

Supporting information

Nb₂C MXene assisted CoNi bimetallic catalysts for hydrogenolysis of aromatic ethers

Sen-Wang Wang,^a Zhen-Hong He,^{b,*} Jian-Gang Chen,^a Kuan Wang,^b Zhong-Yu Wang,^b Pan-
Pan Guo,^b Jie Lan,^b Weitao Wang,^b and Zhao-Tie Liu^{a,b,*}

^aSchool of Chemistry & Chemical Engineering, Shaanxi Normal University, Xi'an 710119,
China.

^bShaanxi Key Laboratory of Chemical Additives for Industry, College of Chemistry and
Chemical Engineering, Shaanxi University of Science and Technology, Xi'an, 710021, China.

*Corresponding authors: hezhenhong@sust.edu.cn (Zhen-Hong He); ztliu@snnu.edu.cn
(Zhao-Tie Liu)

Table S1. Hydrodeoxygenation of diphenyl ether over various heterogeneous catalysts.

Entry	Catalyst	T (°C)	P _{H₂} (bar)	T (h)	Solv.	Conv. (%)	Ref.
1	Ru/SBA-15	130	20	6	[Bmim]PF ₆	100	[1]
2	Ru/C	120	-	10	Isopropanol	>99.0	[2]
3	Pd(OH) ₂ /C	160	1	24	<i>m</i> -Xylene + H ₂ O	>99.0	[3]
4	Pd	130	50	10	[Bmim]PF ₆ + H ₃ PO ₄	>99.0	[4]
5	Pd/C+HZSM-5	200	50	2	H ₂ O	100	[5]
6	Pd/HY	200	34	1	Decalin	>98.0	[6]
7	Pd/C	200	40	48	Methanol	92.0	[7]
8	RuPd ₅ /NH ₂ -SiO ₂	110	10	1	H ₂ O	99	[8]
9	Ru ₁₅ Ni ₈₅	95	1	16	H ₂ O	99	[9]
10	Ru/MMT@IL-SO ₃ H	200	50	2	H ₂ O	100	[10]
11	Ni ₇ Au ₃	100	10	5	H ₂ O	33.7	[11]
12	Pd/Ni	240	N ₂ 10	1.5	2-Propanol	96	[12]
13	RuCo/CeO ₂	200	20	-	Decalin	100	[13]
14	RuFe/CeO ₂	200	20	-	Decalin	100	[14]
15	Ni@SiC	120	6	20	H ₂ O	99	[15]
16	Ni@IRMOF-74(II)	120	10	16	<i>p</i> -Xylene	96	[16]
17	Ni/SiO ₂	150	59	10	H ₂ O	100	[17]
18	Ni(COD) ₂ + SIPr·HCl NaOtBu,	120	1	16	<i>m</i> -Xylene	100	[18]
19	Ni/N-C	200	5	3	<i>n</i> -Hexane	100	[19]
20	Co/C@N	220	20	6	<i>n</i> -Hexane	100	[20]
21	Co ₂ NiO _x + Nb ₂ C	120	5	12	Isopropanol	>99.0	This work

Table S2. ICP-OES results of different catalysts. ^a

Entry	Catalysts	Calculated ^a	ICP-OES tested
1	Co ₁ Ni ₁ O _x	Co ₁ Ni ₁ O _x	Co _{1.06} Ni ₁ O _x
2	Co ₂ Ni ₁ O _x	Co ₂ Ni ₁ O _x	Co _{2.17} Ni ₁ O _x
3	Co ₃ Ni ₁ O _x	Co ₃ Ni ₁ O _x	Co _{3.36} Ni ₁ O _x
4	Co ₅ Ni ₁ O _x	Co ₅ Ni ₁ O _x	Co _{5.21} Ni ₁ O _x
5	Co ₁ Ni ₃ O _x	Co ₁ Ni ₃ O _x	Co ₁ Ni _{3.12} O _x
6	Co ₁ Ni ₅ O _x	Co ₁ Ni ₅ O _x	Co ₁ Ni _{5.08} O _x

^aCalculated from the feed amount of precursor salts.

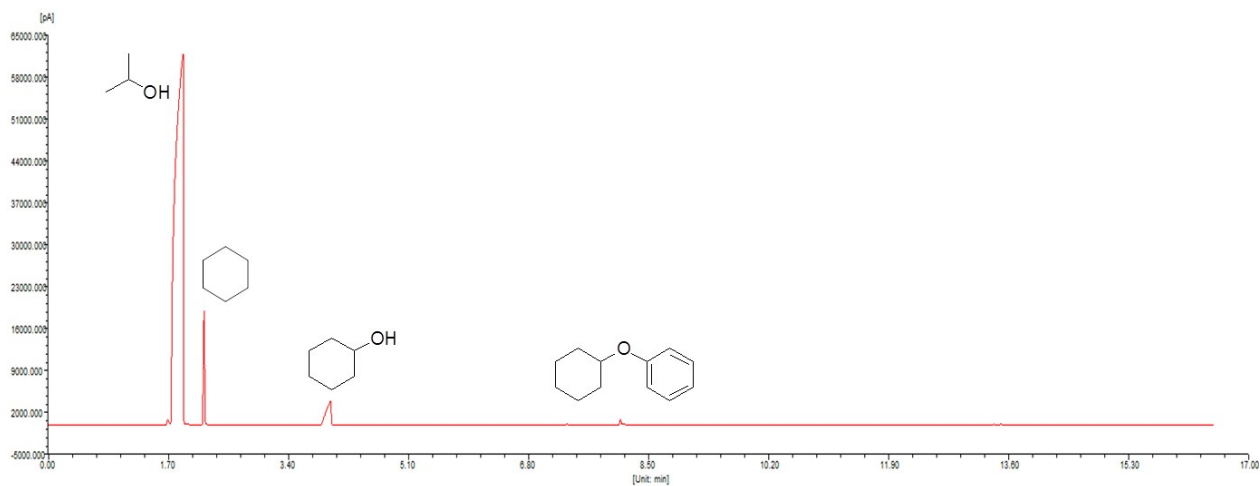


Figure S1. GC analysis diagram of hydrogenolysis products of diphenyl ether. (Table 1, entry 5).

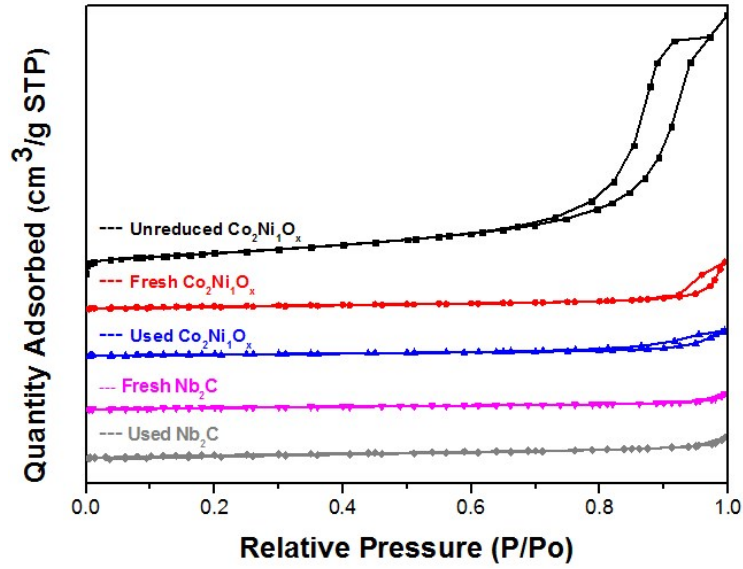


Figure S2. N₂ adsorption/desorption isotherms of catalysts.

Table S3. The analysis results of N₂ adsorption/desorption isotherms for catalysts.

Catalysts	BET surface area (m ² /g)	Pore size (nm)	Pore volume (cm ³ /g)
Unreduced Co ₂ Ni ₁ O _x	69	14	0.22
Co ₂ Ni ₁ O _x	12	16	0.04
Used Co ₂ Ni ₁ O _x	9	15	0.03
Nb ₂ C MXene	9	7	0.01
Used Nb ₂ C MXene	11	12	0.02

^aObtained from the BJH method.

Table S4. Surface elemental concentrations determined by XPS.

Entry	Catalyst	Co 2p (%)			Ni 2p (%)		O 1s (%)			Co (%)	Ni (%)	O (%)	C (%)
		Co ⁰	Co ²⁺	Co ³⁺	Ni ⁰	Ni ²⁺	O-H	V _o	O-M				
1	Co ₅ Ni ₁ O _x	22	29	49	5	95	45	40	15	27	5	47	21
2	Co ₂ Ni ₁ O _x	18	25	57	14	86	42	46	12	15	7	46	32
3	Co ₁ Ni ₃ O _x	20	28	52	16	84	49	32	19	6	18	42	34
4	Co ₁ Ni ₅ O _x	17	29	54	21	79	42	38	20	4	20	35	41
5	Used Co ₂ Ni ₁ O _x	16	37	48	14	86	46	38	16	13	6	41	40

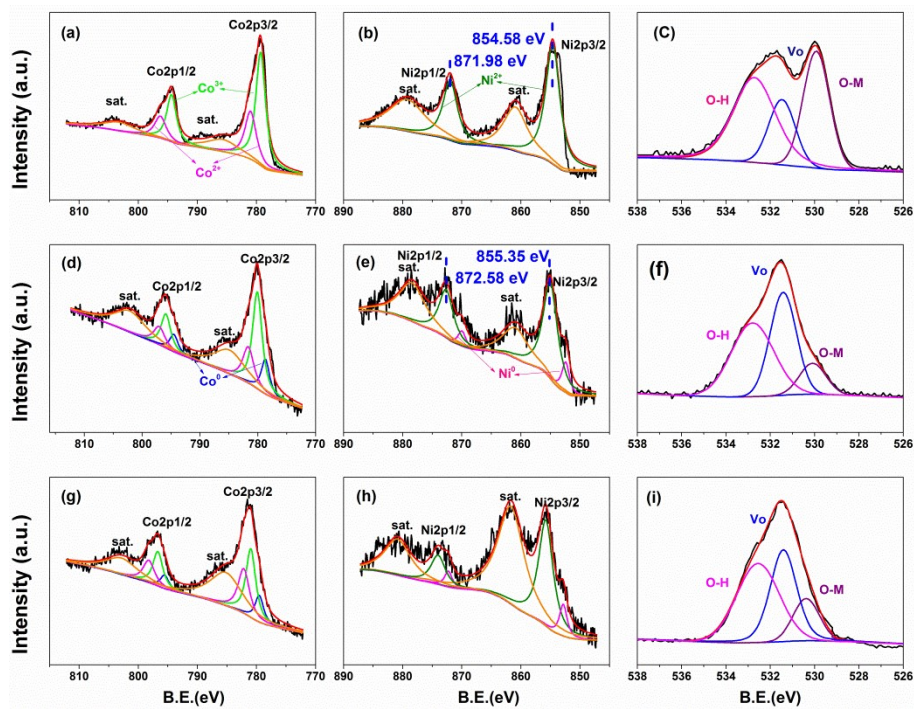


Figure S3. XPS spectra of the unreduced $\text{Co}_2\text{Ni}_1\text{O}_x$ (a, Co 2p; b, Ni 2p; c, O 1s), the fresh $\text{Co}_2\text{Ni}_1\text{O}_x$ (d, Co 2p; e, Ni 2p; f, O 1s), and the used $\text{Co}_2\text{Ni}_1\text{O}_x$ (g, Co 2p; h, Ni 2p; i, O 1s), respectively.

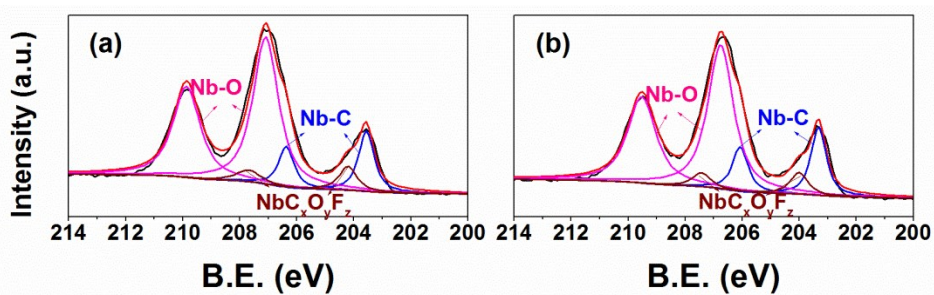


Figure S4. XPS spectra of the fresh (a, Nb 3d) and the used (b, Nb 3d) Nb_2C MXene.

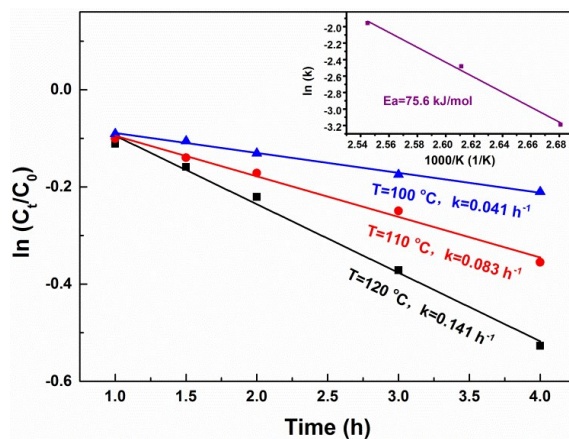


Figure S5. Kinetic studies of the hydrogenolysis of DPE. Reaction condition: $\text{Co}_2\text{Ni}_1\text{O}_x$ 20 mg, Nb_2C 20 mg, DPE 0.5 mmol, isopropanol 2 mL and H_2 5 bar.

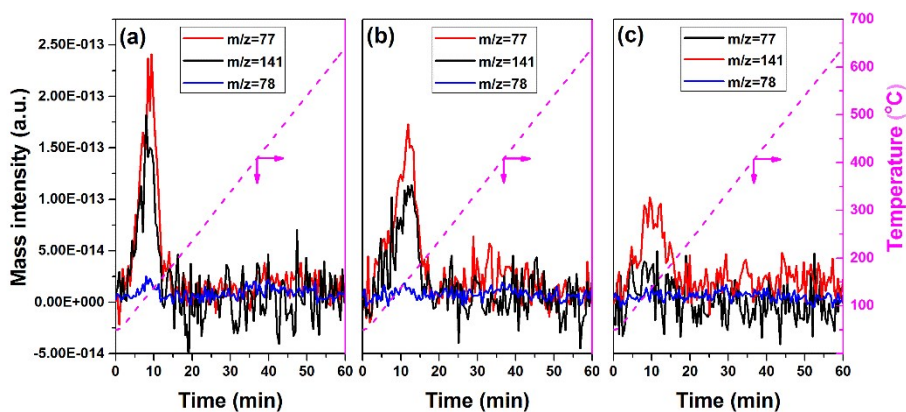


Figure S6. The results of DPE-TPD-Mass by using the same amount (a, $\text{Co}_2\text{Ni}_1\text{O}_x$; b, $\text{Co}_2\text{Ni}_1\text{O}_x+\text{Nb}_2\text{O}_5$; c, $\text{Co}_2\text{Ni}_1\text{O}_x+\text{Nb}_2\text{C}$).

Reference

- [1] S. Yang, X. Lu, H. Yao, J. Xin, J. Xu, Y. Kang, S. Zhang. Efficient hydrodeoxygenation of lignin-derived phenols and dimeric ethers with synergistic [Bmim]PF₆-Ru/SBA-15 catalysis under acid free conditions. *Green Chem.*, 2019, 21, 597-605.
- [2] H. Wu, J. Song, C. Xie, C. Wu, C. Chen, B. Han. Efficient and Mild Transfer Hydrogenolytic Cleavage of Aromatic Ether Bonds in Lignin-Derived Compounds over Ru/C. *ACS Sustain. Chem. Eng.*, 2018, 6, 2872-2877
- [3] H. Zeng, D. Cao, Z. Qiu, C. Li. Palladium-Catalyzed Formal Cross-Coupling of Diaryl Ethers with Amines: Slicing the 4–O–5 Linkage in Lignin Models. *Angew. Chem. Int. Ed.*, 2018, 57, 3752-3757.
- [4] L. Chen, C. Fink, Z. Fei, P. J. Dyson, G. Laurency. An efficient Pt nanoparticle–ionic liquid system for the hydrodeoxygenation of bio-derived phenols under mild conditions. *Green Chem.*, 2017, 19, 5435-5441.
- [5] C. Zhao, J. A. Lercher. Selective hydrodeoxygenation of lignin-derived phenolic monomers and dimers to cycloalkanes on Pd/C and HZSM-5 catalysts. *ChemCatChem*, 2012, 4, 64-68.
- [6] C. A. Scaldaferrri, P. Warakunwit, V. M. Pasa, D. E. Resasco. C–O cleavage of diphenyl ether followed by C–C coupling reactions over hydrophobized Pd/HY catalysts. *Appl. Catal. B-Environ.*, 2019, 259, 118081.
- [7] M. Wang, O. Y. Gutierrez, D. M. Camaioni, J. A. Lercher. Palladium-catalyzed reductive insertion of alcohols into aryl ether bonds. *Angew. Chem. Int. Ed.*, 2018, 130, 3747-3751.
- [8] M. Guo, J. Peng, Q. Yang, C. Li. Highly active and selective RuPd bimetallic NPs for the cleavage of the diphenyl ether C–O bond. *ACS Catal.*, 2018, 8, 11174-11183.
- [9] S. Bulut, S. Siankevich, A. P. Muyden, D. T. Alexander, G. Savoglidis, J. Zhang, P. J. Dyson. Efficient cleavage of aryl ether C–O linkages by Rh–Ni and Ru–Ni nanoscale catalysts operating in water. *Chem. Sci.*, 2018, 9, 5530-5535.
- [10] H. Xu, K. Wang, H. Zhang, L. Hao, J. Xu, Z. Liu. Ionic liquid modified montmorillonite-supported Ru nanoparticles: highly efficient heterogeneous catalysts for the hydrodeoxygenation of phenolic compounds to cycloalkanes. *Catal. Sci. Technol.*, 2014, 4,

2658-2663.

- [11] H. Konnerth, J. Zhang, D. Ma, M. H. Precht, N. Yan. Base promoted hydrogenolysis of lignin model compounds and organosolv lignin over metal catalysts in water. *Chem. Engin. Sci.*, 2015,123, 155-163.
- [12] F. Mauriello, E. Paone, R. Pietropaolo, A. M. Balu, R. Luque. Catalytic transfer hydrogenolysis of lignin-derived aromatic ethers promoted by bimetallic Pd/Ni systems. *ACS Sustain. Chem. Eng.*, 2018, 6, 9269-9276.
- [13] L. Zhang, Y. Wang, L. Zhang, Z. Chi, S. Wan. Hydrogenolysis of aryl ether bond over heterogeneous co-based catalyst. *Ind. Eng. Chem. Res.*, 2020, 59, 17357-17364.
- [14] L. Zhang, Y. Wang, B. Zhang, S. Wang, J. Lin, Y. Wang. Selective hydrogenolysis of aryl ether bond over Ru-Fe bimetallic catalyst. *Catal. Today*, 2020, . doi:10.1016/j.cattod.2020.04.030.
- [15] M. Zaheer, J. Hermannsdorfer, W. P. Kretschmer, G. Motz, R. Kempe. Robust heterogeneous nickel catalysts with tailored porosity for the selective hydrogenolysis of aryl ethers. *ChemCatchem*, 2014, 6, 91-95.
- [16] V. Stavila, R. Parthasarathi, R. W. Davis, F. E. Gabaly, K. L. Sale, B. A. Simmons, M. D. Allendorf. MOF-based catalysts for selective hydrogenolysis of carbon–oxygen ether bonds. *ACS Catal.*, 2016, 6, 55-59.
- [17] M. Wang, Y. Zhao, D. Mei, R. M. Bullock, O. Y. Gutierrez, D. M. Camaioni, J. A. Lercher. The critical role of reductive steps in the Nickel-catalyzed hydrogenolysis and hydrolysis of aryl ether C–O Bonds. *Angew. Chem. Int. Ed.*, 2020, 59, 1445-1449.
- [18] A. G. Sergeev, J. F. Hartwig. Selective, Nickel-catalyzed hydrogenolysis of aryl ethers. *Science*, 2011, 332, 439-443.
- [19] X. Si, Y. Zhao, Q. Song, J. Cao, R. Wang, X. Wei. Hydrogenolysis of lignin-derived aryl ethers to monomers over a MOF-derived Ni/N–C catalyst. *React. Chem. Eng.*, 2020, 5, 886-895.
- [20] Q. Song, Y. Zhao, F. Wu, G. Li, X. Fan, R. Wang, J. Cao, X. Wei. Selective hydrogenolysis of lignin-derived aryl ethers over Co/C@N Catalysts. *Renew. Energ.*, 2020, 148, 729-738.