Supplementary Information:

Water-assisted selective hydrodeoxygenation of phenol to benzene over Ru composite catalyst in biphasic process

Cheng Zhang,[a,c] Chuhua Jia,[c] Yang Cao,[a] Yao Yao,[c] Shaoqu Xie,[c] Shicheng Zhang,[a,b*] Hongfei Lin[c*]

[a] Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention (LAP3), Department of Environmental Science and Engineering, Fudan University, Shanghai 200438, China

[b] Shanghai Institute of Pollution Control and Ecological Security, Shanghai 200092, China.

[c] Gene and Linda Voiland School of Chemical Engineering and Bioengineering, Washington State University, Pullman, WA 99164, USA

[*]Corresponding author:

Shicheng Zhang, E-mail: zhangsc@fudan.edu.cn

Hongfei Lin, E-mail: hongfei.lin@wsu.edu

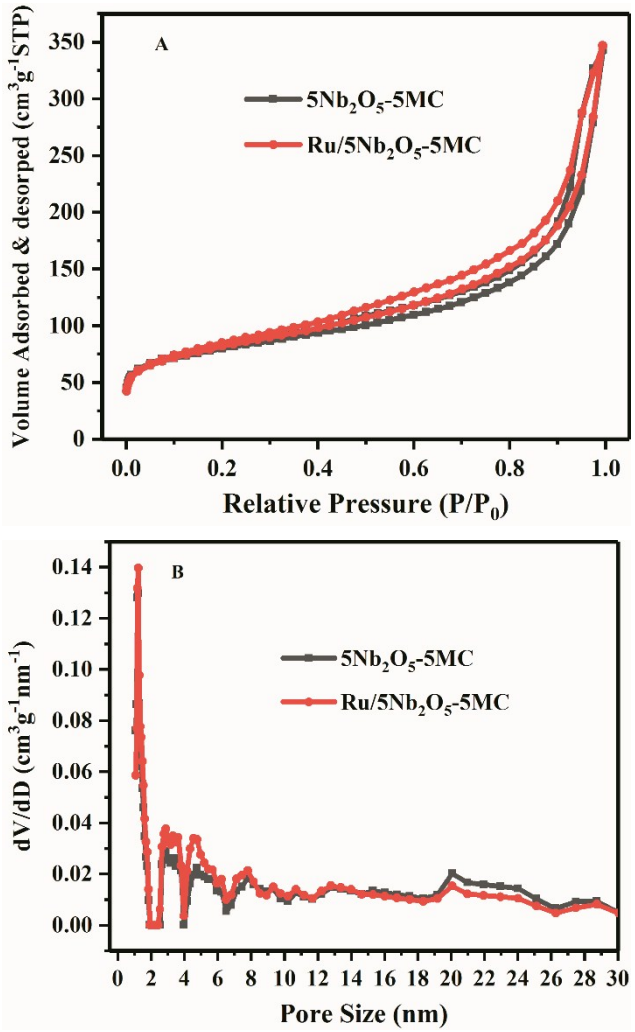

Fig. S1 The nitrogen adsorption-desorption isotherms of support and catalyst (A). The pore size distribution calculated from the adsorption isotherms using DFT method (B).

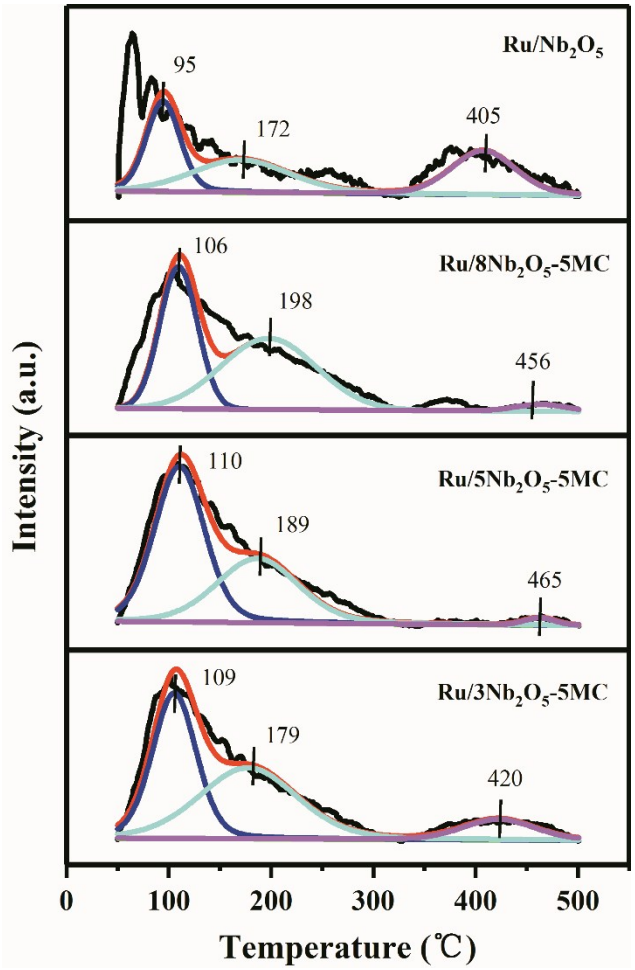

Fig. S2 NH_3-TPD profiles of fresh catalysts.

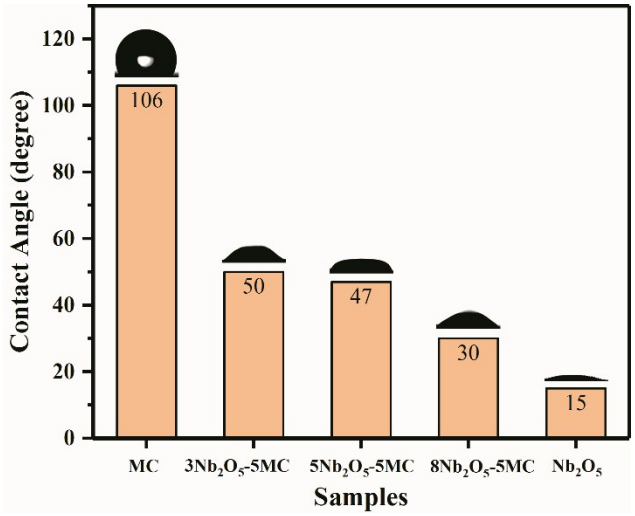

Fig. S3 Air-water contact angles for Ru/MC, Ru/3Nb_2O_5-5MC, Ru/5Nb_2O_5-5MC, Ru/8Nb_2O_5-5MC and Ru/Nb_2O_5 catalysts. The photos were immediately captured after a drop of water was deposited on the surface of the self-supporting pressed sample disc.

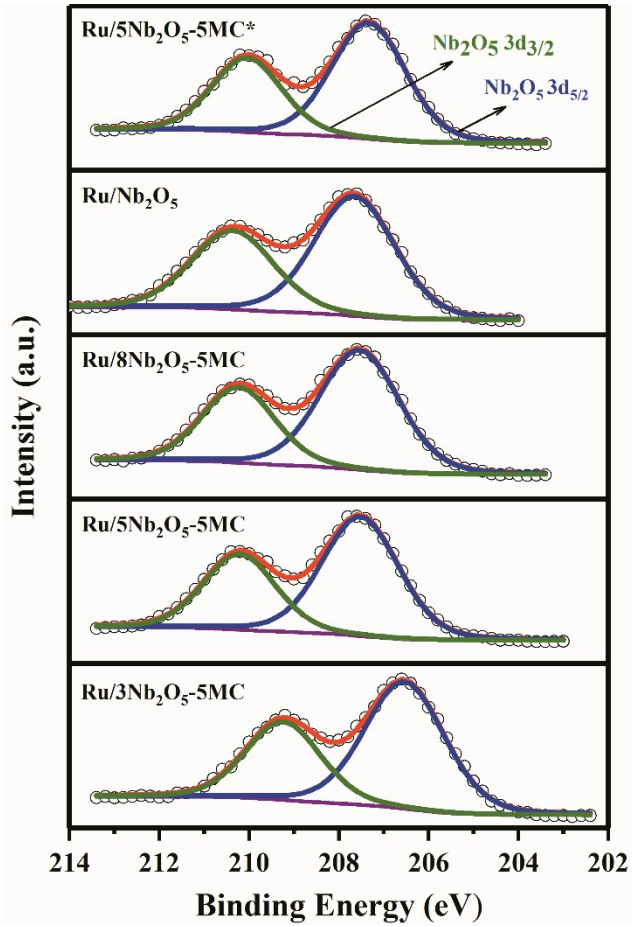

Fig. S4 XPS spectra in the Nb 3d region for the fresh and spent (*) catalysts.

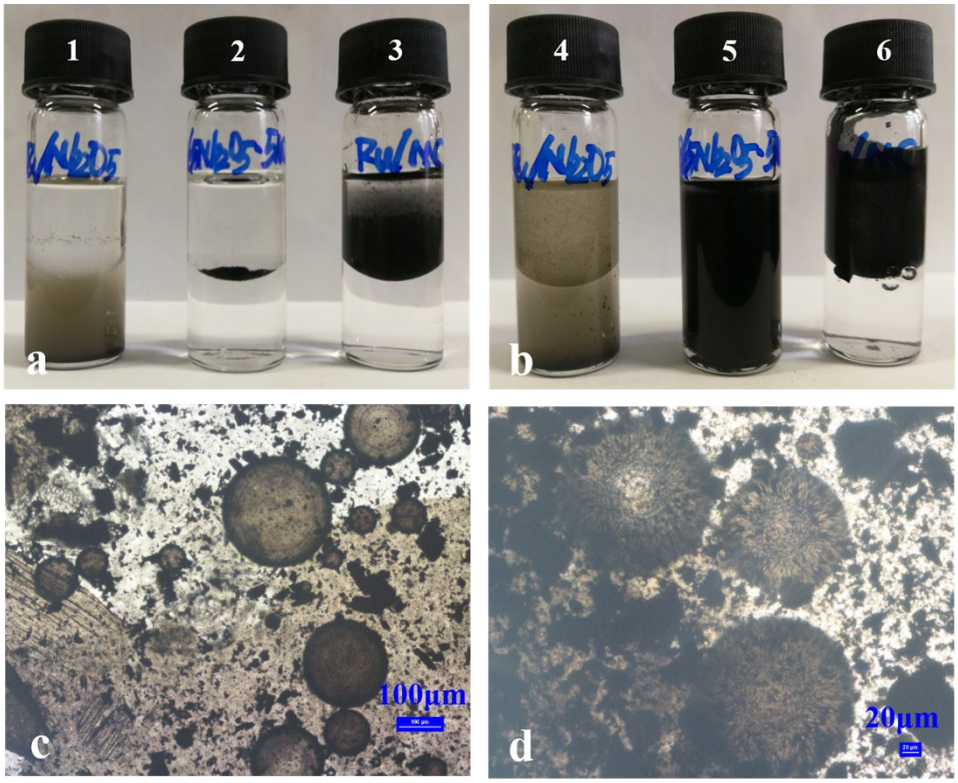

Fig. S5 The images of Ru/Nb_2O_5 (bottle 1, 4), $Ru/5Nb_2O_5$-5MC (bottle 2, 5) and Ru/MC (bottle 3, 6) catalysts in the decalin (upper layer) and water (lower layer) mixture before (a) and after (b) stirring for 30 min. There is no emulsion in biphasic solvent with the Ru/Nb_2O_5 (bottle 4) and Ru/MC (bottle 6) catalysts. A high extent of emulsification and small droplet size are observed with the $Ru/5Nb_2O_5$-5MC catalyst (c, d). We also observed that the $Ru/5Nb_2O_5$-5MC catalyst particles were at the decalin/water interface (c, d).

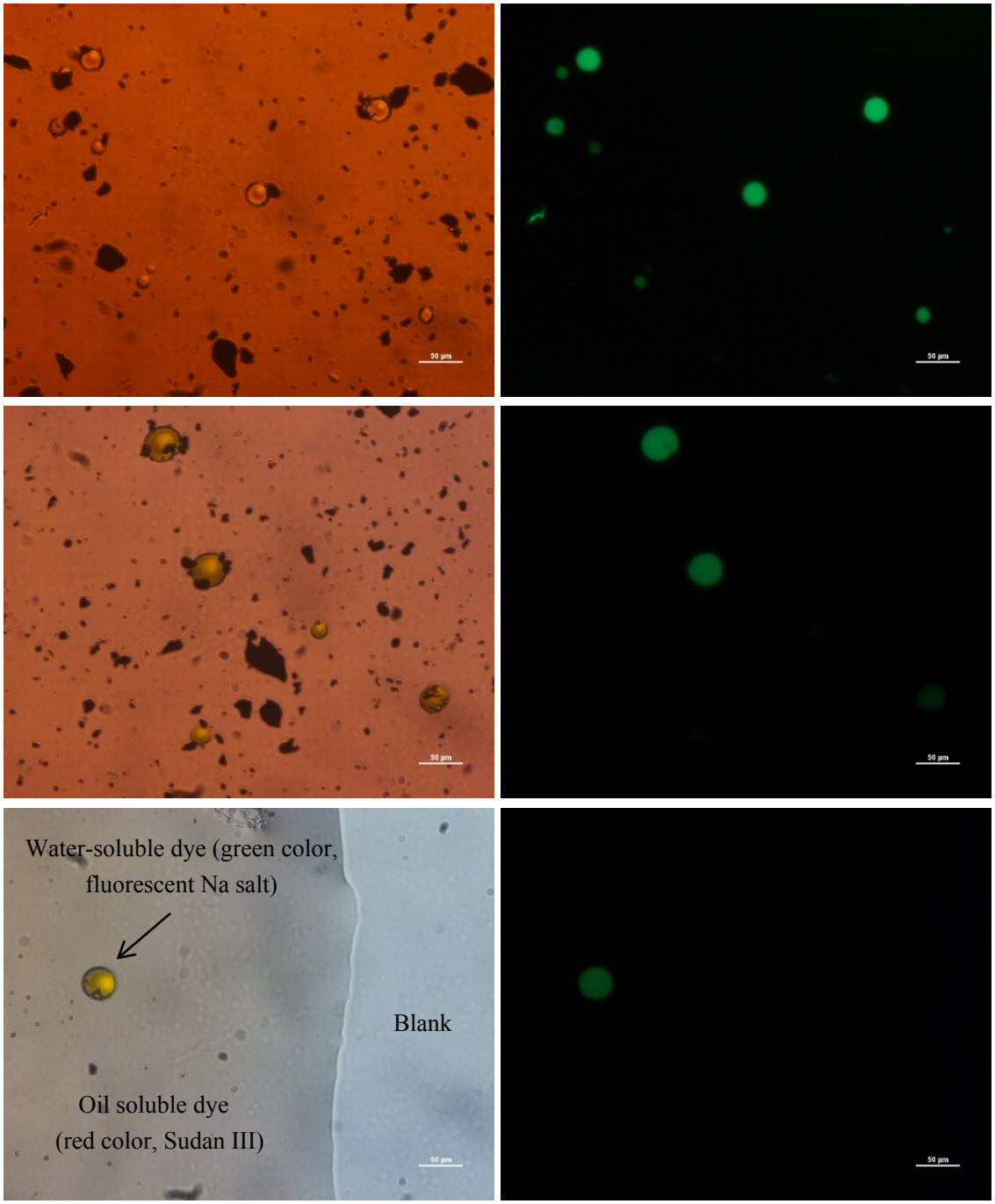

Fig. S6 Color photograph of the emulsion prepared from the Ru/5Nb_2O_5-5MC catalyst. Water-soluble dye (green color, fluorescent Na salt) and oil-soluble dye (red color, Sudan III) were added to identify the water-in-oil type of the emulsion (W/O).

Table S1 Summary of the binding energy in the high-resolution XPS Ru 3d and C 1s spectra of fresh and spent (*) catalysts.

Catalysts	Ru $3d_{3/2}$				C 1s		
	Ru^0	Ru^{x+}	Ru^{y+}	Ru^0%[#]	C-C	C-O	C=O
Ru/MC	283.8	284.7	285.6	27.8	282.9	286.8	288.6
Ru/3Nb_2O_5-5MC	284.4	285.4	286.4	39.6	283.5	287.9	289.3
Ru/5Nb_2O_5-5MC	284.3	285.4	286.5	40.7	283.0	286.8	289.3
Ru/8Nb_2O_5-5MC	284.5	285.4	286.2	36.1	283.8	286.9	289.2
Ru/Nb_2O_5	284.2	285.2	286.3	39.9	283.4	288.4	289.5
Ru/5Nb_2O_5-5MC*	284.5	285.3	286.2	38.0	283.8	287.8	289.3

[#] Ru^0 *100 / (Ru^0 + Ru^{x+} + Ru^{y+}).

Table S2 Summary of the binding energy and full-width half-maximum (FWHM) values in the high-resolution XPS Nb 3d spectra of fresh and spent (*) catalysts.

Catalysts	Nb_2O_5 $3d_{5/2}$		Nb_2O_5 $3d_{3/2}$	
	BE (eV)	**FWHM (eV)**	**BE (eV)**	**FWHM (eV)**
Ru/3Nb_2O_5-5MC	206.5	2.09	209.2	1.96
Ru/5Nb_2O_5-5MC	207.5	2.01	210.2	1.89
Ru/8Nb_2O_5-5MC	207.5	2.08	210.2	1.90
Ru/Nb_2O_5	207.7	2.12	210.4	2.16
Ru/5Nb_2O_5-5MC*	207.3	1.94	210.0	1.83

Table S3 Summary of the binding energy and calculated atomic concentrations in the high-resolution XPS O 1s spectra of fresh and spent (*) catalysts.

Catalysts	O		
	O_α (eV)	O_β (eV)	$O_\alpha / (O_\alpha + O_\beta)$
Ru/MC	533.6	532.1	27.1%
Ru/3Nb_2O_5-5MC	533.1	530.5	59.5%
Ru/5Nb_2O_5-5MC	532.7	530.8	63.0%
Ru/8Nb_2O_5-5MC	533.0	531.0	52.0%
Ru/Nb_2O_5	533.3	531.4	35.4%
Ru/5Nb_2O_5-5MC*	533.0	531.1	48.9%

Table S4 HDO of phenol over the different supports without Ru NPs in biTCP

Entry	Supports	Conversion (wt. %)	Selectivity (C mol. %)			
						
1	Nb_2O_5	0.0	-	-	-	-
2	MC	0.0	-	-	-	-
3	$5Nb_2O_5$-5MC	0.0	-	-	-	-

Conditions: 200 ^oC, 6 bar of H_2, 4 h, 700 rpm