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Supplementary material

Comparative study of WC_x-based catalysts for aqueous phase hydrogenolysis of glycerol into bioadditives

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Quantification method for GC analysis

To quantify the GC results, an internal standard method using n-butanol was used. Typically, certain concentration of n-butanol and substances need to be measured (methanol, 1-PO, 2-PO, 1,2-PDO, 1,3-PDO and EG in this work) were prepared for GC measurement. Calibration factor(f) can be obtained by comparing the peak area and mass of each substance, using equation (1): $f=(A_s/m_s)/(A_r/m_r)$ (A_s and A_r represent the peak area of substance to be tested and n-butanol, respectively; m_s and m_r represent the mass of substance to be tested and n-butanol, respectively). After that, certain amount of n-butanol was added into the liquid product and mixed homogeneously. Using equation (2): $m_i=f*A_i/(A_s/m_s)$ (A_i and m_i represent the peak area and mass of certain compound in the liquid product, respectively) and considering the volume of liquid products and injection sample, the content of each compound can be calculated.

Table S1. ICP results for each catalyst.

catalysts	Cu content (wt.%)	Pt content (wt.%)	Ru content (wt.%)	W content (wt.%)
Cu/WC_x	0.89	/	/	78.84
Pt/WC_x	/	0.92	/	85.69
Ru/WC_x	/	/	0.90	80.98
$CuPt/WC_x$	0.82	0.95	/	72.23
$CuRu/WC_x$	0.85	/	0.98	84.30

Carbon balance calculation

The carbon mass balance was calculated based on the following equation:
Con. by TOC % = (mass of total organic carbon in the liquid phase)/(mass of carbon in the glycerol fed into the reactor)×100%.

Table S2. Carbon balance for glycerol hydrogenalysis over various catalysts.

Carbon balance	Catalyst							
	WC_x	Cu/WC_x	Pt/WO_3	Pt/WC_x	Ru/WO_3	Ru/WC_x	$CuPt/WC_x$	$CuRu/WC_x$
Con. by TOC %	59.3	70.4	72.8	75.2	60.3	80.6	70.9	70.0
Con. by weigh %	64.9	72.0	74.4	79.2	73.5	84.3	80.2	84.5

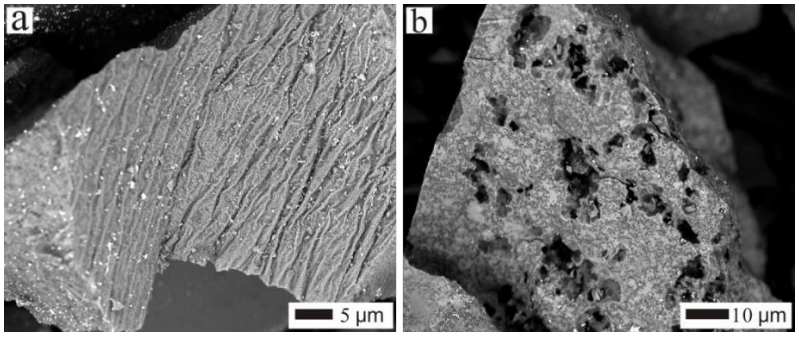

Figure S1. SEM images of $CuPt/WC_x$.

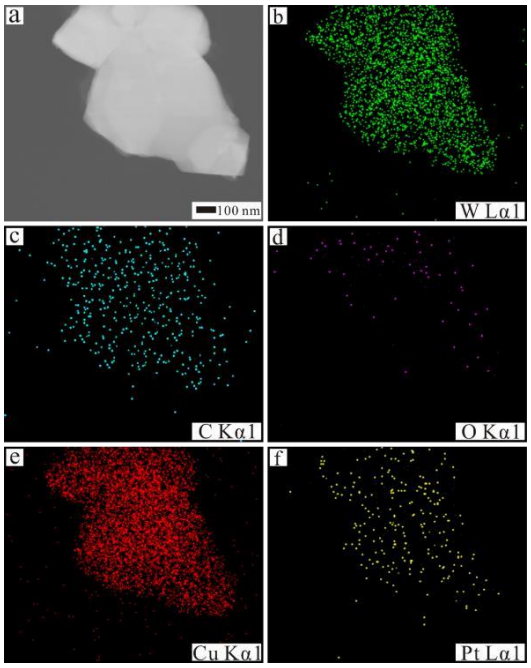

Figure S2. (a) STEM image of $CuPt/WC_x$ and (b–f) the corresponding EDX mapping of $CuPt/WC_x$ at the region shown in (a), indicating spatial distribution of W, C, O, Cu, Pt, respectively.

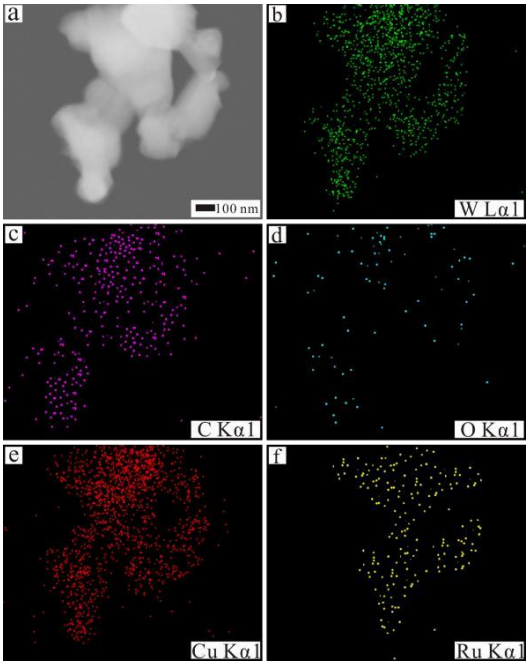

Figure S3. (a) STEM image of $CuRu/WC_x$ and (b–f) the corresponding EDX mapping of $CuRu/WC_x$ at the region shown in (a), indicating spatial distribution of W, C, O, Cu, Ru, respectively.

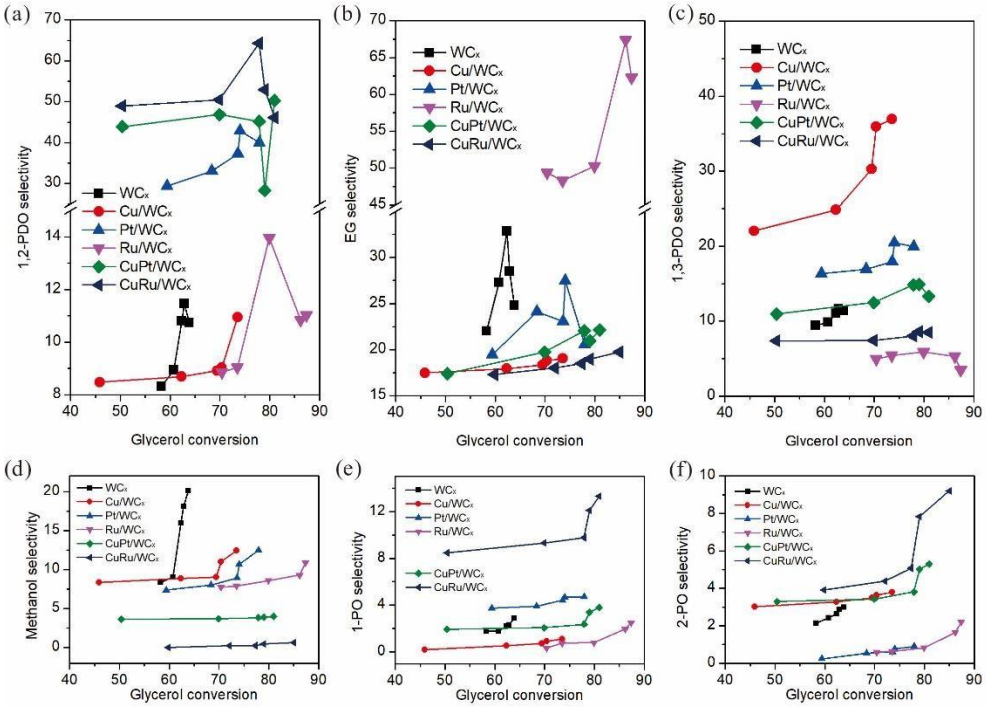

Figure S4. (a) 1,2-PDO selectivity; (b) EG selectivity; (c) 1,3-PDO selectivity; (d) Methanol selectivity; (e) 1-PO selectivity; (f) 2-PO selectivity versus glycerol conversion for each catalyst.

To give more convincing data to Scheme 2, relationship between selectivity versus conversion of each catalyst were studied by selecting five point-in-time with an interval of 30 min (reaction after 6, 6.5, 7, 7.5 and 8 h). An intermittent sampling device was used to get products at each point and sent for analysis. Results show that for most catalysts, selectivity of PDOs and EG both have a tendency to increase and then decrease with the increasing of glycerol conversion. It is reasonable when PDOs and EG exist in the reaction system as the product as well as the reactant. However, we can not get any regular conclusions because of the complexity of the reaction. For methanol, 1-PO and 2-PO, it seems the reaction rate is increasing in later time. Thus, reduce the reaction time may be beneficial for PDOs and EG producing.

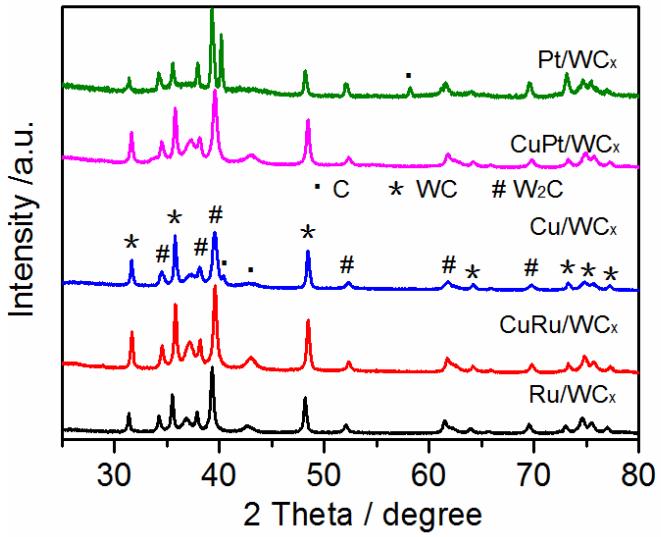

Figure S5. XRD patterns of WC_x-based catalysts (after reaction).

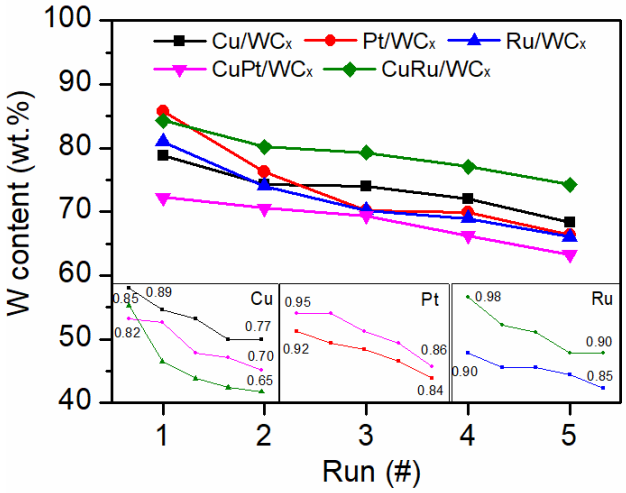

Figure S6. ICP results for catalysts after each run (insets are Cu/Pt/Ru content of each catalyst after each run).