

# Rational design of alkali-resistant catalysts for selective reduction of NO with NH<sub>3</sub>†

Chao Li,<sup>a</sup> Zhiwei Huang,<sup>b</sup> Xiaona Liu,<sup>a</sup> Junxiao Chen,<sup>a</sup> Weiye Qu,<sup>a</sup> Xiaoming Jiang,<sup>c</sup>  
Hu Wang,<sup>c</sup> Zhen Ma,<sup>a</sup> Xingfu Tang,<sup>a</sup> and Yaxin Chen<sup>\*a</sup>

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## Experimental Section

### 1.1. Catalyst syntheses

HWO was prepared by a hydrothermal method according to our previous report.<sup>1</sup> Fe<sub>2</sub>O<sub>3</sub> was prepared by a co-precipitation method. 25 mmol FeSO<sub>4</sub>·7H<sub>2</sub>O and 50 mmol FeCl<sub>3</sub>·6H<sub>2</sub>O were synchronously added into 300 mL ammonia solution (1 mol L<sup>-1</sup>). The as-synthesized slurry was washed by distilled water, dried at 105 °C overnight, and calcinated at 250 °C for 3 h to obtain Fe<sub>2</sub>O<sub>3</sub>. m-WO<sub>3</sub> (monoclinic WO<sub>3</sub>) was prepared by decomposition of (NH<sub>4</sub>)<sub>10</sub>W<sub>12</sub>O<sub>41</sub> at 500 °C for 5 h. Fe<sub>2</sub>O<sub>3</sub>/HWO, Fe<sub>2</sub>O<sub>3</sub>/m-WO<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> were prepared by loading certain amounts of Fe<sub>2</sub>O<sub>3</sub> (0.10 g) onto HWO, m-WO<sub>3</sub>, and TiO<sub>2</sub> (1.00 g) dispersed in distilled water. After drying at 80 °C with stirring, the solid was calcinated at 350 °C for 4 h to obtain the final product. The V<sub>2</sub>O<sub>5</sub>/WO<sub>3</sub>-TiO<sub>2</sub> catalyst was purchased from Shandong Guantong Catalyst Co., Ltd.

K<sup>+</sup> loaded catalysts was prepared by wet impregnation with K<sub>2</sub>SO<sub>4</sub>. The obtained K<sub>2</sub>SO<sub>4</sub>-Fe<sub>2</sub>O<sub>3</sub>/HWO was annealed at 350 °C for 12 h to simulate the aging process in stack gases. The annealed catalyst is denoted as Fe<sub>2</sub>O<sub>3</sub>/K<sub>in</sub>HWO. The K<sup>+</sup> loading amount is 200 μmol/g.

### 1.2. Synchrony X-ray diffraction (SXRD)

Synchrony X-ray diffraction (SXRD) was performed at BL14B1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF). The X-ray wavelength was 0.6883 Å. Refinement was conducted of the collected data using Rietica v1.77 program.

### 1.3. X-ray adsorption spectra (XAS)

X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra at the K K-edge were measured at BL4B7A of the Beijing Synchrotron Radiation Facility (BSRF) with the electron beam energy of 2.21 GeV and a ring current of 300-450 mA. XANES and EXAFS spectra at Fe or W K-edge were obtained at BL14W1 of the SSRF with the electron beam energy of 3.5 GeV and a ring current of 200-300 mA. Data analyses were conducted by using the IFEFFIT 1.2.11 software package.

#### 1.4. Catalyst evaluation

SCR activity measurement was performed in a fixed-bed quartz reactor (i.d. = 8 mm) under atmospheric pressure. 0.500 g sample (40-60 mesh) was used for each run. The feed gas was composed of 1,000 ppm NO, 1,000 ppm NH<sub>3</sub>, 3.0 vol% O<sub>2</sub>, 200 ppm SO<sub>2</sub> (when used), 5 vol% H<sub>2</sub>O (when used), and balanced N<sub>2</sub>. The total flow rate was 500 mL min<sup>-1</sup>. The concentrations of NH<sub>3</sub>, NO, N<sub>2</sub>O and NO<sub>2</sub> in the inlet and outlet gas were measured by a FTIR spectrometer (Thermo Scientific, Antaris IGS Analyzer). The NO conversion and N<sub>2</sub> selectivity were determined as follows:

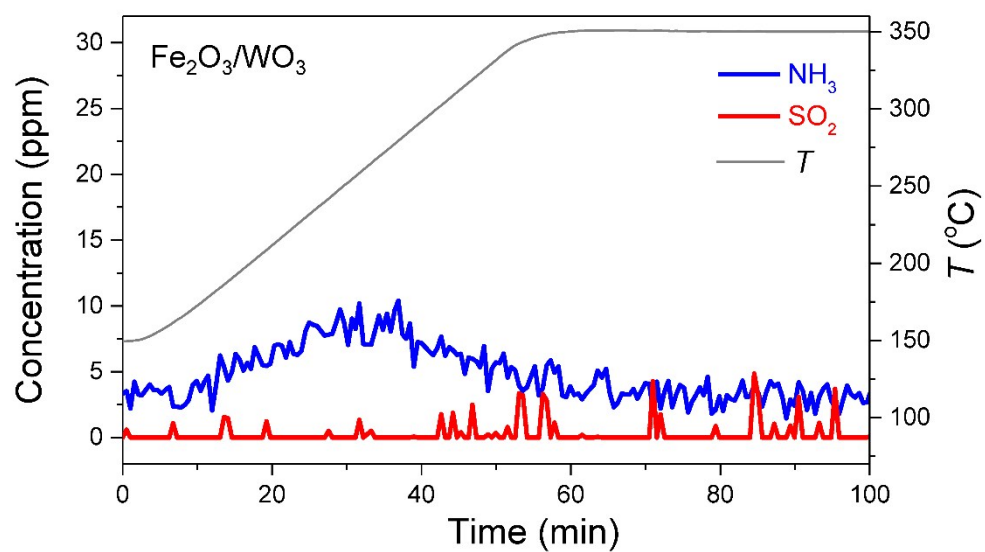
$$\text{NO conversion} = \frac{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}}{[\text{NO}]_{\text{in}}} \times 100\%$$

$$\text{N}_2 \text{ selectivity} = 1 - \frac{[\text{NO}_2]_{\text{out}} + 2[\text{N}_2\text{O}]_{\text{out}}}{[\text{NO}]_{\text{in}} + [\text{NH}_3]_{\text{in}} - [\text{NO}]_{\text{out}} - [\text{NH}_3]_{\text{out}}} \times 100\%$$

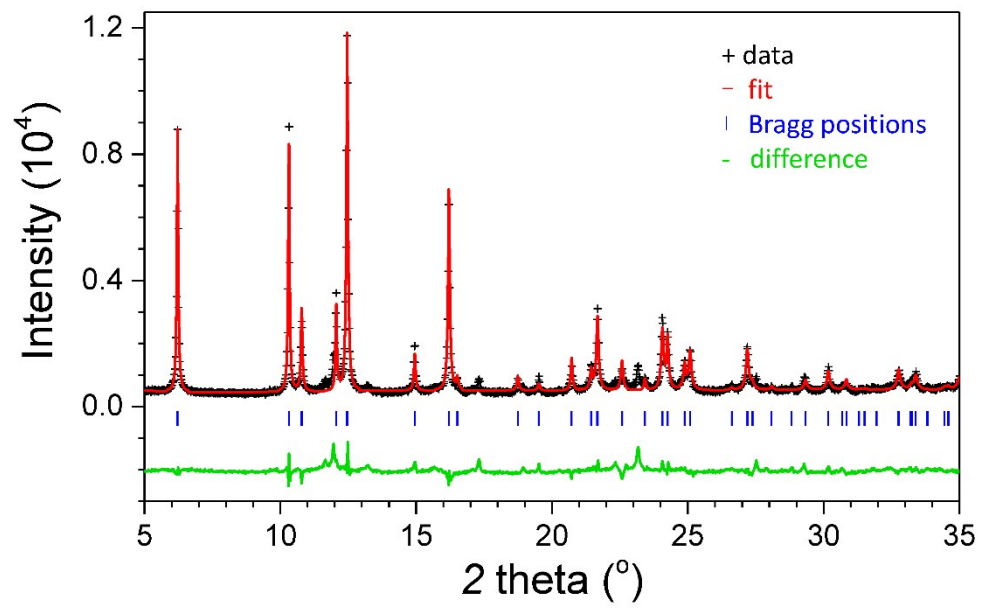
#### 1.5. Temperature-programmed decomposition (TPDC) of K<sub>2</sub>SO<sub>4</sub>

The TPDC experiment was conducted in the above reactor system. 0.500 g sample with deposited K<sub>2</sub>SO<sub>4</sub> (K<sup>+</sup> loading amount = 200 μmol g<sub>cat</sub><sup>-1</sup>) was pretreated at 150 °C for 1 h under N<sub>2</sub> flow of 500 mL min<sup>-1</sup>. The sample was cooled down to 100 °C, then heated to 350 °C at a ramp rate of 5 °C min<sup>-1</sup>. The outlet SO<sub>2</sub> and NH<sub>3</sub> was monitored by FTIR spectrometer (Thermo Scientific, Antaris IGS Analyzer).

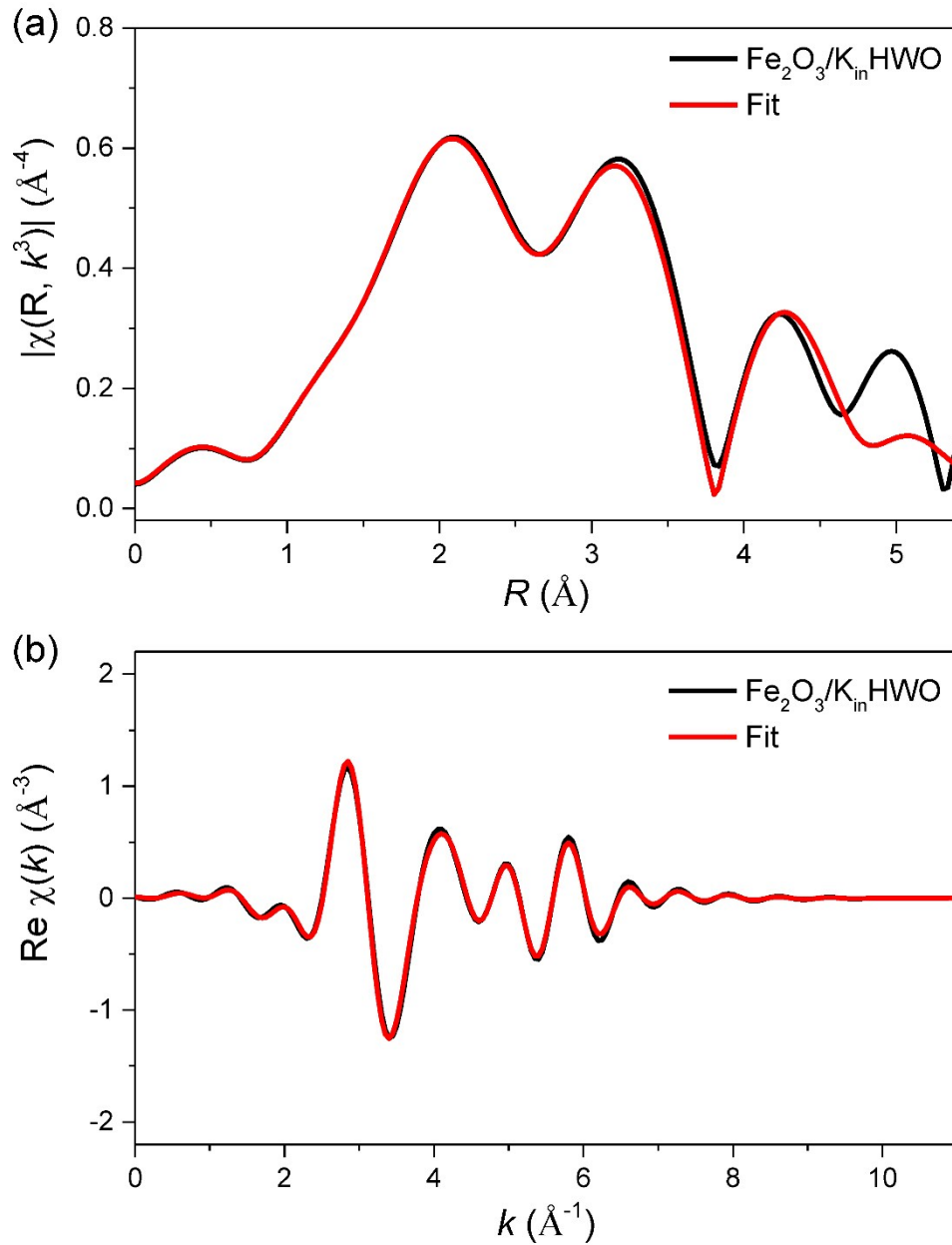
## Figures and Tables



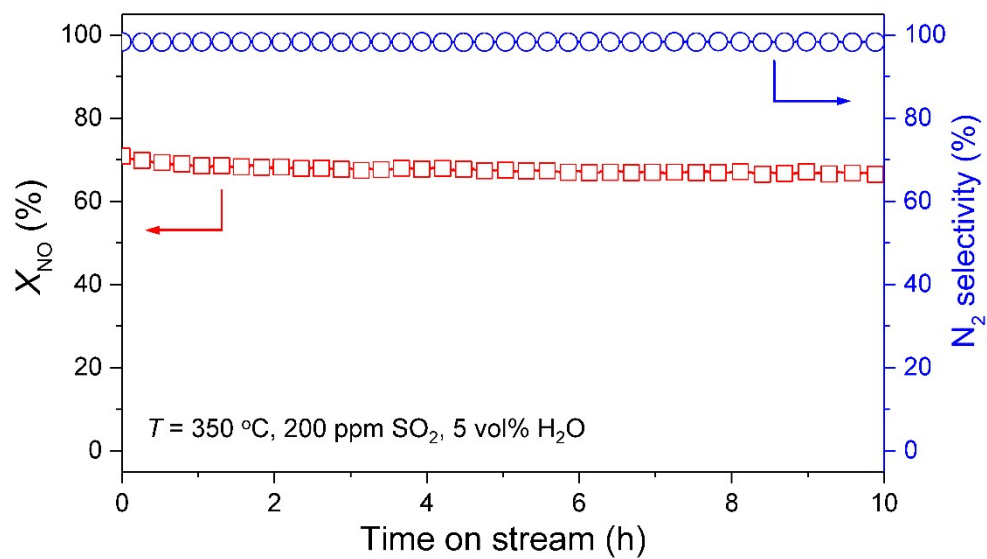
**Fig. S1.** Temperature-programmed decomposition profiles of  $\text{Fe}_2\text{O}_3/\text{WO}_3$  with deposited  $\text{K}_2\text{SO}_4$  ( $\text{K}^+$  loading amount =  $200 \mu\text{mol g}_{\text{cat}}^{-1}$ ) under  $500 \text{ mL min}^{-1} \text{ N}_2$  flow.



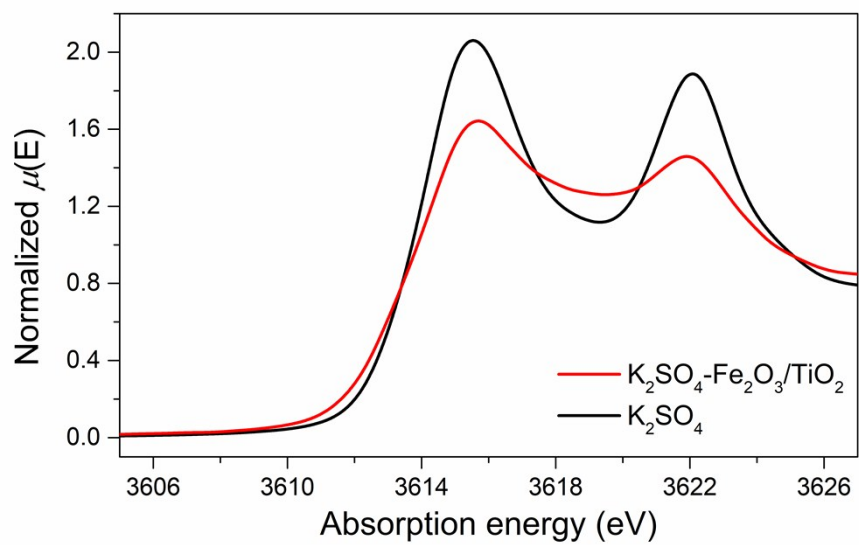
**Fig. S2.** Full-scaled SXRD pattern and the corresponding Rietveld refinement data of Fe<sub>2</sub>O<sub>3</sub>/K<sub>in</sub>HWO.



**Fig. S3.** (a)  $R$ -space ( $\Delta k = 1.6$ - $5.95 \text{ \AA}^{-1}$ ) and (b) inverse FT spectra ( $\Delta r = 1.0$ - $4.7 \text{ \AA}$ ) of  $\text{Fe}_2\text{O}_3/\text{K}_{\text{in}}\text{HWO}$ .



**Fig. S4.**  $X_{\text{NO}}$  and  $\text{N}_2$  selectivity over  $\text{Fe}_2\text{O}_3/\text{HWO}$  with  $\text{K}^+$  loading amount of 200  $\mu\text{mol g}_{\text{cat}}^{-1}$  at 350  $^{\circ}\text{C}$ . Reaction conditions: 1,000 ppm NO, 1,000 ppm  $\text{NH}_3$ , 3.0 vol%  $\text{O}_2$ , 200 ppm  $\text{SO}_2$ , 5 vol%  $\text{H}_2\text{O}$ , and balanced  $\text{N}_2$ . Catalyst mass is 0.500 g. Gas flow rate is 500  $\text{mL min}^{-1}$ .



**Fig. S5.** XANES spectra at the K *K*-edge of  $K_2SO_4$  loaded  $Fe_2O_3/TiO_2$  ( $K^+$  loading amount =  $200 \mu\text{mol g}_{\text{cat}}^{-1}$ ) after annealing at  $350 \text{ }^\circ\text{C}$  (nominated as  $K_2SO_4-Fe_2O_3/TiO_2$ ), together with that of  $K_2SO_4$ .



**Table S1.** K<sup>+</sup> loading amounts, K<sup>+</sup> sources, and data sources of catalysts in Fig. 1.

Catalyst	K <sup>+</sup> loading amount ( $\mu\text{mol g}^{-1}$ )	K <sup>+</sup> source	Data source
HMO	1150	KCl	Reference 2
CeO <sub>2</sub> /TNTs	~590	KNO <sub>3</sub>	Reference 3
V <sub>2</sub> O <sub>5</sub> /HWO	350	K <sub>2</sub> SO <sub>4</sub>	Reference 4
Fe <sub>2</sub> O <sub>3</sub> /HWO			
V <sub>2</sub> O <sub>5</sub> -WO <sub>3</sub> /TiO <sub>2</sub>			
Fe <sub>2</sub> O <sub>3</sub> /TiO <sub>2</sub>	200	K <sub>2</sub> SO <sub>4</sub>	This work
V <sub>2</sub> O <sub>5</sub> /WO <sub>3</sub>			
Fe <sub>2</sub> O <sub>3</sub> /WO <sub>3</sub>			

**Table S2.** NO conversion of pristine catalysts and catalysts with deposited K<sup>+</sup> at 350 °C.

Catalyst	Pristine NO conversion (%)	NO conversion after loading K <sup>+</sup> (%)
Fe <sub>2</sub> O <sub>3</sub> /HWO	92.6%	88.0%
V <sub>2</sub> O <sub>5</sub> -WO <sub>3</sub> /TiO <sub>2</sub>	90.0%	8.0%
Fe <sub>2</sub> O <sub>3</sub> /TiO <sub>2</sub>	47.2%	14.0%
V <sub>2</sub> O <sub>5</sub> /WO <sub>3</sub>	84.1%	8.7%
Fe <sub>2</sub> O <sub>3</sub> /WO <sub>3</sub>	82.8%	3.3%

**Table S3.** Crystallographic data and details of Fe<sub>2</sub>O<sub>3</sub>/K<sub>in</sub>HWO in the data collections and the Rietveld refinements.

Parameters	Crystallographic data
Crystal system	hexagonal
Space group	<i>P6/mmm</i>
$Z^a$	6
$a$ (Å)	7.316
$c$ (Å)	3.825
$V$ (Å <sup>3</sup> )	173.30
$R_p^b$ (%)	8.0
$R_{wp}^c$ (%)	11.4
$R_{exp}^d$ (%)	1.2
$\chi^2^e$	9.8
Wavelength (Å)	0.6883
$2\theta$ range (°)	5-35
$2\theta$ step width (°)	0.02

<sup>a</sup> The number of K<sub>0.04</sub>WO<sub>3</sub> formula units per unit cell

<sup>b</sup> The unweighted profile factor

<sup>c</sup> The weighted profile factor

<sup>d</sup> The expected  $R$  parameter

<sup>e</sup> The goodness of fitting, defined as the square of the ratio of  $R_{wp}/R_{exp}$

**Table S4.** Structure parameters determined by the Rietveld refinement of the SXRD pattern of Fe<sub>2</sub>O<sub>3</sub>/K<sub>in</sub>HWO.

Atoms	<i>x</i>	<i>y</i>	<i>z</i>	Occupation	Isotropic thermal factor
K	0	0	0	0.125	1.5
W	0.5	0	0	1.0	1.9
O1	0.5	0	0.5	1.0	1.1
O2	0.21	0.42	0	1.0	0.2

**Table S5.** Local structure parameters around potassium of Fe<sub>2</sub>O<sub>3</sub>/K<sub>in</sub>HWO estimated by EXAFS analysis at the K *K*-edge.<sup>a</sup>

Shell	CN <sup>b</sup>	R <sup>c</sup> / Å	σ <sup>2d</sup> / Å <sup>2</sup>	ΔE <sub>0</sub> <sup>e</sup> / eV
K-O	6.0	2.63(9)	0.033(9)	-4.686
K-W	6.0	3.67(8)	0.010(5)	-9.506
K-O	12.0	4.01(3)	0.078(8)	11.668

<sup>a</sup> R-factor = 0.00572; R-space fit, Δ*k* = 1.60-5.95 Å<sup>-1</sup>, Δ*r* = 1.0-4.7 Å

<sup>b</sup> The coordination number

<sup>c</sup> The distance between absorber and backscatter atoms

<sup>d</sup> Debye–Waller factor

<sup>e</sup> Energy shift

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