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Selective oxidation of glycerol with O₂ catalyzed by low-cost CuNiAl hydrotalcites

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Abstract

A series of CuNiAl hydrotalcites (HTs) were prepared and used to the selective oxidation of glycerol with O₂. The results revealed that elemental composition, structures and the surface properties of the obtained catalysts significantly influenced their catalytic performance. Among them, amino-functionalized CuNiAl-HTs showed excellent catalytic performance due to their enhanced surface Lewis basicity. Under the optimal reaction conditions, the highest conversion of glycerol reached 68.1% with 76% of the selectivity to glyceric acid; moreover, the catalytic performance remained after being recycled 6 times.

Keywords: Hydrotalcite; surface modification; base; selective oxidation; glycerol

Cool

1. Introduction

In recent decades, the human being has been inspired to find renewable and green energy to deal with the problems of depleting fossil fuels and deteriorating environment. And biodiesel, which was prepared by transesterification of animal and plant oils and produced little pollution in exhaust, is popularly recommended as a renewable and green energy. But 100 kg of glycerol is produced for every ton of biodiesel in biodiesel production, which leads to an increasing amount of glycerol [1-4]. Therefore, it is crucial for biodiesel industry to find new outlets for optimizing the economy of glycerol.

Among a great number (more than 1500) known traditional outlets of glycerol, the selective oxidation of glycerol has aroused a great interest in the academic and industry [1]. This was attributed to the increasing market needs for its value-added oxidation products such as glyceric acid, glyceraldehyde, dihydroxyacetone, glycollic acid and mesoxalic acid [5-13]. However, the commercialization potential of glycerol oxidation is still not ideal due to the wild product distribution. Therefore, there is an urgent need to develop effective catalysts for the selective oxidation of glycerol.

As far as we know, 100% of the selectivity to glyceric acid was reported over Au supported on charcoal or graphite with glycerol conversion approaching to 60% under glycerol/NaOH molar ratio of 1.0 [9]. 37% of the selectivity to glyceraldehyde and 22% of glycerol conversion could be reached over EP50 catalysts [10]. 49.0% of the selectivity to dihydroxyacetone and 91.5% of glycerol conversion have been achieved over 5%Pt-5%Bi/C catalyst with special configure of Pt-Bi nanoparticles [11]. 60% of

the selectivity to glycollic acid has been found using hydrogen peroxide as oxidant over 1.0% Au/C [12]. Though the above noble metal catalysts exhibited high catalytic performance, they had the disadvantages of high price and suffering catalytic deactivation with increasing reaction time. Therefore, more and more researchers began to design low-cost transition metal catalysts for the selective oxidation of glycerol, and some related research had been reported [10,14-18].

In our previous report, we had found that chromium complexes intercalated hydrotalcites were effective in the selective oxidation of glycerol using H_2O_2 as oxidant [18]. The interests in the glycerol oxidation with O_2 prompted us to further explore another effective catalytic system. Hence, in the present work, a series of surface modified CuNiAl-HT were prepared for the selective oxidation of glycerol with O_2 . The roles of composition, structures and surface properties of catalysts in their catalytic performance were discussed in detail. The present oxidation was carried out at mild conditions and the catalysts were low-cost alternatives to traditional noble metal catalysts.

2. Experimental

2.1. Catalyst preparation

The CuNiAl hydrotalcites was synthesized by precipitation followed by controlled hydrothermal treatment [19]. Typically, a 120 mL aqueous solution A contained 0.04 mol of Cu(NO₃)₂•6H₂O, 0.04 mol of Ni(NO₃)₂•6H₂O and 0.04 mol of Al(NO₃)₃•9H₂O, and a 120 mL aqueous solution B contained 0.06 mol of Na₂CO₃. The two solutions

were added dropwise with stirring to 120 mL deionized water at room temperature. The addition was performed over $1.0 \sim 1.5$ h, and the pH value of the obtained mixed solution was maintained close to 10.0 ± 0.5 by addition of appropriate amounts of NaOH. The resulting gel-like slurry was transferred to autoclaves and hydrothermally treated at 373 K for 24 h. The as-prepared product was collected after being filtered and washed with deionized water until pH=7. And then the precipitate was dried at 373 K in air for approximately 12 h. By changing the relative amounts of the three metal salts, the hydrotalcites with different Cu/Ni/Al molar ratios were prepared and denoted as Cu_xNi_yAl_z-HT (where x/y/z is the Cu/Ni/Al molar ratio in solution).



Scheme 1. Preparation and structural representation of modified CuNiAl-HTs

The fresh as-prepared CuNiAl-HT (3.5 g) was degassed at 60 °C under 10⁻² Pa for 2 h. Then, an excess of silane coupling agents (trimethoxymethylsilane, trimethoxy(propyl)silane, 3-Aminopropyl trimethoxysilane and N-[3-(Trimethoxysilyl) propy] ethylenediamine) (0.02 mol) in dry toluene (100 mL) was added, and the

suspension was stirred at reflux temperature under nitrogen flow for a week [20,21]. The resulting solid was filtered, Soxhlet-extracted with ethanol for 48 h and dried in air (at 60 °C under 10^{-2} Pa for 3 h). Then, the organo-modified CuNiAl hydrotalcites were obtained and denoted as CuNiAl-HT-CH₃, CuNiAl-HT-C₃H₇, CuNiAl-HT-C₃H₆NH₂, CuNiAl-HT-C₅H₁₀N₂H₃, respectively (see Scheme 1).

For comparison, gold supported on active carbon (1 wt.% Au/C) was prepared as in the references [22,23].

2.2. Characterization

Elemental chemical analysis was performed using the inductively coupled plasma-optical (ICP) emission spectroscopy (PerkinElmer ICP OPTIMA–3000). Nitrogen adsorption/desorption isotherms were obtained at 77 K on a Micromeritics ASAP-2000 instrument (Norcross, GA), using static adsorption procedures. Samples were degassed at 393 K for a minimum of 5 h under vacuum (10⁻⁶ Torr) prior to the measurement. Surface areas were measured using the BET method. Powder X–ray diffraction (XRD) experiments of samples were carried out on a Rigaku Miniflex diffractometer using a Cu target with a Ni filter in a 2θ range of 5–70°. And the X–ray gun was operated at 50 kV and 30 mA, using a scan speed rate of 0.2°/min. The Fourier transform infrared (FTIR) spectroscopy results of the samples were recorded on a Bruker Tensor-27 FT-IR spectrophotometer after being pressed into 13 mm discs with freshly dried KBr salt. Transmission electron microscope (TEM) studies were performed on a JEOL JEM 2100 microscope. Microcalorimetric adsorption of SO₂ was carried out using a Tian-Calvet heat-flux apparatus. The calorimeter (Setaram

C-80) was connected to a gas handling and volumetric adsorption system, equipped with a Baratron capacitance manometer (MKS, USA) for precision pressure measurements. The differential heat of adsorption versus adsorbate coverage was obtained by measuring the heats evolved when doses of an adsorbate (2-5 umol) were admitted sequentially onto the sample until the surface was saturated by the adsorbate. Before the measurements, the samples were typically dried under vacuum and then evacuated at 393 K for 2 h. The microcalorimetric adsorptions were performed at 308 K. The X-ray photoelectron spectroscopy analyses were conducted using a PHI 5000 VersaProbe X-ray photoelectron spectrometer. The radiation came from monochromatic Al X-rays (1486.6 ev) at 15 mA and 15 kV.

2.3. Catalytic test

The catalytic oxidation of glycerol were carried out under atmospheric pressure in a three neck flask (100 mL) equipped with a heat-gathering style magnetism mixer (DF-II) and gas supply system. For each reactor, 0.2 g of catalyst was suspended in 25 mL aqueous solution of glycerol (0.2 mol/L) and NaOH (25 mL, 0.8 mol/L). Once the required temperature (60 °C) reached, O_2 (99.9%) was introduced into the reactor at 60 mL/min via a mass flow controller. After reaction, catalyst was filtered off, and the aqueous solution was adjusted to neutral by addition of sulfuric acid, and then was analyzed using an Agilent 1200 series high-performance liquid chromatography (HPLC) equipped with refractive index and Uv-Vis detectors. Product separation in the HPLC was carried out using an Aminex HPX-87H column (Bio-Rad) operating at 333 K with 0.01 mol/L H₂SO₄ as eluent flowing at 0.5 mL/min. An injection volume

of 10 uL and a measure time of 30 min were adjusted. The retention times and calibration curves were found using known concentrations of products. During the oxidation reaction, gas in the effluent was collected and analyzed by a BALZERS OMNISTAR QMS200 mass spectrometer.

3. Results and discussion

3.1. Composition, structure and base

The XRD patterns of CuNiAl HTs with different molar ratio of divalent cation $(Cu^{2+} \text{ and Ni}^{2+})$ to trivalent cation (Al^{3+}) are displayed in Fig. 1. The XRD pattern of $Cu_{0.25}Ni_{0.25}Al$ -HT showed mainly $Al_2O_3 \cdot xH_2O$ phase (PDF no. 03-0156), indicating that low Cu^{2+} and Ni^{2+} concentration was not conducive to the formation of hydrotalcite-like phase. For $Cu_{2.5}Ni_{2.5}Al$ -HT with very high Cu^{2+} and Ni^{2+} concentration, besides hydrotalcite phase, another two phases of $Ni(OH)_2$ (PDF no. 02–1112) and $Cu(OH)_2 \cdot xH_2O$ (PDF no. 42–0638) were also found due to the excess divalent cation concentration. In contrast, from $Cu_{0.5}Ni_{1.5}Al$ -HT to $Cu_{2.0}Ni_{2.0}Al$ -HT, they all showed the good pattern characteristic of hydrotalcite [24-26], which suggested the hydrotalcite-like phase could be formed conveniently via controlling the molar ratio of divalent cation to trivalent cation in the range of 2.0–4.0.



Fig. 1. XRD patterns of CuNiAl hydrotalcites with different Cu/Ni/Al molar ratios (□, hydrotalcite; ■, Cu(OH)₂ xH₂O; ●, Ni(OH)₂; ○, Al₂O₃ xH₂O).

The XRD patterns of four CuNiAl-HTs modified by silane coupling agents are showed in Fig. 2. All samples showed the good pattern characteristics of hydrotalcite [24-26], which suggested CuNiAl-HT can be successfully functionalized by different silane coupling agents without demolishing its hydrotalcite-like structure. And the lattice parameters of $a (2d_{110})$ were constant in all the samples, also indicating that the element composition of layer was unchanged during functionalization (see Table 1). Compared to CuNiAl-HT, the (003) peaks of organo-modified CuNiAl-HT shifted to lower 2 θ angles (see Table 1), indicated that the interlayer space increased due to the introduction organic Moreover, from CuNiAl-HT-CH₃ of groups. to CuNiAl-HT-C₅H₁₀N₂H₃, the shift to lower angles increased gradually, which could be attributed to the increasing interlayer space originated from the growing size of organic groups.



Fig. 2. XRD patterns of the prepared samples

The results in Table 1 shows that the Cu/Ni/Al molar ratio in functionalized CuNiAl-HTs was almost the same as that of their parent CuNiAl-HT, suggesting that no element loss occurred during functionalization. The textural properties of samples were valued by N₂ adsorption/desorption measurement. It was found that they all displayed type IV isotherms with clear hysteresis loops (see Fig. 3), confirming that the mesostructure of CuNiAl-HT remained after functionalization by different organic groups. However, a significant decrease in surface area of organo-modified CuNiAl-HTs was observed in comparison with that of CuNiAl-HT (see Table 1), which might be due to the attaching of the organic groups on the surface of CuNiAl-HT.

Samples	Cu/Ni/Al	Lattice parameters (Å)				\mathbf{S}_{BET}
molar ratio	molar ratio	d ₀₀₃	d ₁₁₀	c	a	(m^2/g)
CuNiAl-HT	0.86/0.84/1.00	6.93	1.52	20.79	3.04	77.1
CuNiAl-HT-CH ₃	0.87/0.86/1.00	7.44	1.52	22.32	3.04	66.6
CuNiAl-HT-C ₃ H ₇	0.88/0.83/1.00	7.79	1.52	23.37	3.04	56.2
CuNiAl-HT-C ₃ H ₆ NH ₂	0.86/0.85/1.00	7.86	1.52	23.58	3.04	46.3
CuNiAl-HT-C ₅ H ₁₀ N ₂ H ₃	0.87/0.88/1.00	8.44	1.52	25.32	3.04	40.4

Table 1 Composition, textural and crystalline properties of the prepared samples



Fig. 3 N₂ adsorption/desorption isotherms of the prepared samples

The FTIR spectra of CuNiAl-HT and organo-modified CuNiAl-HTs are illustrated in Fig. 4. The FTIR spectra of organo-modified CuNiAl-HTs showed the characteristic band of Si-O-Si at about 1040 cm-1, implying that they had been successfully prepared [27,28]. Furthermore, for CuNiAl-HT-CH₃, the bands at 2972 and 2862 cm⁻¹ could be attributed to the anti-symmetric and symmetric stretching

modes of the CH₃ moiety. CuNiAl-HT-C₃H₇ showed bands at 2962, 2876 cm⁻¹ and 2930 cm⁻¹ ascribed to C-H stretching modes of CH₃ and CH₂, respectively [29]. CuNiAl-HT-C₃H₆NH₂ and CuNiAl-HT-C₅H₁₀N₂H₃ exhibited bands at 3424 and 1015 cm⁻¹ due to the N-H and C-N stretching modes, respectively [30]. The above characteristic bands were not present in the spectrum of CuNiAl-HT, further confirming that CuNiAl-HT was successfully functionalized by the four kinds of silane coupling agent.



Fig. 4. FTIR spectra of the prepared samples

The TEM images of CuNiAl-HT and CuNiAl-HT- $C_5H_{10}N_2H_3$ are shown in Fig. 5. It was found that they all exhibited typical hydrotalcite-like structures, which was consistent with the results of XRD. In addition, their particle size distribution is about 20-50 nm.



Fig. 5. TEM images of CuNiAl-HT (a) and CuNiAl-HT- $C_5H_{10}N_2H_3$ (b)

Microcalorimetric adsorption of SO2 was performed to determine the surface basicity and basic strength of the prepared samples (see Fig. 6) [31]. Fig. 6(a) shows the coverage of SO_2 adsorption was that significantly increased from CuNiAl-HT-C₃H₇ to CuNiAl-HT-C₅H₁₀N₂H₃, which indicated that their basicity increased gradually. For CuNiAl-HT hydrotalcite-like compounds, their low basicity could be ascribed to the present of -OH groups on the interlayer [26,32]. Obviously, their basicity increased when the -OH groups were replaced by amino-alkyl groups (-C₃H₆NH₂, -C₅H₁₀N₂H₃). In contrast, a decrease in their basicity was found due to the introduction of alkyl group (-CH₃, -C₃H₇). Fig. 6(b) shows that the initial heat of CuNiAl-HT-C₃H₆NH₂ and CuNiAl-HT-C₅H₁₀N₂H₃ obviously increased in comparison with CuNiAl-HT. This suggested that the basic strength also increased when amino-alkyl groups were used as regulators. As a result, more basicity and stronger basic strength were found on the surface of the CuNiAl-HTs modified by amino-alkyl groups.



Fig. 6. Microcalorimetric adsorption of SO₂ on the prepared samples

3.2. Catalytic performance and surface properties

The obtained heterogeneous basic catalysts were investigated in the selective oxidation of glycerol. The results revealed that $Cu_{0.25}Ni_{0.25}Al$ -HT and $Cu_{2.5}Ni_{2.5}Al$ -HT both exhibited relatively low catalytic performance (see Entry 1 and 7 in Table 2). The former could be attributed to the poor hydrotalcite-like structure, while the latter was probably related to the presence of Ni(OH)₂ and Cu(OH)₂•xH₂O phase in hydrotalcite

interlayer which inhibited the accessibility of the reactants to the active sites and the desorption of products. When the reaction was performed over $Cu_{0.5}NiAl$ -HT, CuNiAl-HT, $Cu_{1.5}NiAl$ -HT and $Cu_{2.0}NiAl$ -HT, the glycerol conversion was found to increase gradually to 40.8% with the increasing of Cu content (see Entry 2 to 5 in Table 2). This indicated that that Cu played an important role in the present catalytic system, probably because the Cu species could enhance the oxidation of primary alcohol in glycerol by reacting readily with -CHO group in intermediate of glyceraldehyde [14]. Moreover, with $Cu_{1.5}Ni_{0.5}Al$ -HT and $Cu_{1.5}NiAl$ -HT used as catalysts, the yields of glyceric acid were comparable, suggesting that Ni content was not a decisive factor in the catalytic performance of the obtained CuNiAl-HTs (see Entry 4 and 6 in Table 2). However, the introduction of the appropriate amount of Ni²⁺ benefited the formation of hydrotalcite with regular crystal structure by weakening the Jahn-Teller effect of Cu^{2+} [33].

Entry	Samples	GLY ^b Con. (%)	Selectivity (%)				
			OXAL	TAR	GLYAC	GLYC	FORM
1	Cu _{0.25} Ni _{0.25} Al-HT	7.9	0.8	1.3	55.9	26.8	15.2
2	Cu _{0.5} NiAl-HT	17.0	1.0	1.5	52.6	27.6	17.3
3	CuNiAl-HT	25.1	2.1	1.7	50.4	28.0	17.8
4	Cu _{1.5} NiAl-HT	34.5	2.7	2.4	26.8	29.6	38.5
5	Cu _{2.0} NiAl-HT	40.8	3.2	3.4	28.5	34.5	30.4
6	Cu _{1.5} Ni _{0.5} Al-HT	39.9	3.9	3.3	29.1	31.5	32.2

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Table 2		performance	of samples	in givceroi	oxidation
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7	Cu _{2.5} Ni _{2.5} Al-HT	19.7	1.7	1.3	36.3	30.9	29.8
8	CuNiAl-HT ^b	1.3	2.9	3.4	70.9	25.1	0
9	CuNiAl-HT-CH ₃	20.3	3.1	0.6	54.2	26.4	15.7
10	CuNiAl-HT-C ₃ H ₇	16.3	1.4	2.0	61.4	23.1	14.9
11	CuNiAl-HT-C ₃ H ₆ NH ₂	50.9	2.0	2.7	67.1	20.9	7.3
12	CuNiAl-HT-C ₅ H ₁₀ N ₂ H ₃	68.1	2.4	2.9	76.0	12.2	6.5
13	CuNiAl-HT-C ₅ H ₁₀ N ₂ H ₃ ^c	8.8	1.2	0	85.0	10.3	6.8
14	Au/C	71.2	1.5	4.1	62.3	14.2	17.9

^a Reaction conditions: glycerol 10 mmol, the molar ratio of NaOH and glycerol (n(NaOH/glycerol)) 4, catalyst 0.2 g, O₂ 60 mL/min, 60 °C, 4 h.

^b GLY: glycerol; OXAL: oxalate; TAR: tartronate; GLYAC: glyceric acid; GLYC: glycolic acid; FORM: formic acid.

^cNo NaOH.

In addition, the results in Table 2 also showed that the glycerol conversion decreased sharply to 1.3% under base-free experimental conditions in comparison with 25.1% of glycerol conversion in the presence of NaOH over CuNiAl-HT (see Entry 3 and 8 in Table 2). This could be attributed to the crucial role of hydroxide ions (Bronsted base sites) in NaOH. In the presence of NaOH, the H was readily abstracted from one of the primary hydroxyl groups of glycerol, which overcome the rate limiting step for the oxidation process [5,14]. Simultaneously, such a significant decrease also indicated that the surface free silanols on CuNiAl-HT was not enough to

regenerate hydroxide ions via the catalytic decomposition of peroxide intermediate.

On basis of the yield of glyceric acid, CuNiAl-HT was selected as the representative catalyst to further improve its catalytic performance by surface modification. It was found that the alkyl-modified CuNiAl-HTs (CuNiAl-HT-CH₃ and CuNiAl-HT-C₃H₇) showed lower catalytic performance than their parent CuNiAl-HT (see Entry 9 and 10 in Table 2). Considering their similar composition, textural and crystalline properties (see Table 1), such a difference in catalytic performance could be reasonably ascribed to the decreased surface basicity originated from the surface free silanol (Bronsted base sites) due to the introduction of alkyl groups, which had been confirmed by the afore-mentioned microcalorimetric measurement. This also indicated that the surface basicity of catalysts influenced their catalytic performance under the present base environment.

In order to improve the surface basicity, two amino modifiers were introduced into CuNiAl-HT. catalytic performance The of the obtained CuNiAl-HTs (CuNiAl-HT-C₃H₆NH₂ and CuNiAl-HT-C₅H₁₀N₂H₃) was also listed in Table 2. It could be seen that CuNiAl-HT-C₃H₆NH₂ and CuNiAl-HT-C₅H₁₀N₂H₃ both showed higher catalytic performance than CuNiAl-HT (see Entry 11 and 12 in Table 2). Especially, CuNiAl-HT-C₅H₁₀N₂H₃ with the most basicity showed the highest glycerol conversion of 68.1% and 76.0% of the selectivity to glyceric acid. It is noteworthy that CuNiAl-HT-C₅H₁₀N₂H₃ also showed comparable catalytic performance as the noble metal catalyst of Au/C ((1 wt.%) under the same conditions. The roles of amine groups might mainly lied in two sides. On the one hand, as

depicted by David and Prati, the introduction of amine groups led to the improvement in surface Lewis basicity of catalyst, which could mediate the second and rate determining step of the reaction, *i.e.* the activation of the C-H bond of alkoxy intermediate to form glyceraldehyde [5,7]. This could afford in part the enhanced catalytic activity of catalyst in glycerol oxidation. On the other hand, it had been prevailing accepted that the H₂O₂ detected during the reaction was responsible for C-C bond cleavage, and that H₂O₂ derived from the O₂ reduction by H₂O adsorbed on the catalyst surface. This indicated the formation of H₂O₂ was related to the surface hydrophobicity of catalyst. As a typical hydrophobic groups, the introduction of amine groups improved the surface hydrophobicity of catalyst, and thus could also afford the increased selectivity to glyceric acid to some extent [7,34-35]. Therefore, the above reaction results revealed that Lewis base sites and hydrophobic surface were also catalytically active sites in the selective oxidation of glycerol.

Furthermore, CuNiAl-HT-C₅H₁₀N₂H₃ was also investigated under base-free experimental conditions. However, only 8.8% of glycerol conversion and 85% of the selectivity to glyceric acid were found, though this catalyst also exhibited enhanced catalytic performance than CuNiAl-HT under base-free experimental conditions. Therefore, single Lewis base sites and hydrophobic surface was not enough, and the excellent catalytic performance of CuNiAl-HT-C₅H₁₀N₂H₃ could be attributed to the synergistic catalytic effect of the presence of Cu species, Lewis base sites and hydrophobic surface originated from the introduction of amino groups, and the Bronsted base sites originated from the surface free silanols of catalyst as well as the

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addition of NaOH.

In addition, a leaching test was designed to investigate the stability of $CuNiAl-HT-C_5H_{10}N_2H_3$. After the reaction was run for 2.0 h, half the reaction mixture was filtered. And the filtrate was performed to react continuously. The catalytic performance of the twin reactions with and without the catalyst was showed in Fig 7. In the presence of catalyst, the conversion of glycerol increased with the increased time, whereas the selectivity to glyceric acid decreased significantly. In contrast, in the reaction without catalyst, the conversion of glycerol and the selectivity to glyceric acid almost did not change with the prolonging of reaction time, which indicated that no significant amount of catalyst had leached into reaction mixture.



Fig. 7. Catalytic performance of the twin reactions with and without the catalyst

A further study on the recyclability of CuNiAl-HT- $C_5H_{10}N_2H_3$ was also carried out. After the first catalytic run, the catalyst was separated from the reaction solution, washed several times with water to remove any physisorbed molecules, dried and then

reused in another six catalytic runs. The results in Fig.8 revealed that the catalyst was still active until being reused for six times. Chemical analysis revealed that the recovered catalyst after six times held similar composition (Cu/Ni/Al molar ratio: 0.86/0.87/1.00) as the fresh catalyst. Moreover, the XPS spectra of fresh and used catalysts showed almost the same Cu2p3/2 binding energy around 934.4 ev, corresponding to copper hydroxides [14]. Thus, this catalyst was stable in the present reaction conditions, and the small decrease in the catalytic performance of used catalyst could be ascribed to a small loss of the catalyst during the workup.



Fig.8. Reusability of CuNiAl-HT-C₅H₁₀N₂H₃

Reaction conditions: glycerol 10 mmol, n(NaOH/ glycerol) 4, catalyst 0.2 g, O₂ 60

mL/min, 60 °C, 4 h.

The mechanism of glycerol oxidation is attracting continuous interests, and various mechanistic pathways were suggested. The present reaction fit well in with the mechanism of primary alcohol oxidation under basic environment. Namely, the

glycerol was firstly dehydrogened oxidatively to form glyceraldehyde, and then the glyceraldehyde was rapidly oxidized to glyceric acid. The presence of tartronic acid and C2 or C1 by-product could be attributed to the accompanying side reaction of overoxidation and/or decarboxylation of glyceric acid (see Scheme 2). For detailed mechanism, further research is ongoing.



Scheme 2 possible reaction pathway for glycerol oxidation

4. Conclusions

CuNiAl-HTs with appropriate composition and complete hydrotalcite-like structures were found to be promising catalysts for the selective oxidation of glycerol to glyceric acid with O_2 . Among them, amino modified CuNiAl-HTs were eye-catching due to the synergistic effect of Cu species, Lewis base sites and Bronsted base sites on the hydrophobic surface of catalysts. The Lewis base sites and hydrophobic surface originated from the introduction of amino groups, while the Bronsted base sites were related to the surface free silanols of catalyst and the hydroxide ions of NaOH. When the reaction was performed with a O_2 flow of 60 mL/min at 60 for 4 h, the optimum glycerol conversion reached 68.1% with 76% of the selectivity to glyceric acid over CuNiAl-HT-C₃H₁₀N₂H₃. Moreover, the

catalysts were stable in the present catalytic system, and could be recycled at least 6 times.

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Highlights

- Reaction was performed over low-cost transition metal catalysts.
- Heterogeneous catalysis and recyclability of the catalyst.
- Conversion of glycerol reached 68.1% with 76% of the selectivity to glyceric acid.

A certe Manus

Graphical abstract

Amino modified CuNiAl-HTs were promising catalysts for the selective oxidation of glycerol to glyceric acid with O_2 . This could be attributed to the synergistic effect of Cu species, Lewis base sites (surface amino groups of catalysts) and Bronsted base sites (surface free silanols of catalysts as well as the hydroxide ions of NaOH) on the hydrophobic surface of catalysts. The best glycerol conversion reached 68.1% with 76% of the selectivity to glyceric acid.

