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Research article

Production of C_2 and C_3 polyols from D-sorbitol over hydrotalcite-like compounds mediated bi-functional Ni–Mg–Al–Ox catalysts

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ABSTRACT

Production of C_2 and C_3 polyols from D-sorbitol over $Ni/Mg_xAl_yO_{x+1.5y}$ catalysts with different Mg/Al molar ratio were performed under mild conditions. It was found that this reaction proceeded effectively over these bi-functional catalysts prepared via thermal decomposition and reduction of Ni–Mg–Al hydrotalcite-like compounds. The detected conversion of D-sorbitol over $Ni/Mg_{1.29}Al_{0.06}O_{1.38}$ reached 80.7% at 453 K and further increased to 97.0% at 473 K. Characterizations indicate that the performance of these catalysts depended mainly on its surface basicity.

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1. Introduction

As biomass is one of the most important practical sources of renewable liquid fuel, more and more researches are being conducted to develop new techniques to transform biomass into substituted renewable fuel and chemicals [1–5]. Those popularly reported transformation routines of biomass include transesterification of vegetable oil with methanol or ethanol to biodiesel [6], liquefaction or pyrolysis of biomass to bio-oil [7,8], hydrogenolysis of sugars and cellulose to C_2 and C_3 polyols [9,10], and aqueous phase reforming of sorbitol to C_2 and C_3 polyols [2,11–13]. Among these products, C_2 and C_3 polyols are crucial feedstocks in the manufacture of polyester resins, surfactant, pharmaceuticals and functional fluids [14,15], and these products are currently manufactured from energy intensive transformation of non-renewable raw materials in several steps [2,16,17]. Taking product separation problems into consideration, heterogeneous catalysts, such as SiO_2–Al_2O_3 supported Pt and Pd [18], Pt/NaY [11] and $Pt/ZrO_2 + TiO_2$–WO_x[19] were reported for the hydrogenolysis of sorbitol at 473–513 K and 2–5 MPa H_2. Recently, non-noble metal based catalyst, such as Ni [11,15], attracted attentions of several groups due to its low price and excellent performance in the hydrogenolysis of sorbitol at similar reaction condition as noble metal catalysts.

Hydrotalcite-like compound (HTLc) is an ideal precursor for heterogeneous bi-functional catalysts because of the atomical distribution of metal ions in its framework, controllable surface basicity and stability [20,21]. A series of bi-functional catalysts with homogenously dispersed active sites, such as Cu-solid base [22–24], Ni–Al_2O_3[25,26], and Co–Mg–Al [27] were prepared via controlled calcination and reduction of HTLc precursors. At the same time, it was reported that the basicity of HTLc precursors mediated catalysts could be manually controlled by adjusting composition [22].

In this work, Ni-based catalysts were synthesized through thermal decomposition of Ni–Mg–Al HTLc precursors and applied in hydrogenolysis of D-sorbitol. The basicity of these catalysts was manipulated by adjusting the molar ratio of Mg/Al. The performance of these catalysts was discussed with their physical and chemical properties.

2. Experimental section

2.1. Catalyst preparation

All reagents were purchased at high purified (AR) grade from Sinopharm Chemical Reagent Co., Ltd, China and used without further

Table 1
The physic-chemical properties of $NiO/Mg_xAl_yO_{x+1.5y}$ catalyst.

Catalyst	S_{BET} ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	Surface basicity	
			(μmol-$CO_2\ g^{-1}$)	(μmol-$CO_2\ m^{-2}$)
NiO/Al_2O_3	257.7 ± 6.6	0.57 ± 0.03	76.9 ± 4.3	0.30 ± 0.02
$NiO/Mg_{0.67}Al_{0.56}O_{1.51}$	249.0 ± 2.6	0.55 ± 0.01	322.8 ± 6.3	1.30 ± 0.03
$NiO/Mg_{1.22}Al_{0.12}O_{1.40}$	285.8 ± 6.9	0.55 ± 0.01	337.8 ± 3.8	1.18 ± 0.01
$NiO/Mg_{1.29}Al_{0.06}O_{1.38}$	216.5 ± 7.6	0.46 ± 0.02	375.3 ± 5.2	1.73 ± 0.02
NiO/MgO	208.8 ± 1.2	0.39 ± 0.01	289.0 ± 5.6	1.38 ± 0.03

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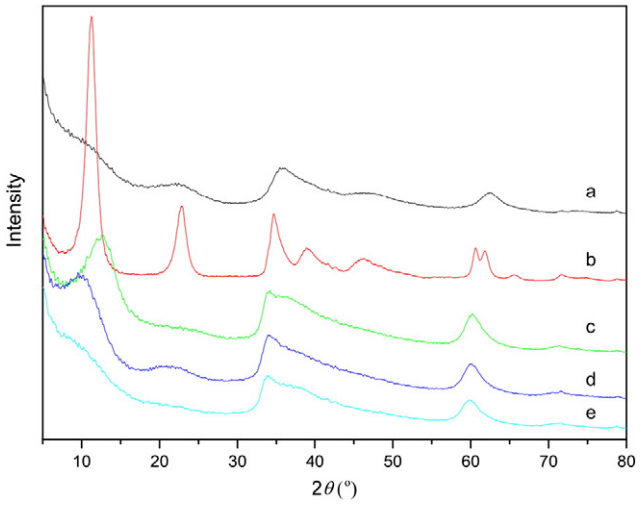

Fig. 1. XRD pattern of fresh Ni–Mg–Al HTLc. (a) $NiAl_{1.08}(OH)_{3.24}CO_3$; (b) $NiMg_{0.67}Al_{0.56}(OH)_{3.02}CO_3$; (c) $NiMg_{1.22}Al_{0.12}(OH)_{2.80}CO_3$; (d) $NiMg_{1.29}Al_{0.06}(OH)_{2.76}CO_3$; (e) $NiMg_{1.37}(OH)_{2.74}CO_3$.

purification. Ni–Mg–Al hydrotalcite-like compounds with the same loading amount of Ni (51.5 wt.% in the reduced samples) were synthesized through a typical co-precipitation method. Calculated amount of $Ni(NO_3)_2{\cdot}6H_2O$, $Mg(NO_3)_2{\cdot}6H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$ were dissolved together into 0.5 L deionized water which was used as the source of metal cations. Meanwhile, 0.4 mol NaOH and 0.125 mol Na_2CO_3 were mixed together in 0.4 L deionized water to form a clear solution. The two kinds of solution mentioned above were simultaneously added into a glass reactor under vigorous stirring at room temperature and the pH value was controlled at 9.5. The resulting slurry was aged at 393 K for 20 h, and then filtrated and washed thoroughly with deionized water. And the products were subsequently dried overnight at 353 K and identified as $NiMg_xAl_y(OH)_{2x\,+\,3y}CO_3$ in which x and y refer to the amount of Mg and Al, respectively.

Before catalytic reaction, these hydrotalcite-like compounds were calcined at 973 K in air for 4 h,followed by hydrogen reduction at 1073 K for 1 h. The resulting catalysts after calcination and reduction were identified as $NiO/Mg_xAl_yO_{x\,+\,1.5y}$ and $Ni/Mg_xAl_yO_{x\,+\,1.5y}$. The compositions of different samples were listed in Table S1 (in supplementary data). X-ray diffraction (XRD) patterns were collected on a Rigaku D/MAX 2550/PC diffractometer (18 kW) using Cu Kα radiation (100 kV, 40 mA, λ = 0.1542 nm). N_2 adsorption of calcined samples was measured at its normal boiling point using an ASAP 2010 analyzer (Micromeritics) after pretreated at 523 K overnight in vacuum (these adsorption–desorption isotherms were shown in Fig. S1, in supplementary data), surface area was calculated using their adsorption isotherms and summarized in Table 1.

2.2. Hydrogenolysis of D-sorbitol

Hydrogenolysis of D-sorbitol was carried out in a 100 mL stainless steel autoclave. Catalyst was calcined at 973 K in air for 4 h and reduced at 1073 K in H_2 for 1 h prior to catalytic reaction. After reduction, 100 mg catalyst was dispersed in the mixed solution of D-sorbitol (500 mg in 10 mL deionized water). The autoclave was sealed, purged with H_2, pressurized to 2.0 MPa, and subsequently stirred with a magnetic stirrer at a rate of 1000 rpm at desired temperature. Finally, the mixture was separated by centrifugation and the aqueous solution was analyzed by an Agilent 1100 series high-performance liquid chromatograph (HPLC) equipped with a refractive index detector (RID) and a Zorbax SAX column (4.6 mm × 250 mm, Agilent) via external calibration method. The conversion of D-sorbitol was calculated as: ((initial mmol of D-sorbitol) − (mmol of D-sorbitol left)) / (initial mmol of D-sorbitol) × 100%. And the selectivity of each product was calculated on the basis of carbon atoms balance, that is: (mmol of product in reaction mixture) × (number of carbon atoms in product) / (((initial mmol of D-sorbitol) − (mmol of D-sorbitol left)) × 6) × 100%. The carbon balance (CB) was also measured.

3. Results and discussion

As Fig. 1 shows, the diffraction peaks at 11.7, 23.6 35.0 and 60.0°, which were assigned to (003), (006), (012) and (110) planes of HTLc materials, could be observed in those samples containing both Mg and Al. Compared with $NiAl_{1.08}(OH)_{3.24}CO_3$ and $NiMg_{1.37}(OH)_{2.74}CO_3$, the intensity of all diffraction peaks in $NiMg_{0.67}Al_{0.56}(OH)_{3.02}CO_3$ is relatively stronger because of the variation of M^{2+}/M^{3+} molar ratio. Though the intensity of these peaks in $NiMg_{1.22}Al_{0.12}(OH)_{2.80}CO_3$ and $NiMg_{1.29}Al_{0.06}(OH)_{2.76}CO_3$ became weak, the framework of HTLc materials could be identified clearly from their XRD spectrum. As Table 1 lists, the BET surface area (S_{BET}) of these samples varied with the addition of Mg. The surface area of $NiO/Mg_{1.22}Al_{0.12}O_{1.40}$ reached 285.8 $m^2\ g^{-1}$, while this value of NiO/Al_2O_3 and NiO/MgO decreased to 257.7 and 208.8 $m^2\ g^{-1}$, respectively. The higher surface area of $NiO/Mg_xAl_yO_{x\,+\,1.5y}$ catalysts than those of NiO/Al_2O_3 and NiO/MgO could be attributed to that mainly Ni–Mg–Al HTLc structured framework formed in precursors of these catalysts. CO_2 temperature-programmed desorption (see Fig. S2 in supplementary data) disclosed that a larger amount of strong basic sites were detected in $Ni/Mg_xAl_yO_{x\,+\,1.5y}$ catalysts than that of Ni/Al_2O_3 and Ni/MgO. The calculated basic sites of these catalysts were summarized in Tables 1 and S2 (in supplementary data).

As listed in Table 2, it was found that the reaction proceeded effectively over these catalysts. The conversion of D-sorbitol on Ni/Al_2O_3 reached 39.3% and it increased continuously with the addition of Mg. The highest conversion of D-sorbitol, which was 80.7%, was detected on $Ni/Mg_{1.29}Al_{0.06}O_{1.38}$ with Mg/Al molar ratio of 21/1. These results indicated that the activity of these catalysts increased with the content of Mg in support, which means that enhancing the basicity of these Ni-

Table 2
Hydrogenolysis of D-sorbitol over reduced Ni–Mg–Al catalyst.[a]

Catalyst	Conversion (%)	Selectivity[b] (%)					CB[c] (%)
		EG	1,2-PD	Glycerol	Erythritol	Xylitol	
Ni/Al_2O_3	39.3	4.8	0	20.5	13.7	41.8	80.8
$Ni/Mg_{0.67}Al_{0.56}O_{1.51}$	70.9	9.8	8.5	40.9	9.9	6.0	75.1
$Ni/Mg_{1.22}Al_{0.12}O_{1.40}$	73.4	12.6	14.8	49.8	5.8	2.9	85.9
$Ni/Mg_{1.29}Al_{0.06}O_{1.38}$	80.7	10.0	18.8	31.4	6.3	2.3	68.8
Ni/MgO	64.8	10.4	19.1	35.0	7.5	3.5	75.5

[a] Reaction condition: 5% aqueous D-sorbitol solution, 10 mL; catalyst amount, 100 mg; reaction temperature, 453 K; 2 h; H_2 pressure, 2 MPa.
[b] The selectivity of products was calculated on the basis of carbon atoms.
[c] Carbon balance, including all the detected organic carbons.

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