

## Electronic Supplementary Information

### Promoter effect of Pd in $\text{CuCr}_2\text{O}_4$ catalysts on the hydrogenolysis of glycerol to 1,2-propanediol

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## 1. Catalyst composition

The composition of synthesized catalysts were examined by ICP and EDS analyses and summarized in Table S1.

Table S1. Composition of synthesized catalysts.

Catalysts	Pd		Cu (at%)	Cr (at%)	O (at%)
	wt%	at%			
Pd <sub>0</sub> -CuCr	0	0	13.87	25.83	60.31
Pd0.3-CuCr	0.25	0.08	13.33	25.24	61.33
Pd0.5-CuCr	0.48	0.14	13.35	24.34	62.16
Pd1-CuCr	1.01	0.30	13.29	24.09	62.31
Pd3-CuCr	2.64	0.87	13.50	27.76	57.87
Pd10-CuCr	9.46	3.03	12.87	25.86	58.24

## 2. Kinetic study

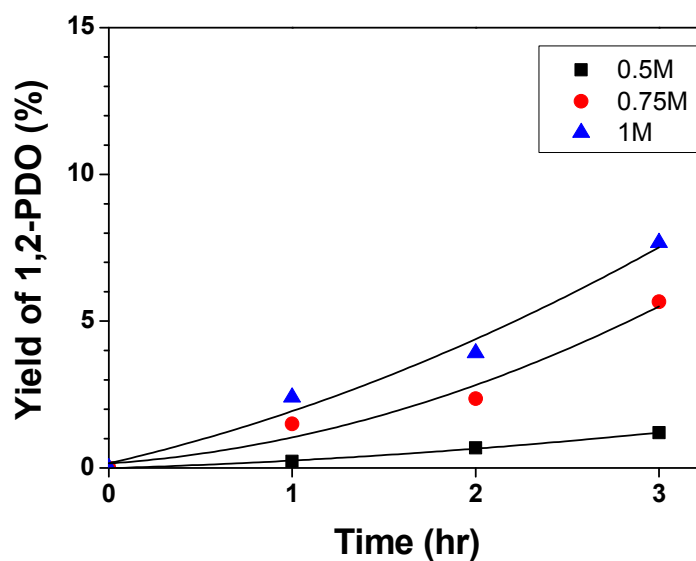


Fig. S1. Hydrogenolysis of glycerol under copper chromite catalyst with the various concentration of glycerol (temperature 220 °C, catalyst 1g and 5 MPa H<sub>2</sub>)

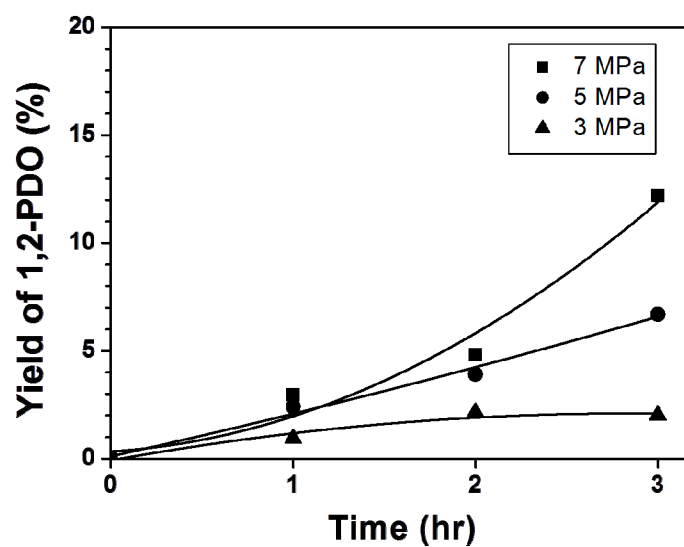


Fig. S2. Hydrogenolysis of glycerol under copper chromite catalyst with the various H<sub>2</sub> pressure (temperature 220 °C, catalyst 1g and 1M glycerol)

### 3. In-situ NH<sub>3</sub>-FT-IR

For further confirmation of the acidic characteristics of the synthesized catalysts, in-situ FT-IR measurements with NH<sub>3</sub> were performed (Fig. S3). Ammonia can be used as the probe molecule, and Brønsted acid sites (B) and Lewis acid sites (L) can be directly distinguished from one another from their spectra. In the spectra, the peaks in the range of 1460~1490 cm<sup>-1</sup> are assigned to the symmetric N-H deformation of NH<sub>4</sub><sup>+</sup>, which is formed by the interaction of NH<sub>3</sub> with Brønsted acid sites. On the other hand, the peaks in the region of 1600~1630 cm<sup>-1</sup> are assigned to the asymmetrical N-H deformation of NH<sub>3</sub> coordinately bound to Lewis acid sites.<sup>1</sup> In the spectra of Pd<sub>0</sub>-CuCr, a very strong characteristic peak for a Lewis acid site, and relatively weak characteristic peaks for Brønsted acid sites were observed, as seen in Fig. S1. In case of the Pd<sub>0.5</sub>-CuCr catalyst, its Lewis acid characteristics decreased to some degree, compared to Pd<sub>0</sub>-CuCr. However, its Brønsted acid characteristics largely increased after adding a small amount of Pd to the CuCr<sub>2</sub>O<sub>4</sub> catalyst. When a 3 wt% of Pd was added to the CuCr<sub>2</sub>O<sub>4</sub> catalyst, the intensity of both spectral signals decreased, indicating that the Lewis and Brønsted acid characteristics had become weakened. These results are in good agreement with the NH<sub>3</sub>-TPD results as shown in Fig. 5. Therefore, it can be concluded that the desorption characteristics peak at the lower temperature of NH<sub>3</sub>-TPD results is corresponding to Brønsted acid sites of the catalysts.

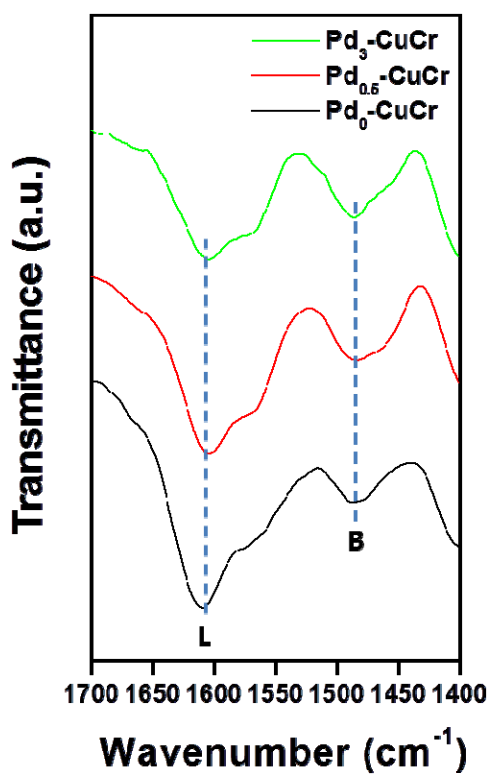
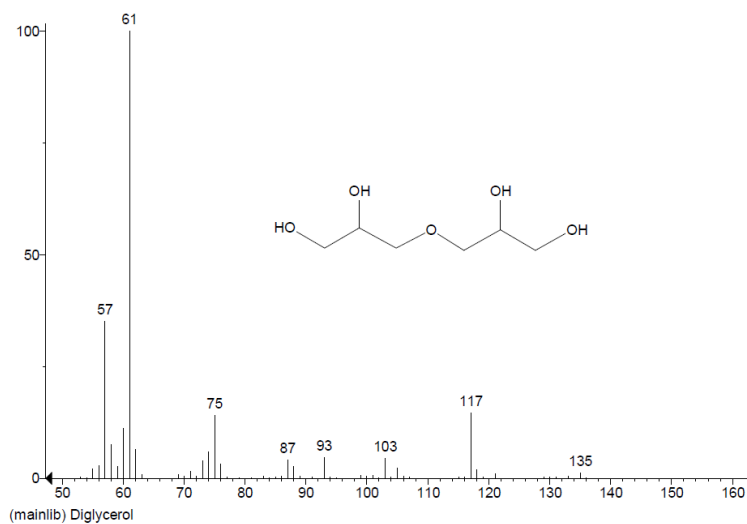
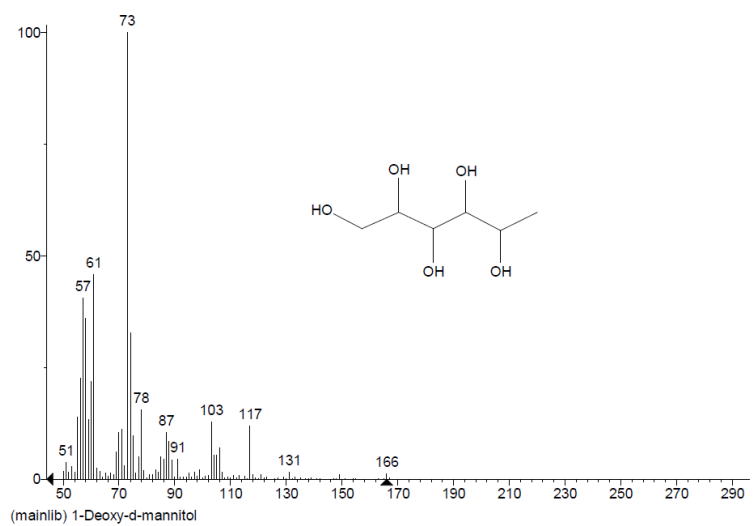
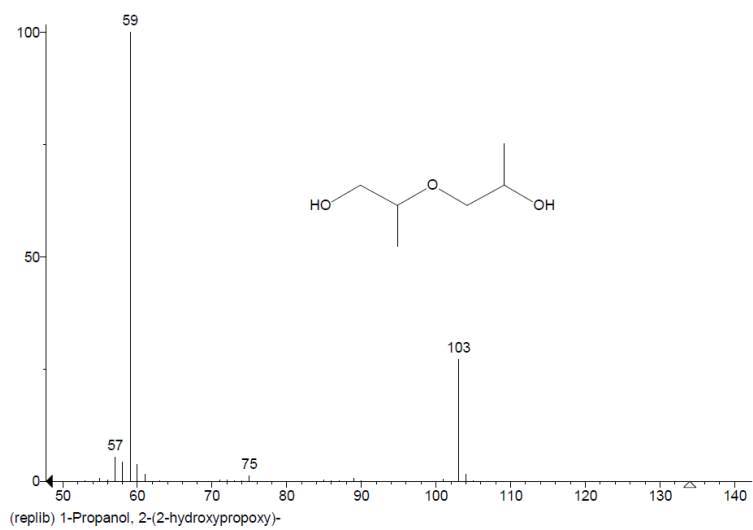


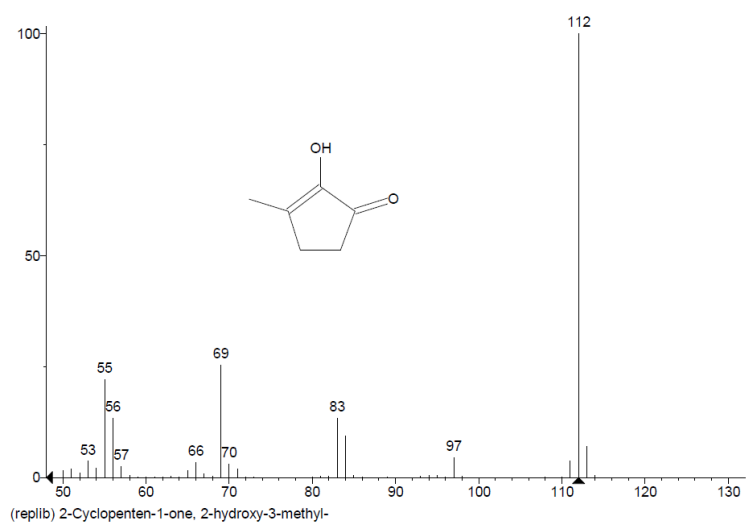
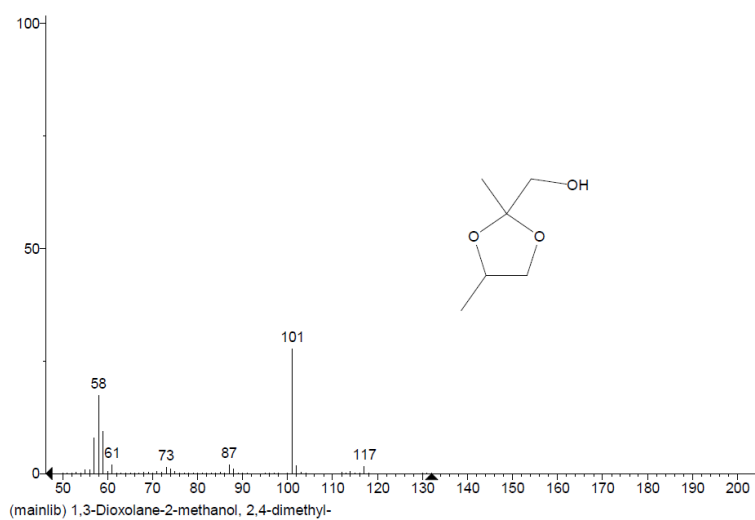
Fig. S3. In-situ FT-IR spectra of NH<sub>3</sub> adsorption for Pd<sub>0</sub>-CuCr, Pd<sub>0.5</sub>-CuCr, and Pd<sub>3</sub>-CuCr catalysts (B = Brønsted acid sites; L = Lewis acid sites).

#### 4. By-product analysis at the beginning of reaction time

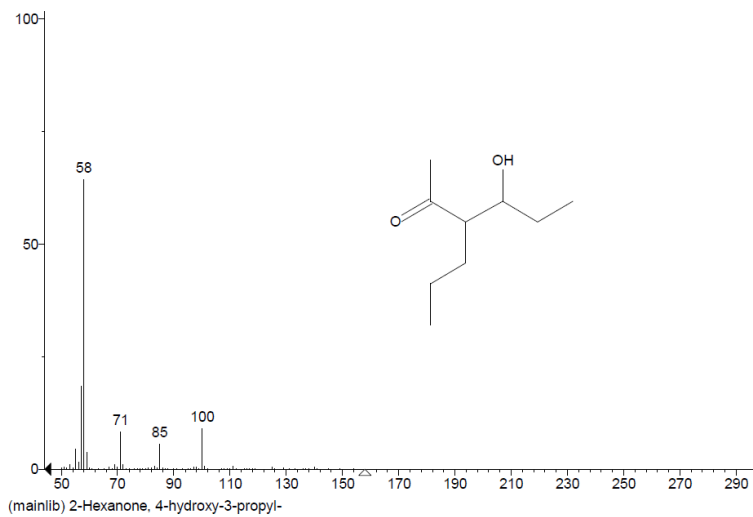
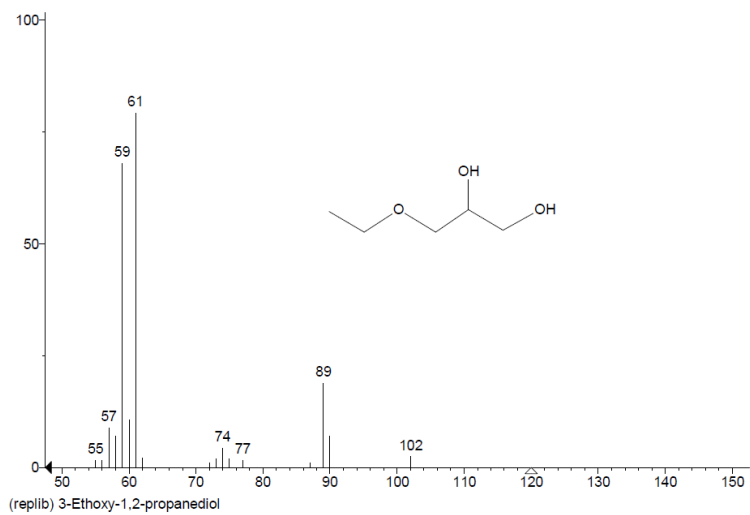
By-products in both liquid and gas phases, which were sampled at the beginning of the hydrogenolysis reaction, were measured by GC-Mass spectroscopic analysis. Representative compounds in the liquid phase are as follows.

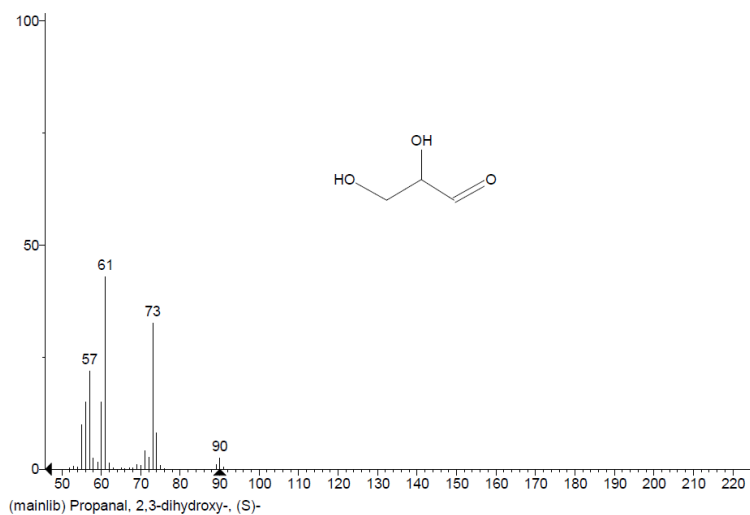












There are also other products present in the gas phase, as shown below.

