Robust CoAl Alloy: Highly Active, Reusable and Green Catalyst in the Hydrogenolysis of Glycerol

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CoAl alloy catalyst is found, for the first time, to be highly active, selective and reusable for the synthesis of diols via the hydrogenolysis of glycerol under mild conditions. The products and the catalyst could be self-separated from the reaction system through a simple reactor.

Keywords CoAl, biomass, glycerol, hydrogenolysis, 1,2-propanediol

Introduction

Due to the dwindling petroleum resources accompanied by escalating energy demand, biomass represents renewable sustainable and carbon-neutral resource for the production of biomaterials, thus attracted much interests.¹⁻³ Readily available and biodegradable in associated with its high functionalization, glycerol has been regarded as one of the most promising platform chemicals to obtain a large number of useful compounds.^{4,5} In recent years, many studies have been devoted to the selective hydrogenolysis of glycerol to 1,2-propanediol (1,2-PDO) and ethylene glycol (EG). Unfortunately, literature reports imply that harsh reaction conditions were often used in the complex catalytic systems. In the case of a multi-metallic catalyst containing Rh, the reaction condition was 8 MPa and 393 K, leading to conversion up to 80% with selectivity higher than 30%.⁶ Using Ru/C in combination with ion-exchange resins, the conversion is only 12.9% under 8.0 MPa at 393 K.

Nowadays, increasing attention has been focused on the inexpensive metals, such as Ni/AC, Ni/NaX, CuO/ZnO and Cu/SiO₂ in glycerol hydrogenolysis.⁸⁻¹⁰ Such catalysts can be used under slightly mild reaction conditions in terms of temperature, whereas careful pre-treatment must be done to afford active catalysts, however, low conversion or poor selectivity was obtained. All of these studies employ harsh reaction conditions, complex catalytic systems, or environmentally toxic catalysts. In addition, such systems always result in low conversion, low selectivity or bad reusability. Therefore, the development of economic metal catalysts with high activity, selectivity and reusability is an important step to further apply this catalytic system in industry.

In our previous study, the hydrogenolysis of glycerol into 1,2-PDO in the absence of hydrogen was developed.¹¹ 100% conversion and 58.2% yield of total diols products (1,2-PDO and EG) were obtained in the presence of a Raney Ni catalyst. The high activity was attributed to active hydrogen atoms produced *in situ* on the catalyst. However, the NiAl alloy powder must be pre-treated with concentrated aqueous NaOH solution for 30 min and washed with distilled water for many times subsequently to afford the fresh catalyst. A large amount of wastewater would be generated in this procedure, which is not consistent with the requirements of sustainable chemistry.

In the present work, we describe the first one pot glycerol hydrogenolysis reaction over a robust CoAl alloy catalyst without any pre-treatment to obtain value-added chemical intermediates. The transformation of glycerol into 1,2-PDO and EG achieves a conversion of 100% and a yield of 66.5% to liquid phase products. After 5 times' recycling, a conversion of 90.6% and a yield of 51.9% could still be attained. In addition, with a smart reactor, the liquid products can be automatically separated from the solid catalyst, which was very useful in a practical industrial plant.

Experimental

Catalyst characterization

The X-ray powder diffraction (XRD) of the catalysts

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Received December 16, 2010; revised March 25, 2011; accepted April 19, 2011.

Project supported by the Major State Basic Resource Development Program (No. 2003CB 615807), the National Natural Science Foundation of China (No. 20973042), the Research Fund for the Doctoral Program of Higher Education (No. 20090071110011) and the Science & Technology Commission of Shanghai Municipality (No. 08DZ2270500).

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was carried out on a Bruker D8 Advance X-ray diffractometer using nickel filtered Cu K α radiation at 40 kV and 20 mA. A JEOL 2011 microscope operating at 200 kV equipped with an EDX unit [Si (Li) detector] was used for the TEM experimets. The samples for electron microscopy were prepared by grinding and subsequent dispersing the powder in ethanol and applying a drop of very dilute suspension on carbon-coated grids. The N₂ physisorption was carried out at 77 K on a Micrometritics TriStar 3000 apparatus.

Activity tests

In a typical test, glycerol aqueous solution (30 mL, 10 wt%) and 1 g CoAl alloy catalyst were added into the stainless steel autoclave (reactor volume, 300 mL). After purging the reactor with H_2 , the reaction was carried out at 473 K for 15 h at a stirring speed of 600 r/min. The temperature was monitored with a thermocouple that was inserted into the autoclave and connected to the thermo-controller. After the reaction was halted, the reactor was cooled to room temperature. The gas phase products were collected in a gasbag and the liquid-phase products were obtained. Internal standards were used to determine the product amount and carbon balance. These products were analyzed by a GC equipped with an FID detector.

Results and discussion

Various reaction conditions have been investigated for the hydrogenolysis of glycerol at optimized reaction conditions. 100% conversion and 66.5% yield could be obtained under optimal reaction conditions (4 MPa H₂ and 473 K) over a commercial CoAl alloy powder without any pre-treatments. In addition, trace amount of ethanol, *n*-propanol, hydroxy acetone and propanoic acid was detected in the liquid products. CO2, CH4, C_2H_6 and C_3H_8 were detected in the gas products. To investigate the effect between cobalt and aluminum, nanosized Co powder and Al powder were used also as catalyst. It is found that neither Co powder nor Al powder shows satisfied activity in this reaction. When Co powder was used, the conversion of glycerol was 31.9%; however, almost no detectable conversion was obtained over the Al powder catalyst although most of the Al powder was consumed after the reaction. When a mechanical mixture of these two metal powders was used as the catalyst, the catalytic performance was greatly enhanced, and 46.7% yield of liquid products was obtained. However, this result is still much lower than that of the CoAl alloy catalyst. All these findings indicated that there was strong synergistic effect between two metals in the alloy. We think that the addition of Al powder in the Co catalyst enhanced the dehydration of glycerol to acetol, thus the chemical equilibrium of dehydration was shifted after the hydrogenation of acetol over cobalt active sites. Also the Co species could be well dispersed on the alumina oxide formed by the hydration of Al powder. It is worthy to note that almost no BET surface area $(14 \text{ cm}^2/\text{g})$ was determined for the CoAl alloy catalyst, suggesting that there is no direct relationship between the BET surface area of the alloy and the activity of the catalyst. However, it is interesting to find that, after the reaction, most of the alloyed Al was leached (only about 5% alloyed Al was left after one cycle reaction), and the BET surface area of the catalyst reached about 80 m²/g, meaning that the leaching process leads to the great enhancement of the BET surface area. This result agrees well with that of the change of BET surface area for NiAl alloy before and after NaOH leaching treatment. Therefore, we can draw a conclusion that it is the alloyed Al that leads to the formation of active Co species in the present hydrogenolysis reaction, which was also stabilized by the alloyed Al because of their difference in electronegativity.

Figure 1 gives the results of glycerol reactions over CoAl alloy catalyst. It is clear that the glycerol conversion as well as the total yield of the diols increased with the reaction time, whereas the yield of diols decreases upon further extending the reaction time. Based on the distribution of the liquid products upon the variation of reaction time, further C—C cleavage could occur when extending the reaction time, *i.e.*, 1,2-PDO can be further degraded to EG.¹² Therefore, a suitable reaction time is necessary for the high yield of diols.



Figure 1 Effect of reaction time on the catalytic performance over CoAl alloy catalyst.

Table 1 shows that higher conversion was obtained at diluted glycerol concentrations over the CoAl alloy catalyst. While it is found that more degraded products would be produced when much lower glycerol concentrations were used. If a 10% aqueous solution of glycerol was used, 100% glycerol conversion was obtained while 66.5% yield of total liquid products could be achieved. So all the experiments were carried out by using 10% glycerol taking into the considerations of industrial application. The conversion of glycerol decreased with increasing the concentration of glycerol, but the selectivity of diols almost unchanged, 100% conversion could also be obtained when properly extending the reaction time. For example, if 20% glycerol was used as the substrate, 100% conversion with 20.4% yield of 1,2-PDO and 6.9% yield of EG could also be obtained after 25 h. The effect of temperature on the hydrogenolysis of glycerol was also shown in Table 1. The conversion of glycerol increased from 42.8% to 100% as the temperature was increased from 433 to 473 K. At the same time, the yield of liquid products was increased from 32.0% to 66.5%. However, the selectivity to 1,2-PDO was slightly decreased from 78.2% to 70.1% correspondingly. It is also found that the selectivity to EG was increased from 21.1% to 28.1%, indicating that higher reaction temperature favoured the degradation products due to C—C bond cleavage. This finding is in agreement with other reports.^{13,14}

Table 1 Effect of glycerol mass concentration, reaction temperature and kinds of catalyst on the catalytic performance overCoAl alloy catalyst^a

Glycerol concentration/%	conversion/%	Yield/%	Sel	Selectivity/%		
			PG	EG	Others	
5	100	28.9	12.4	40.8	46.8	
10^b	42.8	32.0	78.2	21.1	0.7	
10^{c}	69.2	46.3	75.5	23.4	1.1	
10	100	66.5	70.1	28.1	1.8	
10^d	31.9	13.3	61.6	37.5	0.9	
10^{e}	0	0	0	0	0	
10^{f}	75.2	46.7	73.9	23.7	2.4	
20	72.9	48.7	68.3	28.5	3.2	
30	51.2	43.3	64.2	27.7	8.1	

^{*a*} Reaction conditions: 30 mL aqueous glycerol, 473 K, catalyst amount (1 g), H₂ (4 MPa), 15 h; ^{*b*} 433 K; ^{*c*} 453 K; ^{*d*} Co catalyst; ^{*e*} Al catalyst; ^{*f*} mechanical mixture of Co and Al.

Studies on the amount of catalyst in the hydrogenolysis of glycerol over CoAl alloy catalyst were also carried out. In line with the previous studies, when increasing the amount of the catalyst, the glycerol conversion was enhanced significantly, however, the total yield of liquid products decreased, indicating that further C—C cleavage occurred inevitably.

Based on the findings mentioned above, the mechanism of the hydrogenolysis of glycerol over CoAl alloy catalyst was proposed as shown in Scheme 1. 1,2-PDO was formed from the dehydration of glycerol to acetol and the subsequent hydrogenation over active Co sites. EG was formed directly from the reductive cleavage of a C—C bond in glycerol and 1,2-PDO was further degraded to EG.^{7,15}

It is interesting to find that the CoAl catalyst was stable, and can be used for many times. The catalytic performance of the CoAl alloy catalyst decreased a little after recycling for 5 times, which might result from the deactivation of the active cobalt species. As can be observed from the XRD patterns and TEM images (Figures 2 and 3), only a small amount of Co₂Al₉ crystalline was maintained in the alloy catalyst after the reaction (about 4.6% alloyed Al left). Being covered by complex side products as well as oxidized by residual oxygen both might result in the decrease of active Co species, thus leading to the decrease of the catalytic performance of the catalyst. Due to its ferromagnetic property after recycling for 5 times, the used catalyst can be easily gathered from the autoclave. All the results described above imply that the commercial CoAl alloy was a promising candidate in industrial application for the hydrogenolysis of glycerol.

Considering the requirements in industry, an energy-saving and easy-handling process would be very desirable. We report here a fully integrated process in the hydrogenolysis of glycerol. Firstly, a glass vessel was inserted into the autoclave. The vessel inside was designed 2 mm less than the autoclave's inner diameter and 3 cm shorter than the upper side of the autoclave. This design was very smart because the reaction was processed in the glass reactor during the reaction. But after the reaction was stopped, the autoclave was gradually cooled down. During this cooling process, the liquid products would automatically move from the internal glass reactor to the interlayer between the inner tube and the autoclave due to the vapor condensation of the products mixture and the different cooling velocity of stainless steel and glass. After the autoclave was cooled to room temperature, all the solid catalyst was left inside the glass vessel while the liquid products were totally moved to the interlayer between the vessel and the autoclave. It is surprise to find that the glass vessel was floating in the autoclave after the autoclave was opened. With this simple reactor, the centrifugation or filtration was no longer needed for the purification of the products, and the catalyst can be easily reused without any







Figure 2 XRD patterns of CoAl alloy catalyst before and after reaction.







Figure 3 TEM image of the used catalyst.

treatments and loss of active components. This device is much simple and more integrated than that of reactive distillation designed by Suppes and co-workers.¹⁶

Conclusions

In summary, we have demonstrated a facile and efficient one pot catalytic process of glycerol to value added 1,2-PDO and EG over a commercial CoAl alloy catalyst. The reaction conditions for the catalytic process are much milder and the liquid products can be automatically separated from the solid catalyst with a smart design for the reactor. Further improvements can be expected which offered excellent prospects for a fully integrated process, even opened a route to practical applications.

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(E1012162 Lu, Y.; Fan, Y.)