Electronic Supplementary Information

A novel approach for the synthesis of propylene glycol and ethylene glycol from glycerol using Raney Ni as a versatile catalyst

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1. Catalyst preparation.

The Ni-Al alloy was obtained from Sinopharm Chemical Reagent Ltd. Before using, a certain amount of alloy was treated with the NaOH aqueous solution (3 M) for 30 min at 333 K, then the solution was washed with distilled water for several times to afford the fresh Raney Ni catalyst.

2. Procedure for the batch reaction

In a typical test, glycerol aqueous solution (30 ml, 10 wt.%) and 1 g Ni catalyst were added to the stainless steel autoclave (reactor volume, 250 ml). After purging the reactor with N_2, the reaction was carried out at 453 K for 1 h at a stirring speed of 800 rpm. 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 separated from the used catalyst by centrifugation. Internal standards were used to determine the product amount and carbon balance. These products were analyzed by GC.

3. Calculation of the conversion and selectivity.

Conversion of the glycerol in all reaction tests was calculated based on the following equation:

$$Conversion = \frac{\text{total amount of glycerol-amount of remained glycerol}}{\text{total amount of glycerol}} \times 100\%$$

$$Selectivity = \frac{\text{C atoms in each product}}{\text{total C atoms in the products}} \times 100\%$$

Carbon balance is better than 95±3% in this work. According to the proposed reaction pathway, the theoretical selectivity of propylene and ethylene glycol could be calculated as following:

$$C_3H_8O_3 + H_2O \rightarrow C_3H_8O_2 + CO_2 \qquad (1)$$

$$C_3H_8O_3 + H_2O \rightarrow C_2H_6O_2 + CO_2 \qquad (2)$$

According to the two equations listed above and taking the liquid phase products into consideration, the theoretical selectivity of propylene and ethylene glycol is 88% and 68% respectively.

4. Characterization of the catalysts

The X-ray powder diffraction (XRD) of the catalysts was carried out on a German Bruker D8 Avance X-ray diffractometer using nickel filtered Cu Kα 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 investigations. 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 N_2 physisorption was carried out at 77 K on a Micrometritics TriStar 3000 apparatus.

Table S1. Effect of glycerol mass concentration on the products distribution over Raney Ni catalyst.[a]

Glycerol Concentration (%)	Conversion (%)	Yield[b] (%)	Selectivity[c] (%)		
			PG	EG	Ethanol
5	100	23.0	25.0	71.0	4.0
10	100	58.2	43.0	55.0	2.0
20	100	36.7	29.2	64.8	6.0
30	100	30.1	24.6	71.4	4.0
50	71	23.7	37.1	53.6	9.3
100	84	11.1	0	72.1	27.9

[a]Reaction conditions: 453 K, catalyst (1g), N_2 (0.1 MPa), 1 h. [b]Total yield of liquid

products. [c]C-based composition of liquid products/mol%.

Table S2. Effect of amount of catalyst on the catalytic performance over Raney Ni catalyst. [a]

Amount of Catalyst (g)	Conversion (%)	Yield[b] (%)	Selectivity[c] (%)		
			PG	EG	Ethanol
0.5	78	41.5	37.1	59.8	2.7
1.0	100	58.8	42.5	54.4	3.1
1.5	100	37.2	43.0	48.3	8.4

[a]Reaction conditions: 30 ml glycerol aqueous (10 wt.%), 453 K, N_2 (0.1 MPa), 1 h. [b]Total yield of liquid products. [c]C-based composition of liquid products/mol%.

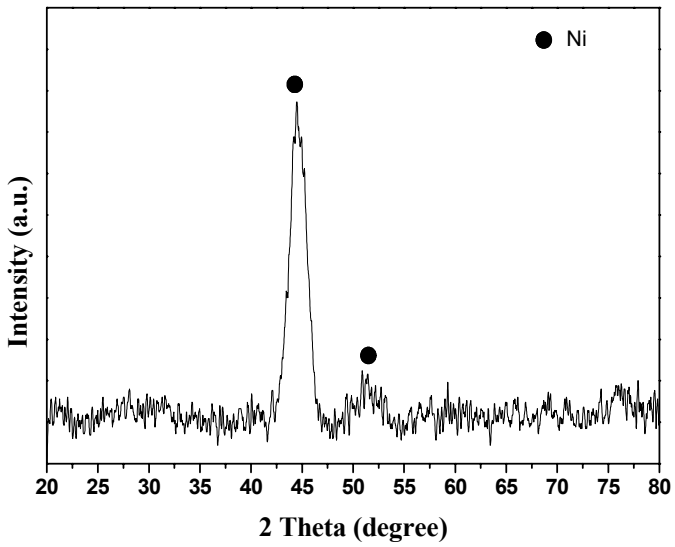

Figure S1. XRD pattern of Raney Ni catalyst.

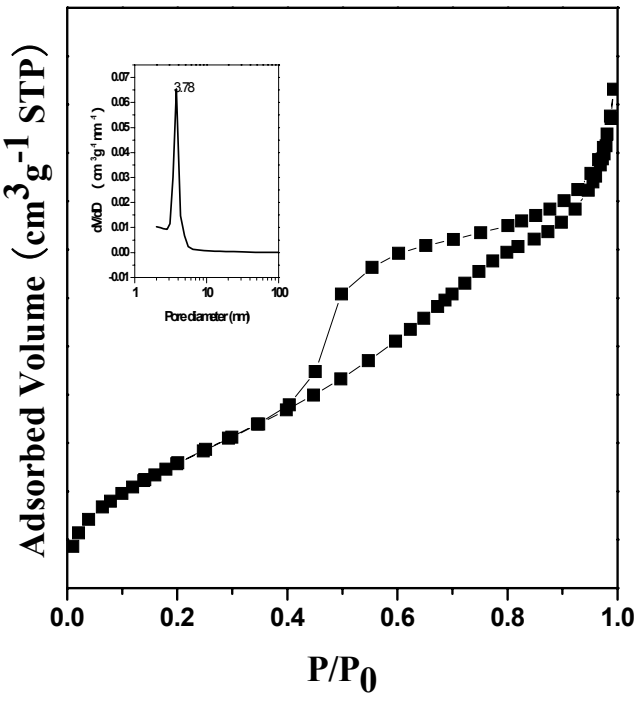

Figure S2. N_2 adsorption-desorption isotherms and pore size distribution curves calculated by BJH equation in desorption branch (inset) of the Raney Ni catalyst.

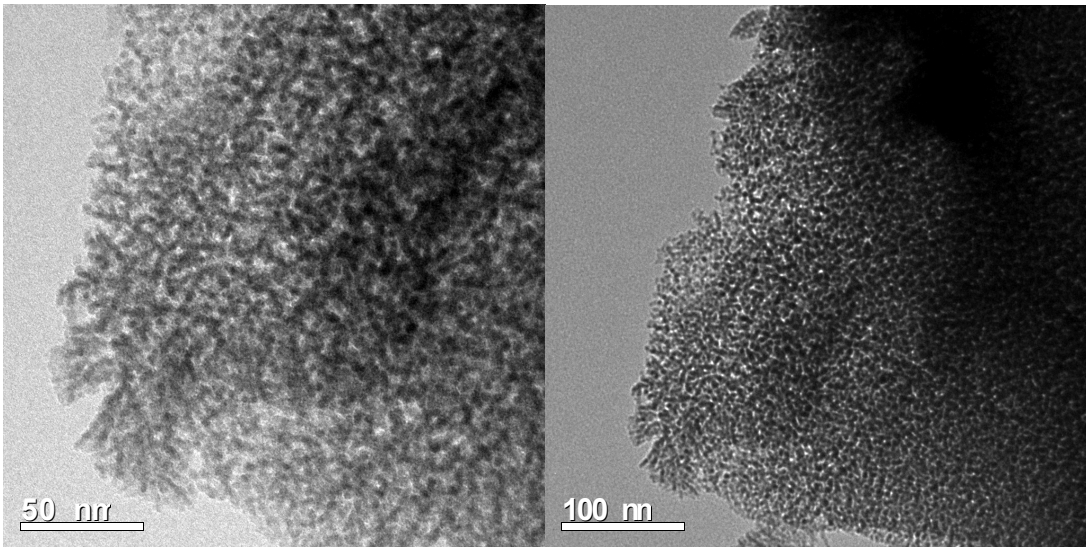

Figure S3. Representative TEM image for Raney Ni catalyst