liu@tue.nl (P. Liu), e.j.m.hensen@tue.nl (E.J.M. Hensen).

urea under solvent-free conditions [25]. However, this reaction must be performed at high temperature ($>120^{\circ}\text{C}$) and low pressure (30–50 mbar) to shift the equilibrium towards GLC formation by isolating produced ammonia continuously from the gaseous phase, and the catalytic activity is found to be due to the leaching of Zn species into liquid phase thus with a homogeneous reaction nature [26]. A more attractive route for GLC synthesis would be transesterification between glycerol and alkyl carbonates, such as dimethyl carbonate (DMC) and diethyl carbonate (DEC), because of the milder and greener process conditions [23]. Uncalcined MgAl hydrotalcites with co-existent hydromagnesite phase were found to be active catalysts for GLC synthesis from glycerol and DMC [27,28], but a larger amount of catalyst ($\sim 50\text{ wt}\%$) and a harmful solvent (*N,N*-dimethyl formamide) are needed for this reaction. Medina and co-workers reported that the rehydrated MgAl hydrotalcites showed higher activity than the calcined MgAl mixed oxides for transesterification of DEC with glycerol, but the active reconstructed hydrotalcite catalysts often deactivate rapidly due to the instability of surface Brønsted basic sites [29–31]. Carbon nanofiber supported MgAl hydrotalcites, however, exhibited a different activity trend with calcined mixed oxides showing higher activity than the rehydrated samples, although the calcined catalyst also deactivated upon reuse and showed lower GLC selectivity ($<90\%$) [32]. Zr-doped MgAl hydrotalcite (Mg/Al/Zr = 3/1/1) showed optimal GLC yield when calcined at 650°C , but without evidence on catalyst stability [33]. Although useful hydrotalcite-based catalysts were reported, it is still a challenging task to develop more efficient and reusable catalysts for synthesis of GLC under mild and solvent-free conditions.

Transition metal-doped hydrotalcites (HT-M) are known to possess tunable surface basic properties that depend on the nature and composition of the transition metal cations [34]. It has been demonstrated that Ni^{2+} or Fe^{3+} containing hydrotalcite-derived mixed oxides are effective solid base catalysts for transesterification in biodiesel production [35–37]. We have recently reported on the benefit of doping transition metal cations into hydrotalcite to render excellent HT-M supported gold nanoparticle catalysts for the aerobic oxidation of alcohols [14]. The basicity of HT-M supports varied with the transition metal ($\text{M} = \text{Cr}^{3+}$, Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+}) cations, which potentially enhance the alcohol dehydrogenation activity. However, the effects of transition metal doping on the basicity of calcined hydrotalcites (HTC-M) and their catalytic performance in the GLC synthesis remain unknown. Herein, we will show that the HTC-M samples by calcination of HT-M precursors are efficient solid base catalysts for GLC synthesis from glycerol and DMC with GLC selectivity up to 100% under moderate (100°C) and solvent-free conditions. Their activity can be tailored by simple adjustment of the calcination temperature. The correlations between the textural, chemical structures and the basic properties of the HTC-M catalysts and the catalytic performance in the glycerol transesterification were investigated. Moreover, the optimal catalyst and reaction conditions were also determined. Our results show that the catalytic activity is proportional to the surface basic site density.

2. Experimental

2.1. Catalyst preparation

A hydrotalcite (HT) precursor with a composition of $\text{Mg}_4\text{Al}_2(\text{OH})_{12}\text{CO}_3$ was prepared by a homogeneous precipitation method using urea hydrolysis [38]. Transition metal-doped hydrotalcite (HT-M, $\text{M} = \text{Cr}^{3+}$, Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+}) precursors, along with a transition-metal-free sample (HT-0), were prepared by using the calcination-reconstruction process

(also known as “memory effect” of HT) [14]. Typically, a thermally decomposed HT (1.0 g calcined at 500°C in air for 6 h) was reconstructed into the layered hydrotalcite structure along with M^{n+} cations by mixing with aqueous M^{n+} nitrate solution ($0.5\text{ mmol M}^{n+}/\text{g}$ HT precursor) in the presence of atmospheric CO_2 (as a source of interlayer CO_3^{2-} anion) under stirring overnight at room temperature. The slurry was filtered and fully washed. The resulting solid was dried at 110°C overnight to obtain the HT-0 and HT-M samples, which were further calcined at 500°C in air for 6 h to yield the HTC-0 and HTC-M catalysts.

2.2. Catalyst characterization

XRD was performed on a Bruker Endeavour D4 with $\text{Cu K}\alpha$ radiation (40 kV and 30 mA). SEM micrographs were taken using a FEI Quanta 200F scanning electron microscope. The BET surface areas were recorded on a Tristar 3000 automated gas adsorption system. The samples were degassed at 180°C for 3 h prior to analysis. Magic-angle spinning (MAS) ^{27}Al NMR spectra were recorded on a Bruker DMX500 spectrometer equipped with a 4-mm MAS probe head operating at an Al NMR frequency of 130 MHz. The ^{27}Al chemical shift is referenced to a saturated $\text{Al}(\text{NO}_3)_3$ solution. In a typical experiment sample (10 mg) was packed in a 2.5 mm zirconia rotor. The MAS sample rotation speed was 25 kHz. The relaxation time was 1 s and the pulse length was $1\ \mu\text{s}$.

X-ray photoelectron spectroscopy (XPS) measurements were performed using a Thermo Scientific K-Alpha spectrometer, equipped with a monochromatic small-spot X-ray source and a 180° double focusing hemispherical analyzer with a 128-channel detector. Spectra were obtained using an aluminium anode ($\text{Al K}\alpha = 1486.6\text{ eV}$) operating at 72 W and a spot size of $400\ \mu\text{m}$. Survey scans were measured at constant pass energy of 200 eV and region scans at 50 eV. The background pressure was 2×10^{-9} mbar and during measurement 3×10^{-7} mbar Argon because of the charge compensation dual beam source. Data analysis was performed using CasaXPS software. The binding energy was corrected for surface charging by taking the C 1s peak of contaminant carbon as a reference at 284.5 eV.

Temperature programmed desorption of CO_2 (CO_2 -TPD) experiments were carried out for the measurement of basicity of the catalysts. After the catalyst (50 mg) was pre-treated at 500°C for 1 h under He stream (50 mL/min), it was cooled down to 90°C and CO_2 (10 vol%) was introduced for adsorption at this temperature for 0.5 h. After the catalyst was swept with He for 60 min to remove the physisorbed CO_2 from catalyst surface, the temperature was increased linearly with rate of $10^{\circ}\text{C}/\text{min}$ in He and the signal of CO_2 ($M/e = 44$) was recorded by online mass spectrometry (quadrupole mass spectrometer, Balzers TPG-300). The amount of CO_2 was quantified by a calibration curve, which was established by thermal decomposition of known amounts of NaHCO_3 .

2.3. Reaction procedure

Transesterification of dimethyl carbonate and glycerol to GLC was carried out using a 10 mL glass tube reactor with a reflux condenser. Typically, the reactor was charged with 5 mmol of glycerol, 10 wt% of catalyst (46 mg), 15 mmol of dimethyl carbonate, and 2 mmol of 1,4-butanediol (internal standard). The resulting mixture was stirred at 100°C for 2 h then 5 mL of ethanol was added to quench the reaction. The used catalyst was separated by centrifugation, washed with ethanol and dried at 200°C . Recovered catalyst can be reused in the next run under the same conditions. The reaction products were quantitatively analyzed by a Shimadzu QP5050 GC-MS (Stabilwax column, $30\text{ m} \times 0.32\text{ mm}$, $d_f = 0.5\ \mu\text{m}$) using an internal standard technique.

Download English Version:

<https://daneshyari.com/en/article/45345>

Download Persian Version:

<https://daneshyari.com/article/45345>

[Daneshyari.com](https://daneshyari.com)