Identification of the reaction pathway and reactive species of the selective catalytic reduction of NO with NH$_3$ over cerium-niobium oxide catalysts

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Temperature programmed desorption of ammonia (NH$_3$-TPD)

The NH$_3$-TPD was used to calculate the surface acidities of the catalysts. The total desorbed amount of ammonia was calculated by the integration of the desorption peak. The result was normalized by the specific surface area of each catalyst. The results are shown in Table S1. The acidities per surface area of different catalysts followed the order: CN500 < CN550 <CN600 < CN700. This result matched well with the XPS result since in our previous study,[1] we found that the niobium oxide species on the surface accounted mainly for the acidity of the binary oxide catalyst.

Table S1

The acidic properties of the Ce-Nb oxide catalysts calcined at different temperatures

Sample	Acidity per surface area / μmol m^{-2}
CN500	0.88
CN550	0.92
CN600	0.94
CN700	1.00

Temperature programmed desorption of NO$_x$ (NO$_x$-TPD)

The NO$_x$-TPD was performed and the desorption of NO$_2$ was shown in Fig. S1. This result was in accordance with the H$_2$-TPR and NO oxidation result. After the saturation of NO+O$_2$, CN500 desorbed the maximum amount of NO$_2$ during the heating procedure, then followed CN550. CN600 desorbed only a very small amount of NO$_2$ while over CN700 no NO$_2$ desorption was found.
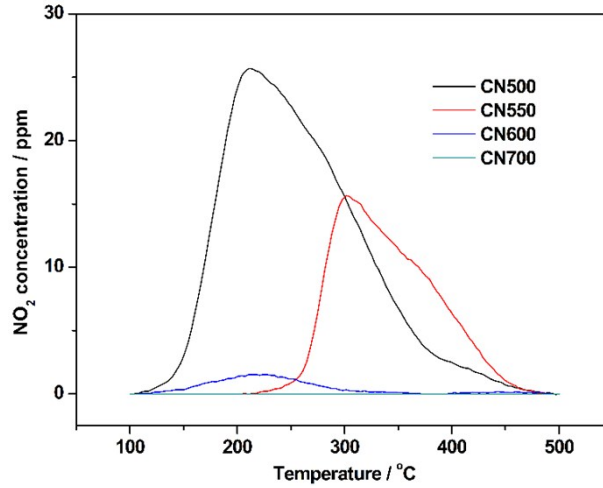
Fig. S1 NO$_x$ –TPD over Ce-Nb oxide catalysts

kinetic study

As demonstrated in the previous report[2], the SCR reaction may follow Eley–Rideal mechanism (E-R) and/or Langmuir–Hinshelwood mechanism (L-H). In Fig. 7, both E-R and L-H mechanisms contributed to the reaction over this catalyst. Thus the total reaction rate can be described as follow:

$$r = r_{E-R} + r_{L-H} \tag{S1}$$

whereas r stands for the total reaction rate, r_{E-R} the reaction rate over E-R mechanism and r_{L-H} the rate over L-H mechanism.

In the L-H mechanism, adsorbed NH$_3$ species reacted with adsorbed NO$_x$ species. Thus the reaction orders with respect to both NH$_3$ and NO should be 0. In the E-R mechanism, adsorbed NH$_3$ species reacted with gaseous NO and the reaction orders with respect to NH$_3$ and NO should be 0 and 1, respectively. Our group has previously developed a method and confirm this claim[3, 4]. Experimentally, the reaction order with respect to NO was measured to be 1 on vanadia-based catalyst,[2, 5, 6] which is known to have a very weak ability to adsorb NO, making the reaction proceed over E-R mechanism mainly. While the value was found to be less than 1 on ferric oxide (0.64) and MnO$_x$-based catalyst (0.4). These catalysts can adsorb NO, making the reaction proceed via both E-R and L-H mechanisms. So r_{E-R} can be described as:

$$r_{E-R} = k_1 [NO] \tag{S2}$$

Considering both (S1) and (S2), we can describe the total reaction rate as:

$$r = k_1 [\text{NO}] + r_{\text{L-H}} \tag{S3}$$

According to (S3), we can vary the gas concentration and measure the total corresponding reaction rate to determine the contributions of E-R and L-H mechanism. The result is shown in Fig. S2. In order to measure the reaction rates at low conversions, we enlarge the GHSV to 600, 000 mL g^{-1} h^{-1}. Good correlations ($r^2 > 0.98$) were found at all the four temperatures. Accordingly the values at [NO]=[NH_3]=500 ppm were selected to form Fig. 8 in the paper. Using the same method, we can calculate the values over other catalysts, *i.e.* CN550, CN600 and CN700, and the result is shown in Fig. 9.
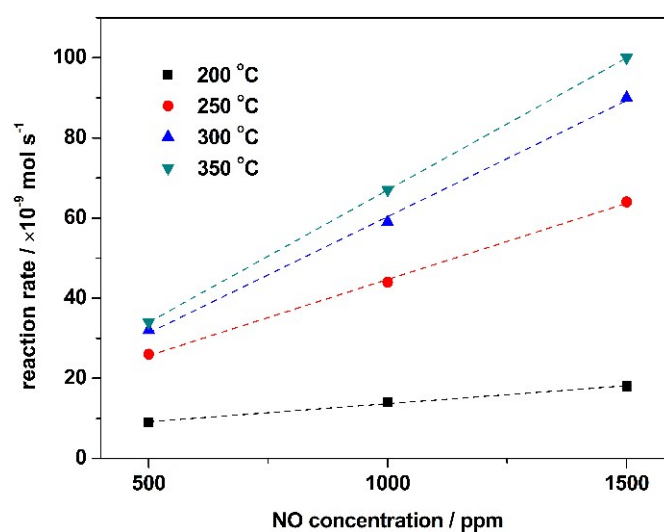

Fig. S2 reaction rates over CN500 catalyst at different NO and NH_3 concentrations

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