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Improved NO_x reduction in the presence of alkali metals by using hollandite Mn-Ti oxides promoted Cu-SAPO-34 catalysts

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Catalyst Characterization.

The X-ray diffraction (XRD) experiments were performed in a D/MAX2200V PC X-ray diffractometer and the XRD patterns were recorded using a scanning speed of 8°/min in the 2θ range of 10° to 90°. The nitrogen adsorption-desorption isotherms and the specific surface areas of the samples were obtained at 77 K on an automated analyser (Autosorb-IQ2, Quantachrome Corporation) for surface and pore size by nitrogen adsorption/desorption. HRTEM and TEM were implemented on a JEM-2100F and a JEM-200CX, respectively. The ammonia temperature-programmed desorption (NH₃-TPD) was tested on a Tianjin XQ TP-5080 automatic adsorption instrument, and the NH₃ was detected by a TCD. 80 mg of each sample was pre-treated with N₂ for 30 min at 300 °C before the TPD run. The samples were switched to a flow of NH₃ for adsorption for 1 h after cooling down to 100 °C. Finally, the temperature was increased to 500 °C for gas desorption with a rate of 10 °C·min⁻¹.

In situ DRIFTs measurements were performed on a Nicolet 6700 spectrometer. All DRIFT spectra were gathered using a wavenumber range of 1800 cm⁻¹ to 1000 cm⁻¹ in the Kubelka-Munk format, accumulating 64 scans per minute at 4 cm⁻¹ resolution. Prior to each test, each sample was pre-treated at 300 °C under N₂ flow for 0.5 h, then regulated to the target temperature to obtain a background spectrum, which should be deducted from the sample spectra. For the adsorption of NH₃ or NO + O₂ studies, the catalysts were held at 300 °C and the background spectra were obtained for different temperatures, then were exposed to a flow of 500 ppm of NH₃ or NO + O₂ at 30 °C for 1 h. The desorption process was then performed under a flow of N₂ and was recorded for the corresponding temperatures of the background spectrum. After the same

pretreatment, for the transient reactions between NO + O_2 (NH₃) and pre-adsorbed NH₃ (or NO + O_2), the catalysts were exposed to 500 ppm NH₃ (or NO + O_2) for the adsorption. An hour later, the samples were switched to a flow of NO + O_2 (or NH₃) and the reaction process was recorded as a function of time.



Fig. S1. (a) NO conversions and (b) N₂ selectivity over Cu-SAPO-34 catalysts with different copper ion exchange times during the NH₃-SCR reaction. Reaction conditions: total flow rate is 260 mL/min, [NO] = [NH₃] = 500 ppm, 5 vol% O₂, GHSV = 40000 h⁻¹.



Fig. S2. NO conversions over hollandite-type Mn-Ti oxides (HMT) and K⁺ poisoned HMT samples.

The chemical composition of hollandite-type Mn-Ti oxides was $K_xMn_{0.25}Ti_{0.75}O_2$. The chemical valence state of Mn in $K_xMn_{0.25}Ti_{0.75}O_2$ was lower than Mn^{4+} , indicating that the redox property of Mn was relatively weak. On the other hand, the Mn elements in the hollandite structure were too stable to change chemical valence. Therefore, the NO conversion is very low over the hollandite-type Mn-Ti oxides. The pristine HMT showed weak SCR activity and HMT@Cu-S showed similar curves of NO conversion with Cu-S catalysts. In fact, the HMT had a little contribution on NO_x reduction due to their SCR activity, but this contribution was negligible. We consider that the Cu-S was dominant on NO_x reduction in HMT@Cu-S catalysts.



Fig. S3. NO conversions over K-HMT@Cu-S without acid treatment, K-Cu-S and Cu-S catalysts during the NH₃-SCR reaction. Reaction conditions: total flow rate is 260 mL/min, $[NO] = [NH_3] = 500$ ppm, 5 vol% O₂, GHSV = 40000 h⁻¹.



Fig. S4. N_2 adsorption-desorption isotherms of K-HMT@Cu-S, HMT@Cu-S, K-Cu-S and Cu-S catalysts.



Fig. S5. Reaction rates normalized to the surface area in NH₃-SCR reation as a function of temperature over K-HMT@Cu-S, HMT@Cu-S, K-Cu-S and Cu-S catalysts.



Fig. S6. XRD patterns of hollandite-type Mn-Ti oxides before and after acid treatment.



Fig. S7. TEM images of the (a) Cu-S, (b) K-Cu-S, (c) HMT@Cu-S and (d) K-HMT@Cu-S catalysts.

In fact, the hydrothermal treatment for Cu/SAPO-34 catalysts at relatively low temperature (around 70 °C) could cause the collapse of SAPO-34 framework at zero or low Cu loadings. Furthermore, the copper content increase could enhance the hydrothermal stability. As for our catalysts, an incipient wetness impregnation method was used at around 45 °C and Cu-S catalysts were ion exchanged with Cu²⁺ at 80 °C for 3 h. As shown in Fig. 4 and Fig. S7, distinct cuboids with well-defined crystal structures for typical SAPO-34 were observed for all the catalysts. The uniform distributions of different elements were found in the frameworks. Therefore, for HMT@Cu-S and K-HMT@Cu-S catalysts, their frameworks were not destroyed after wetness impregnation.



Fig. S8. Pore size distribution profiles of the (a) Cu-S, (b) K-Cu-S, (c) HMT@Cu-S and (d) K-HMT@Cu-S catalysts.



Fig. S9. In situ DRIFTs of the transient reactions at 250 °C over (a), (b) Cu-S and (c), (d) HMT@Cu-S catalysts between NO+O₂ and pre-adsorbed NH₃ as a function of time.



Fig. S10. In situ DRIFTs of the transient reactions at 250 °C over (a), (b) Cu-S and (c), (d) HMT@Cu-S catalysts between NH_3 and pre-adsorbed $NO+O_2$ as a function of time.

Catalysts	Temperatures	Alkali Metal Loading	NO _x Conversions
	(°°)	Amounts	(%)
V ₂ O ₅ -WO ₃ /TiO ₂ ^[1]	350	0.5 wt % K	12
V ₂ O ₅ /ZrO ₂ (SO ₄ ²⁻) ^[2]	350	K/V molar ratio 0.4	75
Ce/TiO ₂ ^[3]	350	0.5 wt % K	20
CeO ₂ -WO ₃ ^[4]	300	1 wt % K	82
V ₂ O ₅ /CeO ₂ ^[5]	350	0.5 wt % K	55
V _{0.4} -Ce ₅ W ₅ /Ti ^[6]	350	1 wt % K	20
V-TNTs ^[7]	300	0.8 wt % K	88
Ce-TNTs ^[8]	300	Na/Ce molar ratio	82
		1	
HMO ^[9]	350	0.5 wt % K	90
V ₂ O ₅ /HWO ^[10]	350	1.3 wt % K	72
Cu-S (this work)	350	0.5 wt % K	71
HMT@Cu-S (this work)	350	0.5 wt % K	92

Table S1. NO_x conversions of various catalysts after alkali metal loading from references and this work.

As shown in Fig.1, after 0.5 wt% K poisoning, the NO conversions of Cu-S catalysts in the whole temperature range of 90-360 °C decreased obviously. In the meantime, the NO conversions of HMT@Cu-S catalysts in the relatively low temperature range also decreased somewhat after poisoning, although the maximal NO conversion could reach nearly 92 %. This means that although most of alkali metal ions could be trapped by the HMT, there are still some little alkali metal ions get into the Cu-S thus influence catalytic performance slightly. Combining the Table S1, it seems that it is impossible to maintain catalytic performance of catalysts in the whole temperature range after addition of alkali metal ions. But in this case of 0.5 wt% K poisoning, our new catalysts show great alkali resistance compared to other catalysts. Furthermore, this catalyst should need to be regenerated when the catalytic performance in the operating temperature range start to decline because of the enrichment of alkali metal ions.

In the 'Preparation of catalysts' section, the potassium extraction process of prepared hollandite-type Mn-Ti oxides was conducted via acid treatment. When the catalysts were poisoned by alkali metal, this potassium extraction process should be implemented. After potassium extraction treatment, the catalysts which have new free tunnels to trap alkali metal ions are regenerated. In addition, we consider that the catalysts could be regenerated by electrophoresis method.

The HMT@Cu-S catalysts were developed via the isolation of active sites and alkali metal trapping sites. The Cu-S mainly provided SCR catalytic activity and the HMT mainly trapped the alkali metal ions. From Fig. 1 and Fig. S3, it can be known that the HMT@Cu-S catalysts with less free tunnels could also trap the K⁺, and that the acid treatment could create more tunnels for K⁺ trapping and increase alkali resistance. If we increase the content of HMT in HMT@Cu-S catalysts, we think that the alkali resistance would also be improved. On the contrary, we consider that the SCR performance of HMT@Cu-S catalysts would be dropped with the addition of overmuch HMT. Therefore, the determination of appropriate proportion between HMT and Cu-S in HMT@Cu-S catalysts would need more investigations and studies.

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