

Electronic Supporting Information:

Low-valence or tetravalent cation doping of manganese oxide octahedral molecular sieve (K-OMS-2) materials for nitrogen oxides emission abatement

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1. Raman spectra

The Raman experiment was performed by using an inVia-reflex Renishaw spectrometer equipped with an optical microscope at room temperature. The Raman spectra of the M-K-OMS-2 materials are shown in Fig. S1. A strong peak at 632 cm^{-1} together with a weak shoulder peak at 571 cm^{-1} was characteristic of the Mn-O stretching vibrations of the pure K-OMS-2 material.^[S1,S2] They were indicative of a well-developed tetragonal structure with 2×2 tunnels. Intuitively, the Raman spectra of Fe-K-OMS-2 and V-K-OMS-2 showed these 2 characteristic lines but much enlarged than those of K-OMS-2, indicating that they were incorporated into the framework of the K-OMS-2 and provoked small distortion of the lattice arrangement of the K-OMS-2 structure. For M-K-OMS-2 (M=Zn, Fe, and Zr), The absence of a Raman active feature of 439 cm^{-1} ^[S3] in Zn-K-OMS-2, 276 and 387 cm^{-1} ^[S4] in Fe-K-OMS-2, 278 and 318 cm^{-1} ^[S5] in Zr-K-OMS-2, suggested that no extra free ZnO, Fe_2O_3 and ZrO_2 particles were present, respectively. For V-K-OMS-2, an additional band centered at $\sim 835\text{ cm}^{-1}$ was observed, ascribed to the V-O vibrations in K-OMS-2.^[S6]

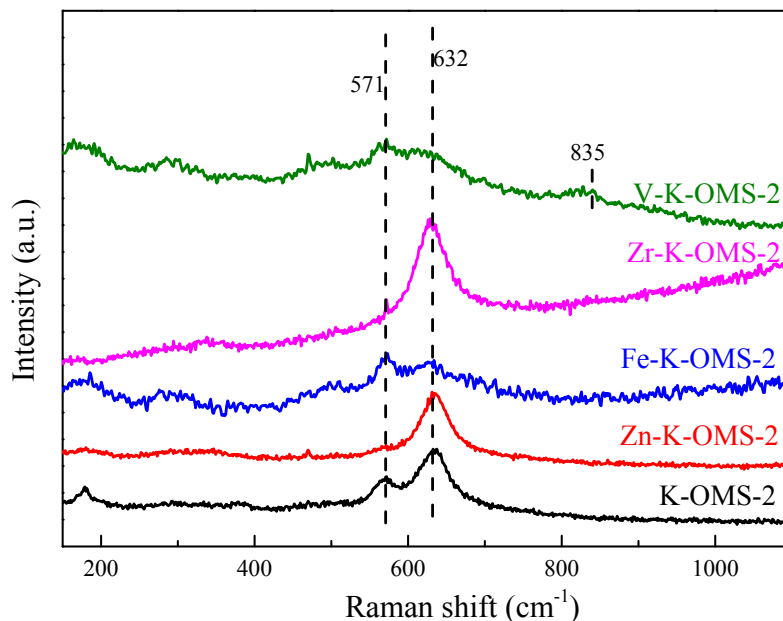


Fig. S1 Raman spectra of the M-K-OMS-2 (M=Zn, Fe, Zr, and V) materials.

2. N₂ selectivity

Fig. S2 gives the N₂ selectivity of the M-K-OMS-2 (M=Zn, Fe, and Zr) catalysts. It can be seen that the N₂ selectivity of both K-OMS-2 and Zn-K-OMS-2 decreased obviously with increasing reaction temperature in the temperature range of 100-150 °C (Fig. S2(a)), which could be ascribed to the formation of N₂O (Fig. S2(b)). However, after doping with Fe and Zr, the N₂ selectivity of Fe-K-OMS-2 and Zr-K-OMS-2 catalyzed reactions were also very remarkable, remaining higher than 88% even at 150 °C. The results indicated that the N₂ selectivity of the K-OMS-2 catalyst can be improved by doping with Fe and Zr.

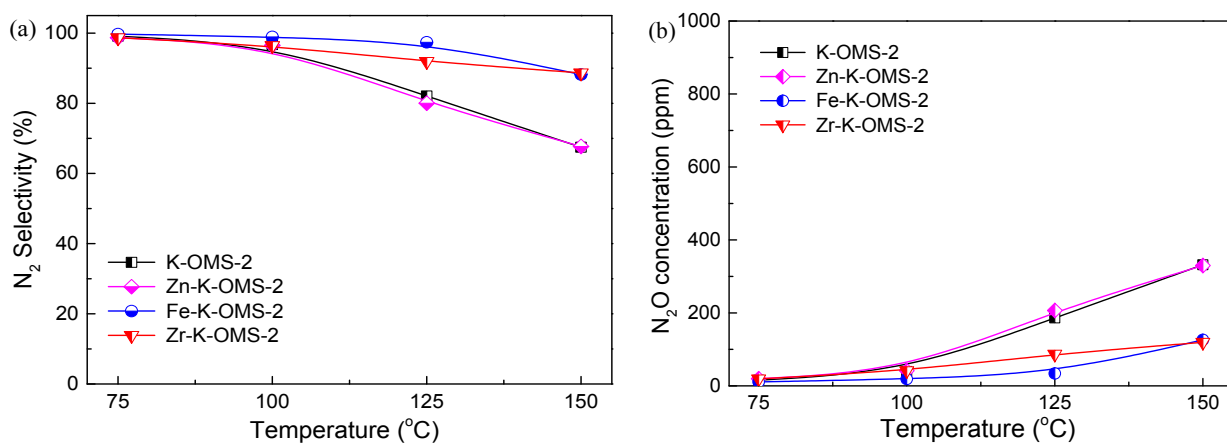


Fig. S2 The N₂ selectivity (a), and N₂O concentration (b) during the NH₃-SCR reaction at different temperatures.

3. NH₃-TPD

The ammonia temperature programmed desorption (NH₃-TPD) was performed on an automated catalyst characterization system (Micromeritics Autochem 2920) with a TCD detector. 100 mg of the sample was pretreated at 300 °C and saturated with NH₃ (1 vol% NH₃/He, 100 mL/min) at room temperature (RT). After being purged with pure He at RT, NH₃ desorption took place at a ramp of 10 °C/min in a He flow of 100 mL/min and the temperature range of 30-600 °C.

The NH₃-TPD was conducted to study the adsorption and activation of NH₃ on the active sites of the materials, and their NH₃-TPD profiles are presented in Fig. S3. Each of the samples had obvious NH₃ desorption in the temperature range of 50-400 °C. The profile of each sample could be roughly deconvoluted into three peaks of ~148, ~229, and ~307 °C, corresponding to weak, moderate, and strong acidic sites [S7]. The peak at ~148 °C was ascribed to desorption of the physical adsorption NH₃ and some NH₄⁺ bounded to the weak Brønsted acid sites. The band at ~229 °C was due to NH₄⁺ bounded to the strong Brønsted acid sites, and the peak at ~307 °C was due to the coordinated NH₃ bounded to the Lewis acid sites [S8]. The results indicated that all of the samples possessed the basically similar high intensities of weak and moderate acidic sites with low intensity of strong acidic sites. Moreover, the doped metals (Zn, Fe, Zr and V) incorporated into the K-OMS-2 material could significantly enhanced the weak acidic sites and moderate acidic sites, thus greatly increasing the adsorption capacity of NH₃. The total acidity decreased in the sequence of Zr-K-OMS-2 > V-K-OMS-2 > Fe-K-OMS-2 > Zn-K-OMS-2 ~ K-OMS-2.

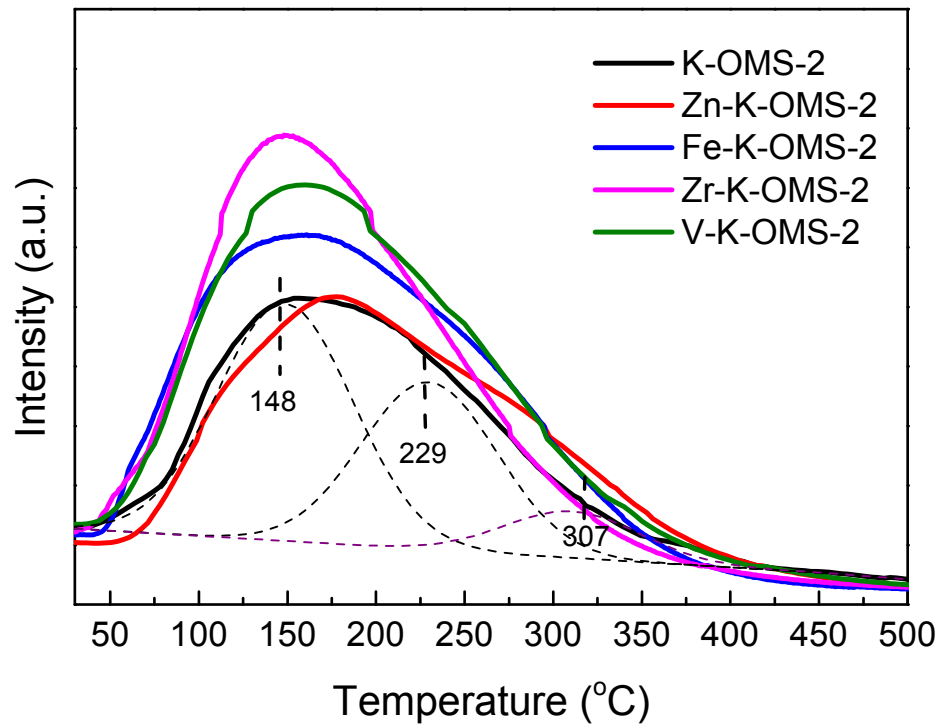


Fig. S3 NH₃-TPD profiles of the M-K-OMS-2 (M=Zn, Fe, Zr, and V) materials.

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