# Relationship between structure and activity of MoO<sub>3</sub>–CeO<sub>2</sub> catalysts on NO removal: influences of acidity and reducibility

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**Supporting Materials** 

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# **Experimental Section**

#### **Catalyst preparation**

The catalysts are prepared by a co-precipitation method. Appropriate amounts of cerium nitrate and ammonium molybdate are dissolved and excess urea solution is added with stirring, resulting in the precipitation of a solid. The precipitated solids are collected by filtration and then washed with distilled water, followed by drying at 120 °C for 12 hours and calcination at 500 °C for 5 hours. Finally, the catalysts are crushed and sieved to 40–60 mesh. The sample, denoted as the MoxCe, suggests a mass percent ratio of MoO<sub>3</sub> to CeO<sub>2</sub>.

#### Activity measurement

Activity measurements are performed in a fixed-bed quartz reactor (inner diameter of 5 mm) using 100 mg of catalyst measuring 40–60 mesh. The feed gas mixture contains 500 ppm NO, 500 ppm NH<sub>3</sub>, 3 % O<sub>2</sub>, and the balance is N<sub>2</sub>. The total flow rate of the feed gas is 200 cm<sup>3</sup>·min<sup>-1</sup> and the gas hourly space velocity is approximately 120,000 h<sup>-1</sup>. Here, to ensure the reaction order is zero with respect to the NH<sub>3</sub>, the concentration of NH<sub>3</sub> is usually slightly higher (5–10 ppm) than that of NO. The concentrations of the gases (NO, NO<sub>2</sub>, N<sub>2</sub>O, and NH<sub>3</sub>) are continually monitored by an FTIR spectrometer (MultiGas TM 2030 FTIR Continuous Gas Analyzer). The concentration data are collected when the reaction reaches a steady state after 30 min at each temperature. To better evaluate the catalytic activity, kinetic parameters are calculated according to the following equation, applied to the NO<sub>x</sub> conversion:

$$k = -\frac{V}{W} \times \ln(1-x) \tag{1}$$

In the above equation, k is the reaction rate constant  $(\text{cm}^3 \cdot \text{g}^{-1} \cdot \text{s}^{-1})$ , V is the total gas flow rate  $(\text{cm}^3 \cdot \text{s}^{-1})$ , W is the mass of catalyst in the reactor, and x is the NO conversion in the testing activity. The equation is based on the understanding that the reaction is first order dependent on NO and zero order dependent on NH<sub>3</sub>.<sup>1, 2</sup>

#### **Catalyst characterization**

Characterization of the BET surface area of the samples is carried out with a Micromeritics ASAP 2020 apparatus. The crystal structure is determined using X-ray diffraction (XRD) measurements (Rigaku, D/max-2200/PC) between 20 ° and 80 ° at a step rate of 10 °·min<sup>-1</sup> operating at 40 kV and 30 mA using Cu K $\alpha$  radiation. X-ray photoelectron spectroscopy (XPS) is performed with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al K $\alpha$  radiations. The binding energies are referenced to the C1s line at 284.8 eV. The temperature programmed desorption (TPD) of NH<sub>3</sub> and temperature programmed reduction (TPR) of H<sub>2</sub> experiments are performed on a chemisorption analyzer (Micromeritics, ChemiSorb 2920 TPx) under a 10 % NH<sub>3</sub>/He or 10 % H<sub>2</sub>/Ar gas flow (50 mL·min<sup>-1</sup>) at a rate of 10 °C·min<sup>-1</sup> up to 550 °C for NH<sub>3</sub>–TPD and 750 °C for H<sub>2</sub>–TPR. Each sample is pretreated in He for 1 h at 350 °C before testing.

#### In situ Raman spectroscopy

In situ Raman spectra are measured using a Raman microscope (InVia Reflex, Renishaw) equipped with a deep-depleted thermoelectrically cooled charge-coupled device (CCD) array detector and a high-grade Leica microscope (long working distance objective  $50\times$ ). The sample is placed into the sample cell, which is specially designed for catalytic reactions carried out at high temperature and pressure (CCR 1000, Linkam fitted with quartz windows). The samples (25 mg) with larger than 60 meshes are mounted on unreactive disposable ceramic fabric filters, placed inside the ceramic heating element, which is capable of heating samples from ambient up to 1000 °C. The 532 nm line (5 mW at sample) of laser is used for recording the Raman spectra. The sample is pretreated in flowing N<sub>2</sub> at 350 °C for 1 h then cooled down to room temperature and switch to N<sub>2</sub> purging. The gas used for the experiments is a mixture 500 ppm NO/N<sub>2</sub> and 5 %  $O_2/N_2$  with a total flow rate of 50 cm<sup>3</sup>·min<sup>-1</sup>.

### In situ IR spectroscopy

In situ IR spectra are recorded on a Fourier transform infrared spectrometer (FTIR, Nicolet 6700) equipped with a SMART collector and an MCT detector cooled by liquid  $N_2$ . Diffuse reflectance measurements are performed *in situ* in a high-temperature cell with a ZnSe window. The catalyst with larger than 60 meshes is loaded in the Harrick IR cell and heat to 350 °C under  $N_2$  at a total flow rate of 100 cm<sup>3</sup>·min<sup>-1</sup> for 1 h to remove any adsorbed impurities. The background spectrum is collected in a flowing  $N_2$  atmosphere and subtracted from each sample spectrum. The spectra are recorded by accumulating 32 scans at a resolution of 4 cm<sup>-1</sup>. Here, to diminish the influence of absorbance for different catalysts, the absorbance intensity was set to 3.00 for every sample at 100 °C when collecting the background spectra.

## Basic properties of the Mo<sub>x</sub>Ce catalysts

**Table 1** summarizes the basic physic-chemical properties of the prepared catalysts. BET surface areas and labile surface oxygen (O $\alpha$ ) continuously decrease, while surface Mo:Ce ratio calculated and Mo surface density increase with elevating MoO<sub>3</sub> content.

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	$S_{BET}$	Oα ratio	Surface Mo:Ce	Mo surface density
	$(m^2/g)$	(%)		$(Mo/nm^2)$
Mo5Ce	69.4	58.1%	0.11	2.9
Mo10Ce	57.4	55.8%	0.26	6.6
Mo20Ce	46.0	46.9%	0.41	15.1
Mo50Ce	39.8	45.1%	0.74	35.0
Mo100Ce	31.7	26.7%	0.93	65.9
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Table 1. Basic properties of the Mo<sub>x</sub>Ce catalysts.

#### **Comparison of the SCR catalysts**

**Fig. S1** shows the activities of state-of-art SCR catalysts under GHSV of 60000 h<sup>-1</sup>. CeO<sub>2</sub>-WO<sub>3</sub> exhibited remarkable high NO<sub>x</sub> removal efficiency than the other two catalysts, while CeO<sub>2</sub>-MoO<sub>3</sub> exhibited more active than  $V_2O_5$ -WO<sub>3</sub>/TiO<sub>2</sub> at low temperature. The loss of activity at 400 °C for CeO<sub>2</sub>-MoO<sub>3</sub> could be responsible for the NH<sub>3</sub> oxidation.



Fig. S1 Comparison of the SCR activity on CeO<sub>2</sub>-MoO<sub>3</sub>, CeO<sub>2</sub>-WO<sub>3</sub> and V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalysts.

#### Phase structures of the MoxCe catalysts

**Fig. S2** shows the XRD patterns of the MoxCe catalysts, all the peaks can be attributed to the cubic fluorite phase of CeO<sub>2</sub> (PDF# 34–0394). With increasing the MoO<sub>3</sub> content, the diffraction peaks are broadened, accompanied by a decrease in their intensities. This can be attributed to a transformation from the bulk, regular crystals to an amorphous structure. The MoO<sub>3</sub> phase cannot be directly determined through the XRD results, indicating that MoO<sub>3</sub> could be highly dispersed on the CeO<sub>2</sub> surface.



Fig. S2 XRD patterns of the MoxCe catalysts.

#### Raman peaks assignments

The main peak at 464 cm<sup>-1</sup> can be assigned to the  $F_{2g}$  mode of oxygen atoms around cerium ions in the cubic phase CeO<sub>2</sub>, the peaks at 267 cm<sup>-1</sup> and 594 cm<sup>-1</sup> can be assigned to a second-order transverse acoustic mode and a defect-induced mode of CeO<sub>2</sub>, respectively.<sup>3, 4</sup> The peaks at 998 and 980 cm<sup>-1</sup> can be attributed to the Mo=O vibrational modes,<sup>5</sup> and the peaks at 886 and 786 cm<sup>-1</sup> can be assigned to the Mo–O–Mo vibrational modes. The bands (327, 814 and 945 cm<sup>-1</sup>) can be assigned to Ce<sub>2</sub>Mo<sub>4</sub>O<sub>15</sub>.<sup>6, 7</sup>

# **XPS** results

The XPS results of Ce 3d are shown in **Fig. S3(a)**. The bands labeled  $\mu$ ,  $\mu$ '',  $\mu$ ''',  $\nu$ ,  $\nu$ '' and  $\nu$ ''' represent the 3d<sup>10</sup>4f<sup>0</sup> state of Ce<sup>4+</sup>, whereas u' and v' represent the 3d<sup>10</sup>4f<sup>1</sup> state, corresponding to Ce<sup>3+,8</sup> and the corresponding Mo 3d spectra are shown in **Fig. S3 (b)**.





Fig. S3 XPS spectra of (a) Ce 3d and (b) Mo 3d for the MoxCe catalysts.

The XPS spectra of O 1s for the MoxCe catalysts are shown in **Fig. S4**. The O 1s peaks can be fitted into two peaks, referred to as the lattice oxygen at 529.3–530.3 eV (O $\beta$ ) and the chemisorbed surface oxygen at 530.9–531.9 eV (O $\alpha$ ).<sup>8</sup> The O $\alpha$  appears highly active in oxidation reactions due to its higher mobility than the lattice oxygen O $\beta$ . The ratio of the O $\alpha$  (Table S1) decrease with increasing MoO<sub>3</sub> content, suggesting that surface active oxygen species in ceria might be covered by molybdenum oxides.



Fig. S4 XPS spectra of O 1s for the MoxCe catalysts.

## NH<sub>3</sub> adsorption at 100 °C

**Fig. S5** displays the *in situ* IR spectra of  $NH_3$  adsorption on the MoxCe catalysts at 100 °C. The band centered in the range of 1100–1200 cm<sup>-1</sup> can be assigned to the Lewis acid sites, while the peaks at 1440 and 1660 cm<sup>-1</sup> can be attributed to the Brønsted acid sites.<sup>9</sup> Lewis acid sites decrease while Brønsted acid sites are remarkably improved with elevating the MoO<sub>3</sub> content. Moreover, two distinct peaks for the Lewis acid sites over Mo5Ce could be due to the different sites for  $NH_3$  adsorption on surface cerium or

molybdenum atoms. The similar IR spectra can be also found when study the vanadia supported on ceria.



Fig. S5 In situ IR spectra of NH<sub>3</sub> adsorption on the MoxCe catalysts at 100 °C.

#### NH<sub>3</sub>-TPD

**Fig. S6** shows the NH<sub>3</sub>–TPD profiles of the MoxCe catalysts in the temperature range of 80–500 °C. Two peaks, at 175 and 260 °C for the Mo5Ce catalyst can be assigned to the weak acid sites and strong acid sites, respectively. Both the peaks move to the low temperature, indicating the weakened stability of surface acidity. Considering the NH<sub>3</sub> desorption behaviors from in situ IR spectra (**Fig. S7(b)-(f)**), the unstable acid sites are originated from the Brønsted acid sites, especially for the Mo50Ce and Mo100Ce catalysts. It appears that the Ce<sub>2</sub>Mo<sub>4</sub>O<sub>15</sub> compound on the catalysts significantly decreases the acid sites and shows the influences on the acid stability.



Fig. S6 NH<sub>3</sub>-TPD for the MoxCe catalysts in the temperature range of 80-500 °C.

## NH<sub>3</sub> desorption in IR spectra in the range of 100-300 °C

**Fig. S7 (a)–(f)** shows the *in situ* IR spectra of  $NH_3$  desorption in the temperature range of 100–300 °C. All the samples decrease in intensities with the elevated temperature.













Fig. S7 In situ IR spectra of NH<sub>3</sub> desorption on the MoxCe catalysts in the temperature range of 100-

300 °C.

## NO<sub>x</sub> adsorption at 100 °C

**Fig. S8** shows the ad-NO<sub>x</sub><sup>-</sup> (mainly nitrate or nitrite species) on the MoxCe catalysts at 100 °C. The bands centered at 1606, 1580, 1514, 1468, 1306 and 1237 cm<sup>-1</sup> can be attributed to the bridged, bidentate and monodentate nitrate and bridged, bidentate, monodentate nitrite species, respectively.<sup>9</sup> The ad-NO<sub>x</sub><sup>-</sup> for all the catalysts decrease with increasing the MoO<sub>3</sub> content, only weak bridged and monodentate nitrate species are observable on the Mo100Ce catalyst.

**Fig. S9** (a)–(f) presents the NO<sub>x</sub> desorption on the MoxCe catalysts in the temperature range of 100–300 °C. Correlated with the surface structures of molybdenum oxides, the monomeric [MoO<sub>x</sub>] units could slightly promote nitrite species, while the polymeric or cerium molybdenum compound suppress the ad-NO<sub>x</sub><sup>-</sup>.



Fig. S8 In situ IR spectra of NO<sub>x</sub> adsorption on the MoxCe catalysts at 100 °C.













Fig. S9 In situ IR spectra of  $NO_x$  desorption on the MoxCe catalysts in the temperature range of 100-

300 °C.

#### **Reaction details on the Mo20Ce catalyst**

First the reactive ad-NH<sub>3</sub> are studied shown in **Fig. S10** (a). Nearly after NO and O<sub>2</sub> are introduced to the IR cell for 10 min, part of Lewis and Brønsted acid sites bands are consumed. Considering the low SCR activity of the catalyst at 150 °C, it appears that Lewis and Brønsted acid sites are reactive on the CeO<sub>2</sub>-MoO<sub>3</sub> catalysts. When the gas order is reversed, the ad-NO<sub>x</sub><sup>-</sup> stable exist on the spectra within 10 min of NH<sub>3</sub> purging, while the ad-NH<sub>3</sub> appear and grow at 3 min. The results indicate that ad-NO<sub>x</sub><sup>-</sup> is inactive. The same reaction are carried out at 250 °C and shown in **Fig. S11**. Both Lewis and Brønsted acid sites can be consumed by NO and O<sub>2</sub> purging for 10 min, and the pre-adsorbed NO<sub>x</sub><sup>-</sup> nearly unchange during the whole experiment.



Fig. S10 In situ sequential Raman spectra of the Mo20Ce catalyst at 150 °C



Fig. S11 In situ sequential Raman spectra of the Mo20Ce catalyst at 150 °C

#### Influences of SO<sub>2</sub> and H<sub>2</sub>O on the Mo20Ce at 300 °C

**Fig. S12** shows the SO<sub>2</sub> and H<sub>2</sub>O resistance on the Mo20Ce catalyst at 300 °C for 12 h. SO<sub>2</sub> significantly decreases the NO<sub>x</sub> conversion of the Mo20Ce catalyst. When shut down the SO<sub>2</sub> gas flow, the SCR activity cannot be recovered. That indicates the sulfate or

sulfite species strongly boned to the surface active sites. Considering the similar acid/base properties of  $SO_2$  with  $NO_2$ , we assume that the sulfate could occupy the surface defect sites. When  $SO_2$  and  $H_2O$  are sequentially introduced to the gas flow, the NO conversion of the Mo20Ce catalysts decreases from approximately 85 % to 45 %. As soon as shutting down the  $SO_2$  and  $H_2O$ , the catalyst activity is partly recovered, the NO conversion are similar as that the  $SO_2$  influence alone showed. That indicate the influence of  $H_2O$  on the Mo20Ce catalyst is temporary and recovered.



**Fig. S12** Influences of SO<sub>2</sub> and  $H_2O$  on the Mo20Ce catalyst at 300 °C.

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