Supporting Information

Selective hydrogenation of dimethyl terephthalate over potassium-modified Ni/SiO₂ catalyst

Han Xiao,[a],§ Chao Zhang,[a],§ Jiaojiao Zhao,[b],* Zhaohui Zheng, [c] Yuehui Li [b],*

*a*School of Chemical Engineering, Guizhou Minzu University, Guiyang 550025, PR China

*b*State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics (LICP), Chinese Academy of Sciences, Lanzhou 730000, PR China

*c*College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266000, PR China

§These two authors contributed equally.

* To whom correspondence should be addressed.

EXPERIMENTAL SECTION

Catalyst Characterization

The X-ray diffraction (XRD) patterns of the samples were obtained on a SmartLab 9KW powder diffractometer (Cu Kα radiation, λ= 1.5406 Å) with a scanning angle (2θ) ranging from 10 to 90°. Based on the Ni (111) diffraction peak, the average particle size was calculated using the jade software based on the Scherrer equation.

$$D=k\lambda/(\beta\cos\theta)$$

where k (k=0.89) is the Scherrer constant, β is the full width at half of the maximum intensity (FWHM), and θ denotes the diffraction angle.

N_2 physical adsorption/desorption measurement was carried out at liquid nitrogen temperature on a Micromeritics 2020 instrument. Samples were pre-degassed at 200 ℃ for about 3 h to remove water and other physically adsorbed species. The specific surface area was determined by the Brunauer-Emmett-Teller (BET) method. The pore size was obtained using the desorption isotherm through the Barrett-Joyner-Halenda (BJH) method.

The element contents of Ni and K were determined with an ICP-mass spectrometer (Shimadzu 2030). Calcined samples were used, and a typical procedure was as follows: 10 mg samples were fully dissolved in 10 ml of aqua regia (HCl: HNO_3=3:1, V: V), 10/100 times were diluted, and then measured with Shimadzu 2030 ICP-MS.

Transmission electron microscopy (TEM) observations were carried out on an FEI Talos 200A transmission electron microscope.

The temperature-programmed reduction (TPR) and temperature-programmed desorption (TPD) profiles of the samples were both recorded using a Micromeritics ChemiSorb 2920 with a thermal conductivity detector (TCD). For the H_2-TPR studies, the sample (100 mg) was placed in a quartz U-tube reactor and was pretreated under flowing argon at 400 ℃ for 30min to remove traces of water. Then, the TPR profile was assessed in a stream of H_2/Ar (1:9, v/v; 50 mL min^{-1} total flow) with a heating rate of 5 ℃ min^{-1} from 50 to 800 ℃. The silver oxide was chosen as a standing sample to

calibrate the TCD signal and the reducibility of each catalyst was calculated based on the hydrogen consumption. For the NH_3-TPD process, the sample (200 mg) was first sealed and reduced in the reactor in H_2/Ar (50 mL min^{-1}) at 550 °C for 3 h. Subsequently, the reduced sample was purged with Ar at 550 °C for 30 min to remove the excess hydrogen. Then the sample was cooled to 50 °C and NH_3 (10% NH_3-90%Ar) was absorbed for 60 min. Finally, a stream of Ar (50 mL min^{-1}) was introduced to perform the TPD measurement with a temperature ramp of 10 °C min^{-1} from 50 to 600 °C. For the H_2-TPD process, the sample (200 mg) was first sealed and reduced in the reactor in H_2/Ar (50 mL min^{-1}) at 550 °C for 3 h. Subsequently, the reduced sample was purged with Ar at 550 °C for 30 min to remove the excess hydrogen. Then the sample was cooled to 50 °C and H_2 (10% H_2-90%Ar) was reabsorbed for 60 min. Finally, a stream of Ar (50 mL min^{-1}) was introduced to perform the TPD measurement with a temperature ramp of 10 °C min^{-1} from 50 to 800 °C. The dispersion of Ni was calculated based on the molar of chemisorbed H_2 using the following simplified equation:[31]

$$D_i(\%) = \frac{A_i \times m(Ag2O) \times M(Ni) \times SF}{A(Ag2O) \times M(Ag2O) \times m_i \times P_i \times R_i} \times 100$$

where Ag_2O is used as a standard, A_i and $A(Ag_2O)$ are the desorption area of chemisorbed H_2 in the TPD procedure; m_i and $m(Ag2O)$ denote the weight of the sample (g); $M(Ni)$ and $M(Ag)$ are the molecular weight of Ni(58.693) and Ag_2O(231.730), respectively; P_i is the weight fraction of Ni in the sample as determined by ICP; R_i is the reduction degree of Ni; and SF is the stoichiometric factor (Ni:H molar ratio in the chemisorption) which is taken as 1.

X-ray photoelectron spectroscopy (XPS) was performed on an Axis Supra+ (Shimadzu Company, JAPAN) with a vacuum sample disk. An X-ray photoelectron spectrometer operated at a pressure of 2×10^{-9} Pa using monochromatized Al $K\alpha$ radiation (1486.6 eV) energy scans ranges from 1100 to -10 eV. The extrinsic C (C 1s =284.6 eV) was used for calibration. Typical reduction conditions of samples are as follows: Samples were reduced in a tube furnace in pure H_2 flow (30 mL/min) for 4 h at 550 °C. To avoid being oxidized, the quartz tube was equipped with globes valves at both ends, after the reduction procedure, the sample was cooled to room temperature in H_2, then the quartz

tube was transferred to the glove box with both ends sealed by globe valves, the sample was transferred to a vacuum sample disk, finally, the disk was transferred to the Axis Supra+ (Shimadzu Company, JAPAN) X-ray photoelectron spectrometer.

Evaluation of the Catalytic Performance

Typically, the catalytic experiment was conducted in 4 mL glass vials. The vials were filled with 50 mg catalyst, 2 mL isopropanol, 0.1 g dimethyl terephthalate (DMT), and a stirring bar in sequence, and closed with a septum cap. To allow gas exchange, a needle was pierced through a septum. The vials were placed on a steel plate in a 250 mL steel autoclave (Microreactor, Yanzheng Instrument Ltd. Shanghai). The closed reactor was washed three times with H_2 and filled with 4 MPa H_2. After stirring for 15 min at room temperature, the reaction was performed for 4 h under different temperatures while stirring (500 rpm) the reaction mixtures. After the reaction was completed, the reactor was cooled to room temperature and depressurized. The vials were removed from the autoclave, and biphenyl was added as a standard to the reaction solutions. After using centrifugation to remove the solid catalyst, the liquid products were quantitatively analyzed using a gas chromatograph (Agilent GC 7890A) equipped with a flame ionization detector (FID).

$$\text{conversion (\%)} = \frac{\text{moles of reactant converted}}{\text{moles of reactant in feed}} * 100$$

$$\text{product selectivity (\%)} = \frac{\text{moles of product formed}}{\text{moles of reactant converted}} * 100$$
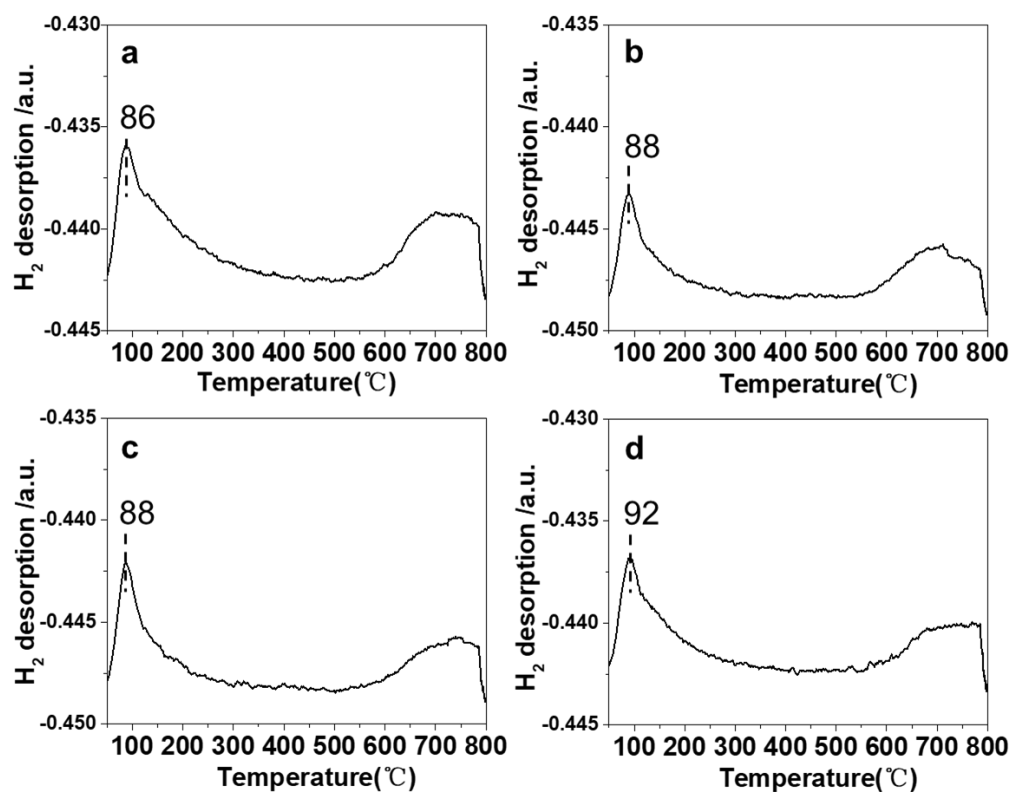
Figure S1. H_2-TPD profiles of (a) Ni/SiO$_2$; (b) KVO$_3$-Ni/SiO$_2$; (c) KOH-Ni/SiO$_2$; (d) KF-Ni/SiO$_2$.

Table S1 The reducibility, and dispersion of catalysts.

Catalysts (M-Ni/SiO$_2$) [a]	Area	Mass/g	Reducibility % [b]	Dispersion % [c]	Temperature Range/ ℃
Ag$_2$O	1.6366	0.0154	100		
Ni/SiO$_2$	3.5568	0.1000	58.87		200-750
KVO$_3$-Ni/SiO$_2$	4.1821	0.1001	66.83		200-750
KOH-Ni/SiO$_2$	3.7755	0.1004	65.42		200-750
KF-Ni/SiO$_2$	3.9954	0.1005	68.66		200-750
Ni/SiO$_2$	0.5734	0.2014		8.41	50-300
KVO$_3$-Ni/SiO$_2$	0.3595	0.2042		4.21	50-300
KOH-Ni/SiO$_2$	0.4217	0.2029		5.82	50-300
KF-Ni/SiO$_2$	0.8645	0.2007		10.84	50-300

[a] M stands for potassium dopant. [b] measured by H_2-TPR. [c] measured by H_2-TPD.

Figure S2. XRD patterns of catalysts reduced at 400 °C for 4 h. From the bottom to top: (a) Ni/SiO₂; (b) KVO₃-Ni/SiO₂; (c) KOH-Ni/SiO₂; (d) KF-Ni/SiO₂.

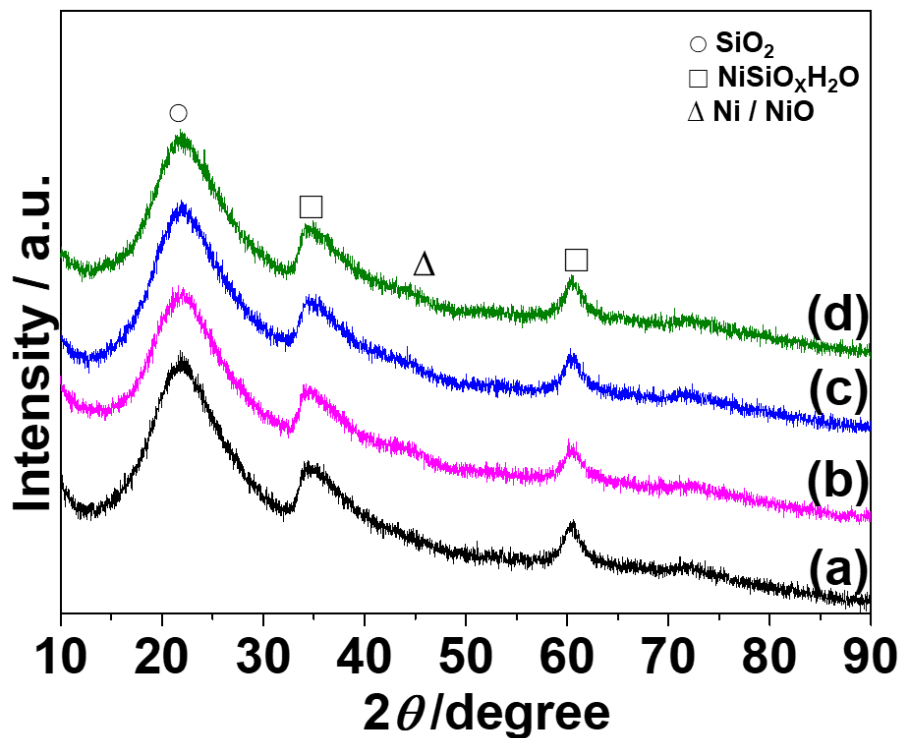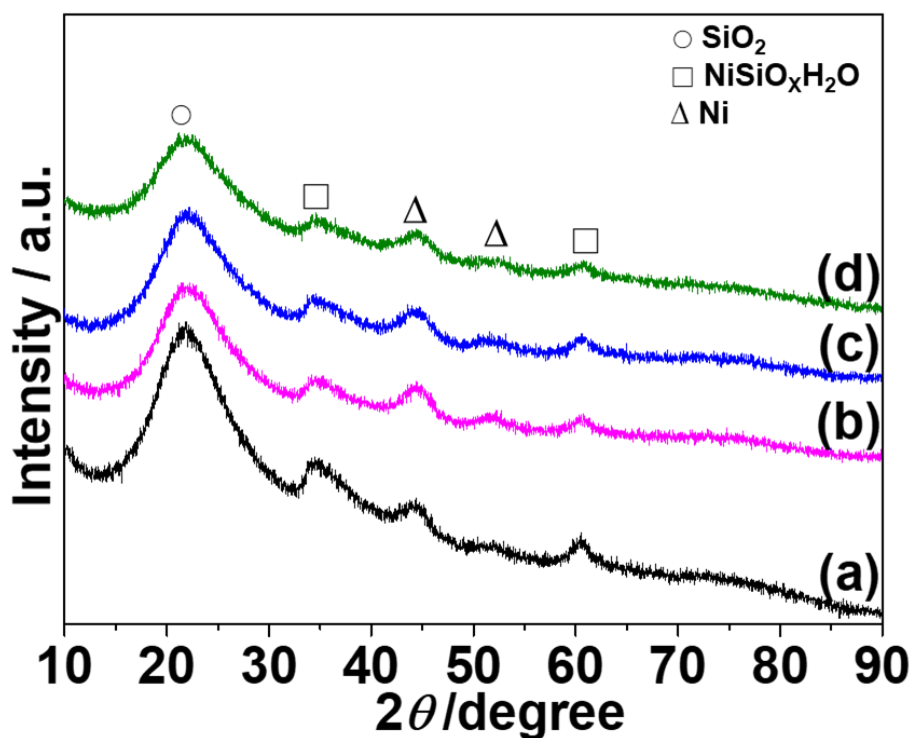

Figure S3. XRD patterns of catalysts reduced at 500 °C for 4 h. From the bottom to top: (a) Ni/SiO₂; (b) KVO₃-Ni/SiO₂; (c) KOH-Ni/SiO₂; (d) KF-Ni/SiO₂.

Table S2 The deconvoluted area and fraction of Ni species in XPS results (Figure 5).

Catalysts (M-Ni/SiO$_2$)	Area					Ni^0/ (Ni^0+Ni^{2+})	Ni^0/Ni^{2+} (NiO)	Ni^0/Ni^{2+} (phyllosilicates)
	Ni^0	Ni^{2+} /NiO	Ni^{2+} /1:1Ni-PSi	Ni^{2+} /2:1Ni-PSi	Ni^{2+} $_{Sat.}$			
Ni/SiO$_2$	20389	28855	20032	6666	5181	0.27	0.71	0.76
KVO$_3$-Ni/SiO$_2$	21150	25067	13940	6580	3418	0.35	0.84	1.03
KOH-Ni/SiO$_2$	17365	25193	12916	5958	3188	0.31	0.69	0.92
KF-Ni/SiO$_2$	16224	21288	17412	5395	4791	0.30	0.76	0.71

Table S3 The detailed DMT conversion and selectivity of the products (Figure 6).

Catalysts (M-Ni/SiO$_2$) [a]	DMT/Conv.%	DMCD/S%	MMB/S%	BDCAMMEE/S%	MMCHC/S%
Ni/SiO$_2$ [b]	0	0	0	0	0
KVO$_3$-Ni/SiO$_2$[b]	0	0	0	0	0
KOH-Ni/SiO$_2$[b]	0	0	0	0	0
KF-Ni/SiO$_2$[b]	0	0	0	0	0
Ni/SiO$_2$[c]	25	81	9	10	0
KVO$_3$-Ni/SiO$_2$[c]	13	74	4	22	0
KOH-Ni/SiO$_2$[c]	20	82	4	14	0
KF-Ni/SiO$_2$[c]	21	77	2	21	0
Ni/SiO$_2$[d]	38	87	12	1	0
KVO$_3$-Ni/SiO$_2$[d]	54	94	6	0	0
KOH-Ni/SiO$_2$[d]	68	95	5	0	0
KF-Ni/SiO$_2$[d]	98	95	5	0	0
Ni/SiO$_2$[e]	64	84	16	0	0
KVO$_3$-Ni/SiO$_2$[e]	78	93	7	0	0
KOH-Ni/SiO$_2$[e]	89	94	6	0	0
KF-Ni/SiO$_2$[e]	99	93	6	0	1

[a] M stands for potassium dopant. [b] The catalyst was calcined at 450 ºC for 4 h. [c] The catalyst was reduced at 400 ºC for 4 h. [d] The catalyst was reduced at 500 ºC for 4 h. [e] The catalyst was reduced at 550 ºC for 4 h. Reaction conditions: catalyst, 50 mg; DMT, 0.1 g; IPA, 2 mL; the initial pressure of H$_2$, 5MPa; reaction temperature, 90 ºC; reaction time, 4 h.

Table S4 The detailed DMT conversion and selectivity of the products (Figure 7).

Entry	Catalysts (M-Ni/SiO$_2$) [a]	DMT/Conv.%	DMCD/S%	MMB/S%	BDCAMMEE/S%	MMCHC/S%
1	Ni/SiO$_2$[b]	30	87	13	0	0
2	KVO$_3$-Ni/SiO$_2$[b]	30	95	5	0	0
3	KOH-Ni/SiO$_2$[b]	49	97	3	0	0
4	KF-Ni/SiO$_2$[b]	64	97	3	0	0
5	Ni/SiO$_2$[c]	41	83	15	1	0
6	KVO$_3$-Ni/SiO$_2$[c]	57	93	6	1	0
7	KOH-Ni/SiO$_2$[c]	81	95	4	1	0
8	KF-Ni/SiO$_2$[c]	95	96	4	0	0
9	Ni/SiO$_2$[d]	64	84	16	0	0
10	KVO$_3$-Ni/SiO$_2$[d]	78	93	7	0	0
11	KOH-Ni/SiO$_2$[d]	89	94	6	0	0
12	KF-Ni/SiO$_2$[d]	99	93	6	0	1
13	Ni/SiO$_2$[e]	99	84	13	0	3
14	KVO$_3$-Ni/SiO$_2$[e]	99	90	8	0	2
15	KOH-Ni/SiO$_2$[e]	100	92	0	0	8
16	KF-Ni/SiO$_2$[e]	100	93	0	0	7

[a] M stands for potassium dopant. [b] Reaction temperature, 80 ºC. [c] Reaction temperature, 90 ºC. [d] Reaction temperature, 100 ºC. [e]Reaction temperature, 110 ºC. All the catalysts were reduced at 550 ºC for 4 h. Reaction conditions: catalyst, 50 mg; DMT, 0.1 g; IPA, 2 mL; the initial pressure of H$_2$, 5MPa; reaction time, 4 h.