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Short communication

An effective and stable Ni_2P/TiO_2 catalyst for the hydrogenation of dimethyl oxalate to methyl glycolate

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ABSTRACT

An effective and stable bifunctional Ni_2P/TiO_2 catalyst was proposed for gas-phase hydrogenation of dimethyl oxalate to corresponding alcohols. A 93.0% conversion of DMO with a selectivity of 88.0% to methyl glycolate was observed under 210 °C. Moreover, the catalyst showed an excellent stability which can be performed for 3600 h under the reaction conditions of 230 °C, 3 MPa H_2 and the weight space velocity of 0.1 h^{-1}.

1. Introduction

Methyl glycolate (MG) is an important fine chemical intermediate, which can be used as a raw material for the synthesis of polyglycolic acid and other organic chemicals [1]. Ethylene glycol (EG) has benign properties and versatile functions, and it has been proposed as a raw material for producing many chemicals, including polyester, dynamite manufacture and antifreeze [2].

Several approaches envisioned for the production of MG have been reported [3,4]. Typically, severe reaction conditions were required to obtain a high yield of MG. For the production of EG, the primary route was the hydration of ethylene or fermentation of sugars [5–7]. However, these routes were limited for the shrinking oil and expensive bioprocesses. In contrast, the hydrogenation of dimethyl oxalate (DMO) to MG or EG is attractive as it is a more efficient and greener catalytic process (as seen in Scheme 1) [8].

EG can be achieved efficiently over copper-based catalysts via selective hydrogenation of DMO [9–11]. However, low MG yields (<83%) were obtained over copper-based catalysts [10,12], and the instability of the catalyst limited its further application. To improve the selectivity to MG in hydrogenation of DMO, introducing a noble metal to the catalytic system is required. For example, CuAu alloy nanoparticles and a silver-based catalyst were applied for the hydrogenation of DMO to obtain a high yield of MG (>90%) [13–15]. However, the large requirement of the noble metal limited its further application in industry. Thus, it is desirable but more challenging to design an efficient non-noble metal catalyst to catalyse the hydrogenation of DMO to MG under mild conditions. Because of their high catalytic efficiency and stability, the transition metal phosphides have been attracting increasing attention. Recently, many efforts demonstrated that the transition metal phosphide catalysts showed excellent activities for hydrodesulfurization, hydrodenitrogenation and hydrodeoxygenation owing to its strong noble metallic properties [16–20]. To the best of our knowledge, the transition metal phosphides have scarcely been reported in the hydrogenation of esters to their corresponding alcohols. Based on the above understandings, we hypothesise that it would be a huge breakthrough if the transition metal phosphides could replace the noble metal and be used for the DMO hydrogenation efficiently.

In this work, a bifunctional Ni_2P/TiO_2 catalyst was proposed. The catalyst exhibited superior catalytic performance for the hydrogenation of DMO to MG. A high selectivity of 88.0% to MG with a 93.0% conversion of DMO was obtained under 210 °C. More importantly, the Ni_2P/TiO_2 catalyst displayed an excellent stability, which can be successively performed for 3600 h without deactivation under 230 °C.

2. Experimental

The Ni_2P/TiO_2 catalyst was prepared by temperature-programmed reducing method. The catalysts were characterized by ICP, XRD, TEM, XPS, BET, H_2-TPR, and NH_3-TPD. The catalytic performance evaluation was performed in a vertical fixed-bed reactor (i.d. 12 mm, length 600 mm) made of a stainless steel tube. Details of catalyst preparation,

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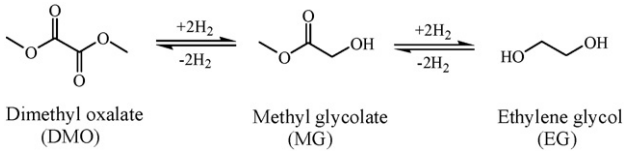

Dimethyl oxalate (DMO) Methyl glycolate (MG) Ethylene glycol (EG)

Scheme 1. The hydrogenation process of the DMO.

catalyst characterization, and catalyst evaluation are available in the supporting material.

3. Results and discussion

3.1. Catalyst characterization

The textural properties derived from N_2 adsorption–desorption isotherms of the TiO_2 and Ni_2P/TiO_2 catalysts are listed in Table 1. Compared with TiO_2 support, the BET surface area and average pore diameter of the Ni_2P/TiO_2 catalyst decreased while the average pore volume enhanced. To understand the structures of the Ni_2P/TiO_2 catalyst, XRD, TEM and XPS characterizations were performed. Fig. 1A shows the XRD patterns of the TiO_2 support and the as-prepared Ni_2P/TiO_2 catalyst. For the Ni_2P/TiO_2 catalyst, the three peaks positioned at $2\theta = 40.8$, 44.7, 47.5 are assigned to the (111), (021) and (210) lattice planes of Ni_2P (JCPDS 65-9706), respectively. Fig. 1B shows the typical TEM (a) and HRTEM (c) images of the Ni_2P/TiO_2 catalyst. The HRTEM analysis revealed that the crystal domains within Ni_2P NPs had an interfringe distance of 0.22 nm, which is close to the lattice spacing of the (111) plane in face-centred cubic (fcc) Ni_2P crystal (0.221 nm) [21,22]. Fig. 1C (a) displays the XPS spectra of the Ni_2P/TiO_2 catalyst. The XPS spectrum for the fresh Ni_2P/TiO_2 catalyst shows Ni (2p3/2) and P (2p3/2) peaks at 856.5 and 133.3 eV, respectively. The Ni (2p3/2) binding energy is consistent with the range of those reported for Ni (855.6–856.6 eV) in $Ni(OH)_2$ [23,24] while the P (2p3/2) binding energy is in good agreement with a value reported for P (133.3 eV) in $Ni_3(PO_4)_2$ [24,25]. As a result, the peaks at 856.5 and 133.3 eV are assigned to Ni^{2+} and P^{5+} species in the Ni_2P, respectively. Meanwhile, additional peaks are observed in the Ni (2p3/2) and P (2p3/2) regions at 852.9–853.3 eV and 129.1–129.5 eV, respectively, which are assigned to reduced $Ni^{\delta+}$ ($0 < \delta < 2$) and $P^{\delta-}$ ($0 < \delta < 1$) in Ni_2P [26,27]. The XPS for Ni metal and elemental phosphorus are reported to be at (852.5–852.9) and 130.2 eV, respectively [28]. A positive shift of 0.25–0.65 eV to 853.15 eV was observed for Ni ($2p_{3/2}$) binding energies in the Ni_2P catalyst (Fig. 1C), while a negative shift of 0.7 eV for the P (2p3/2) signal to 129.5 eV was obtained. These results verified that a few electrons were transferred from Ni to P. These results, combined with the X-ray powder diffraction (XRD) and TEM results further corroborated the formation of Ni_2P NPs. In addition, the accessible surface acidic sites of the catalysts were probed by NH_3-TPD (Fig. S1 in ESI†). Compared with TiO_2 and Ni/TiO_2, the NH_3 desorption temperature of the Ni_2P/TiO_2 catalyst shifted towards higher temperature. This result reflected that the addition of P increased the acidity and acid strength of the catalyst, as the formation of P-OH in the surface increased the Brønsted acid and the formation of electron-deficient state of Ni verified by XPS improved the Lewis acid [27].

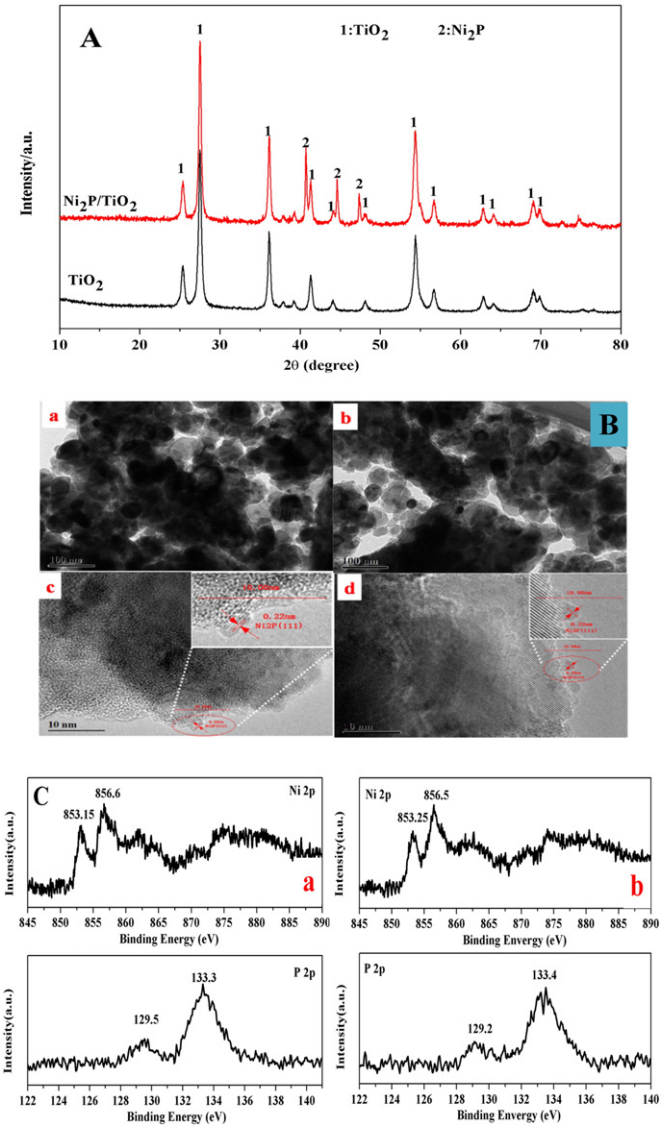

Fig. 1. (A) XRD patterns of as-prepared Ni_2P/TiO_2 catalyst and TiO_2 support. (B) TEM and HRTEM images of the as-prepared (a and c) and spent (b and d) Ni_2P/TiO_2 catalysts. (C) XPS spectra in the Ni (2p) and P (2p) regions for the as-prepared (a) and spent (b) Ni_2P/TiO_2 catalysts.

3.2. Catalytic test

Table 2 presents the results of the hydrogenation of DMO over TiO_2 (entries 1–2), Ni_2P (entries 3–8), and Ni_2P/TiO_2 (entries 9–15) catalysts. As shown in Table 2, the pure support of TiO_2 was inactive towards DMO hydrogenation, while a 38.2% conversion of DMO was observed with Ni_2P as the catalyst at 200 °C (entry 3). Therefore, the Ni_2P sites account for the catalytic hydrogenation performance. Additionally, it can be observed that the Ni_2P catalyst exhibited a good selectivity of 90.5% to MG

Table 1
The physicochemical properties of TiO_2 and Ni_2P/TiO_2 catalysts.

Catalyst	S_{BET} ($m^2\ g^{-1}$)	D_{pore} (nm)	V_{pore} ($cm^3\ g^{-1}$)	Ni content[a] (mol/g)	P content[a] (mol/g)	Ni:P[a] (mole/mole)
TiO_2	24.64	0.120	17.41	–	–	–
Ni_2P/TiO_2-fresh	15.43	0.097	22.65	1.62×10^{-3}	1.0×10^{-3}	1.62
Ni_2P/TiO_2-spent	16.35	0.106	22.02	1.33×10^{-3}	0.85×10^{-3}	1.56

[a] Determined by ICP.