catalysts

Supplementary Materials

DRIFT Study on Promotion Effect of the Keggin Structure over V_2O_5-MoO_3/TiO_2 Catalysts for Low Temperature NH_3-SCR Reaction

Rui Wu [1,†], Ningqiang Zhang [1,†], Lingcong Li [1], Hong He [1,2,*], Liyun Song [1,*] and Wenge Qiu [1]

[1] Laboratory of Catalysis Chemistry and Nanoscience, Department of Chemistry and Chemical Engineering, College of Environmental and Energy Engineering, Beijing University of Technology, Beijing 100124, China; wuruicoco@sina.com (R.W.); zhangningqiang08@163.com (N.Z.); lilingcong1988@163.com (L.L.); qiuwenge@bjut.edu.cn (W.Q.)
[2] Collaborative Innovation Center of Electric Vehicles in Beijing, Beijing 100081, China
* Correspondence: hehong@bjut.edu.cn (H.H.), songly@bjut.edu.cn (L.S.)
† These authors contributed equally.

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1. Characterization

The powder X-ray diffraction (XRD) measurements were carried out on a Bruker D-8 system with Cu radiation (λ=0.15418 nm) at 40 kV and 100 mA. The experiments data were collected in the 2θ range of 10–80° at a step of 0.02 °/0.3 s for determining the crystal structure.

The N_2 adsorption-desorption isotherms were obtained at −196 °C using a Micromeritics ASAP 2020 automated gas sorption system. The specific surface areas of the samples were evaluated from these isotherms by the Brunauer–Emmett–Teller (BET) model (ASAP 2020, Micromeritics). The element of the catalyst was analyzed by X-ray fluorescence (XRF) measurements (Magix PW2403, Netherlands)

Total acidities of the catalysts were investigated by the temperature programmed desorption of ammonia (NH_3-TPD) and sulfur dioxide (SO_2-TPD) on a chemisorption instrument equipped a thermal conductivity detector (TCD) (Quantachrome Chem BET Pulsar TPR/TPD, American). Before the experiment, the catalysts were pretreated in pure He at 400 °C for 60 min. Then the samples were saturated with 5% NH_3/He or SO_2/He at a flow rate of 30 mL/min for about 30 min. Desorption was carried out by heating from 50 to 900 °C with a heating rate of 10 °C/min.

In situ DRIFTS studies were performed on a Nicolet 6700 FTIR spectrometer (Thermo, American) equipped with an in situ cell. The samples were pretreated at 300 °C under a 50 mL/min N_2 for 1 h and cooled down to the desired temperature. In the studies of NH_3 or NO+O_2 adsorption, the background spectra was obtained at 250 °C in a N_2 atmosphere. The reaction conditions were as follows: 500 ppm NO + 5% O_2, 500 ppm NH_3, balance with N_2. The total flow rate of gas mixture was kept at 50 mL/min.

FTIR studies were recorded with a Nicolet 6700 FTIR spectrometer (Thermo, American) using the KBr wafer technique for sample preparation.

In situ Raman spectra were recorded on a high-resolution Raman spectrometer system (Renishaw inVia Reflex) equipped with five laser excitations (785, 633, 532, 325, and 244 nm). The 532-nm line was used for recording the Raman spectra. The samples (ca. 20 mg of loose powder) were loaded in an *in situ* cell with a quartz window, which could be treatments at desired temperatures and gas flows. The samples were heated to 250 °C under N_2 atmosphere at a total flow rate of 50 ml/min for 30 min to remove any adsorbed impurities. Subsequently, 500ppm NO/N_2, 500ppm NH_3/N_2, and 6% O_2 were add to simulate the SCR condition. Finally, the NO, NH_3 and O_2 were cut off and N_2 was purged. During every stage, the spectra were recorded.

2. XRD and Raman results

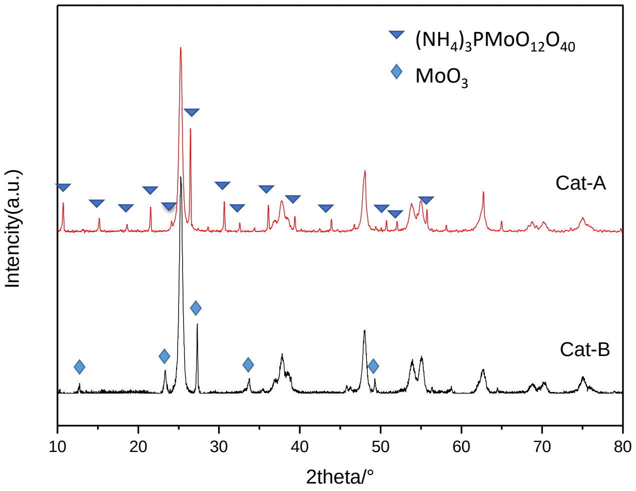

Figure S1. XRD patterns of Cat-A and Cat-B.

The XRD patterns of the samples was shown in Fig.1. All catalysts exhibited the characteristic pattern of TiO_2-anatase peaks (PDF-JCPDS-65-5724) with diffraction lines at 2*θ* =25.2°, 37.7°, 48.1°, 53.8°, 55.0°, 62.7°. On the XRD profile of the Cat-A samples, the peaks at 10.5°、15.5°、26.5°、30.5° could be found, which could be indexed to Keggin-type $(NH_4)_3PMoO_{12}O_{40}$ (PDF-JCPDS-43-0315) [1] and no MoO_3 peaks were observed. For the Cat-B catalysts, the characteristic diffraction peaks at around 11.5°、24.5°、27.5°、34.5° could be assigned to orthorhombic MoO_3 [2].

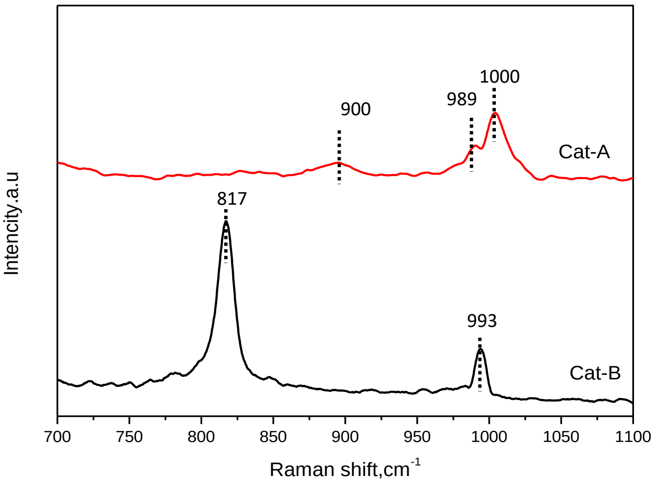

Figure S2. Raman spectra of Cat-A and Cat-B.

The Raman spectra in the range 700-1100 cm^{-1} under ambient condition provides the evidence for different structures. For Cat-A, one can find three intense peaks that could be due to the Keggin anion. The peak at 900 cm^{-1} could be assigned to the vibration of Mo-O-Mo, while peaks at 989 cm^{-1} and 1000 cm^{-1} could be caused by the vibration of Mo-O in Keggin anion [3, 4]. For Cat-B samples, the peaks at 817and 993 cm^{-1} could be attributed to the symmetric stretch of Mo-O-Mo and the vibration of Mo=O, respectively [5, 6]. The results further confirmed that the materials possessed different structures.

Table S1. Compositions and BET surface area of Cat-A and Cat-B.

Catalysts	**Element content (wt. %)**				**S_{BET}(m^2·g)**
	Ti	Mo	P	V	
Cat-A	48.2	11.6	0.4	0.5	53
Cat-B	48.0	11.8	0.4	0.5	52

3. NH_3-TPD results

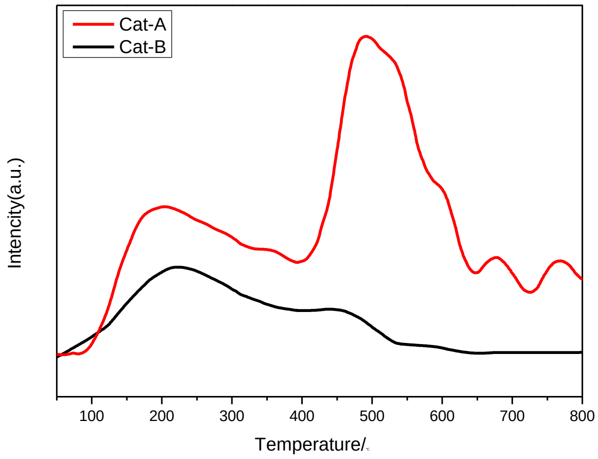

Figure S3 NH_3-TPD profiles of the catalysts.

4. In situ sequential Raman spectra results.

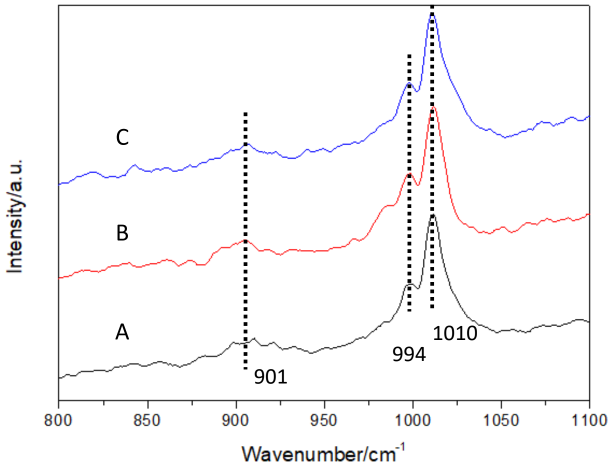

Figure S4 In situ sequential Raman spectra of Cat-A at 250 °C under various atmospheres: (A) the catalyst was treated by N_2; (B) after then, NO+NH_3+O_2 was added; (C) NO+NH_3+O_2 was stopped and the catalyst was treated by N_2 again.

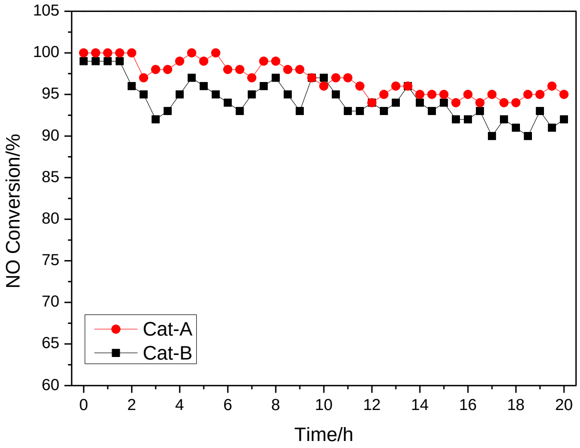

Figure.S5 The time-on-stream stability of the catalysts at 250°C under the conditions: NO 1000ppm, $NH_3/NO=1$, O_2 5%, H_2O 5%, SO_2 350ppm, N_2 balance, and GHSV=40,000 $h^{-1.}$

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