Tailored Alkali Resistance of DeNO$_x$ Catalysts by Improving Redox Properties and Activating Adsorbed Reactive Species

**HIGHLIGHTS**

Fe-decorated SO$_4$$^{2-}$/CeZr catalysts exhibit superior alkali resistance. Improved redox properties compensate for the loss of the acidity. Higher reactivity of NH$_x$ species makes up their decreased quantity. Alkali resistance is enhanced via improving the redox and reactivity of NH$_x$ species.
Tailored Alkali Resistance of DeNO$_x$ Catalysts by Improving Redox Properties and Activating Adsorbed Reactive Species

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SUMMARY
It is still challenging to develop strongly alkali-resistant catalysts for selective catalytic reduction of NO$_x$ with NH$_3$. It is generally believed that the maintenance of acidity is the most important factor because of neutral effects of alkali. This work discovers that the redox properties rather than acidity play decisive roles in improving alkali resistance of some specific catalyst systems. K-poisoned Fe-decorated SO$_4^{2-}$/Co-modified CeZr oxide (Fe/SO$_4^{2-}$/Co/CeZr) catalysts show decreased acidity but reserve the high redox properties. The higher reactivity of NH$_x$ species induced by K poisoning compensates for the decreased amount of adsorbed NH$_x$, leading to a desired reaction efficiency between adsorbed NH$_x$ and nitrate species. This study provides a unique perspective in designing an alkali-resistant deNO$_x$ catalyst via improving redox properties and activating the reactivities of NH$_x$ species rather than routinely increasing acidic sites for NH$_x$ adsorption, which is of significance for academic interests and practical applications.

INTRODUCTION
Concerns about the severe acid rain and haze problems caused by NO$_x$ excessive emission have triggered extensive researches on effective abatement controls of NO$_x$ (deNO$_x$) via NH$_3$ selective catalytic reduction (NH$_3$-SCR) (Han et al., 2019a, 2019c; Paolucci et al., 2017; Qu et al., 2020). Since the ultra-low emissions of NO$_x$ have been almost attained for the power plants, it is more pressing to reduce NO$_x$ emissions in some non-electrical industries such as steel plants, biomass burning boilers, and waste incinerators. There is an increasing demand for novel alkali-resistant SCR catalysts because the commercial vanadia-based catalysts tend to be poisoned by the alkali metals such as K and Na released from the flue gas (Hao et al., 2019; Huang et al., 2013; Marberger et al., 2016; Peng et al., 2016). A generally recognized deactivation mechanism is the proton exchange of alkali-metal ions onto the active Bronsted acid sites, which results in the loss of acidity over the neutralized acid sites (Hao et al., 2019; Hu et al., 2015b). A feasible approach to improve the alkali tolerance is adopting strongly acidic supports that supply sufficient acidic sites to interact with alkali ions and thus protect the active sites. Sulfated metal oxides supports such as TiO$_2$ and ZrO$_2$ as well as sulfated titanosilicate nanotubes have effectively improved alkali resistance (Due-Hansen et al., 2007; Gao et al., 2014; Putluru et al., 2012; Wang et al., 2015). However, this approach impairs the catalytic activity to some extent because of the sacrificial acidity of acidic supports. Another efficient strategy of alkali resistance is constructing the alkali-trapping sites that separate active sites and alkali-poisoned sites. Such a measure could reserve the original activity of catalysts on account of the intact acidic and redox sites. Hollandite manganese oxide and hexagonal WO$_3$ have been demonstrated to be effective for strengthening alkali resistance owing to the trapping effects of internal tunnels without destroying active sites (Hu et al., 2015b; Zheng et al., 2016). These strategies could protect active sites from alkali poisoning through precise structural designs. However, the stringent specification of acidity strength, pore tunnels, and type of oxides restrict the alkali-resistant applications. Actually, the alkali-resistant strategy is still lacking to develop highly efficient catalysts.

So far, less research effort has been devoted to the variation of redox sites and the reactivity of adsorbed nitrate and NH$_x$ species associated with alkali poisoning, which are decisive to SCR activity. In this study, we discover an unexpected result that redox properties rather than acidity play decisive roles in improving alkali resistance of Fe-decorated SO$_4^{2-}$/CeZr oxide (Fe/SO$_4^{2-}$/CeZr) catalysts. Herein, Ce-Zr mixed...
oxides combining the highly refractory property of ZrO2 with the superior oxygen storage capacity of CeO2 are used as the model catalyst, which are usually served as supports for SCR catalysts (Ding et al., 2015; Li et al., 2008; Sánchez Escribano et al., 2009). SO4\(^{2-}\) modification is performed on Ce-Zr mixed oxides to increase the acidic sites and improve the SCR activity (Zhang et al., 2017), whereas the SCR activity of SO4\(^{2-}\)/CeZr is largely decreased after alkali poisoning because of the loss of acidity and redox properties associated with the decreased reactivity of adsorbed nitrate and NH\(_x\) species. Via decorating Fe on SO4\(^{2-}\)/CeZr, the redox properties are enhanced after K poisoning owing to the promoted electron transfer between K, Fe, Ce, and Zr as well as sufficient Ce\(^{3+}\) and active oxygen species. Although the acid amount of K/Fe/SO4\(^{2-}\)/CeZr catalysts decreases more severely than K/SO4\(^{2-}\)/CeZr, the enhanced redox properties compensate for the loss of acidity, which notably improves the reactivity of adsorbed NH\(_x\) and meanwhile maintains the high reactivity of adsorbed nitrate species. Therefore, the K-poisoned Fe/SO4\(^{2-}\)/CeZr catalyst exhibits satisfactory SCR activity. This finding is of significance in revealing novel alkali-resistant mechanisms and paves a novel way for developing alkali-resistant catalysts in the future research.

RESULTS
Originally, one strategy of increasing acidity was attempted to improve the SCR activity via introducing SO4\(^{2-}\) onto the surface of CeZr oxides. As expected, SO4\(^{2-}\)/CeZr shows higher SCR activity (300–480\(^\circ\)C, NO conversion above 90%, Figure 1) compared with the pristine CeZr mixed oxides (the highest NO conversion of 80% at 330\(^\circ\)C, Figure S1). K-poisoned CeZr catalyst is almost deactivated with the highest NO conversion of only 16.7% at 360\(^\circ\)C (Figure S1) and K-poisoned SO4\(^{2-}\)/CeZr catalyst also displays poor activity with the maximum 64.8% NO conversion at 360\(^\circ\)C (Figure 1). This result indicates that introducing more acidic sites is not enough to maintain the SCR activity of CeZr catalysts after K poisoning. Besides, Fe-decorated CeZr (without SO4\(^{2-}\) modification) shows lower activity than SO4\(^{2-}\)/CeZr and inferior K resistance because of the less acidity (Figure S2). Via tuning the amount of Fe decoration on SO4\(^{2-}\)/CeZr, 1.5Fe/SO4\(^{2-}\)/CeZr exhibits the optimum SCR activity with a broad temperature window (270–420\(^\circ\)C, NO conversion above 90%) (Figure S3). After K poisoning, 1.5Fe/SO4\(^{2-}\)/CeZr still exhibits more than 85% NO conversion within 270–420\(^\circ\)C (Figure 1), indicating that Fe decoration notably improves the alkali resistance of SO4\(^{2-}\)/CeZr. Besides, the fresh/K-poisoned SO4\(^{2-}\)/CeZr and 1.5Fe/SO4\(^{2-}\)/CeZr catalysts all show good N\(_2\) selectivity above 90% within 150–480\(^\circ\)C (Figure S4).

To probe the effects of Fe decoration on the alkali resistance of SO4\(^{2-}\)/CeZr, the structural and textural features of fresh and K-poisoned SO4\(^{2-}\)/CeZr and 1.5Fe/SO4\(^{2-}\)/CeZr were first investigated. The X-ray diffraction patterns (Figure S5) and Raman spectra (Figure S6) both evidence the formation of Ce-Zr solid solution over fresh/K-poisoned SO4\(^{2-}\)/CeZr and 1.5Fe/SO4\(^{2-}\)/CeZr catalysts. Besides, no FeO\(_x\)-related X-ray diffraction peaks or Raman bands are observed, indicating the FeO\(_x\) is highly dispersed on the surface of SO4\(^{2-}\)/CeZr. The scanning electron microscope mapping of the representative K-poisoned 1.5Fe/SO4\(^{2-}\)/CeZr catalyst shows that Fe,
Ce, and Zr active components are highly dispersed with each other and K is also uniformly dispersed on the surface of catalysts (Figure S7). The Brunauer-Emmett-Teller (BET) surface areas of fresh SO$_4^{2-}$/CeZr and 1.5Fe/SO$_4^{2-}$/CeZr are 60.06 and 44.42 m$^2$/g, whereas they increase to 70.37 and 66.29 m$^2$/g after K poisoning, respectively. The increase of surface area after K poisoning is likely due to the contribution of K$_2$O nanoparticle on catalyst surface (Table S1). There is no correlation between surface area and SCR activity, indicating that the surface area of catalysts is not decisive to the SCR activity of catalysts.

The exposure of catalysts to alkali metals could reduce the acid sites for NH$_3$ adsorption/activation, thus causing a severe decrease of catalytic activity. It is necessary to probe the changes in acidity of SO$_4^{2-}$/CeZr and 1.5Fe/SO$_4^{2-}$/CeZr catalysts before/after K poisoning. Herein, NH$_3$ temperature-programmed desorption combining with mass spectrum (NH$_3$-TPD-MS) was performed to study the acidic properties of catalysts (Figure 2A). The NH$_3$ desorption peaks below 300°C on all the catalysts are attributed to the weakly acidic sites, and the peaks above 300°C are attributed to the strongly acidic sites (Park et al., 2016). K poisoning obviously decreases the amount of weakly acidic sites over SO$_4^{2-}$/CeZr and 1.5Fe/SO$_4^{2-}$/CeZr. The quantitative analysis of NH$_3$-TPD-MS reveals that the total acid amount of SO$_4^{2-}$/CeZr decreases from 292.2 to 182.9 mmol/g (decrease by 37.4%), whereas that of 1.5Fe/SO$_4^{2-}$/CeZr decreases from 257.6 to 115.2 mmol/g (decrease by 55.3%) after K poisoning. The fresh 1.5Fe/SO$_4^{2-}$/CeZr (257.6 mmol/g) owns less acidity than the fresh SO$_4^{2-}$/CeZr (292.2 mmol/g) likely because FeOx species occupy some SO$_4^{2-}$ acidic sites. The acid amount of 1.5Fe/SO$_4^{2-}$/CeZr decreases more severely than SO$_4^{2-}$/CeZr (decrease by 55.3% versus 37.4%) after K poisoning, which is likely because more weakly acidic sites derived from Fe-OH are lost (Sugawara et al., 2007). This is also evidenced by that K/1.5Fe/SO$_4^{2-}$/CeZr almost lost all the weak acid but K/SO$_4^{2-}$/CeZr still possesses some weak acid (Figure 2A). It is notable that the total acid amount of K/1.5Fe/SO$_4^{2-}$/CeZr is even less than K/SO$_4^{2-}$/CeZr, implying that the acid amount is not the essential reason for the strong K resistance of 1.5Fe/SO$_4^{2-}$/CeZr catalysts. Besides, SO$_2$ signal (m/z = 64) was observed above 600°C over all fresh and K-poisoned catalysts during NH$_3$-TPD-MS (Figure S8), indicating that SO$_4^{2-}$ strongly bonds on CeZr catalysts and is thermally stable during the whole SCR active temperature region (<500°C).
As mentioned above, the acid amount is notably reduced for K-poisoned 1.5Fe/SO\textsubscript{4}\textsuperscript{2−}/CeZr. One question arises: Does the increased redox property associated with Fe decoration improve the alkali resistance? To check the changes of redox properties along with Fe decoration, H\textsubscript{2} temperature-programmed reduction (H\textsubscript{2}-TPR) and X-ray photoelectron spectroscopy (XPS) were carried out for Fresh and K-poisoned catalysts. As shown in Figure 2B, SO\textsubscript{4}\textsuperscript{2−}/CeZr shows two fitted reduction peaks around 600°C, which are related to the reduction of CeO\textsubscript{2} that is not interacted with ZrO\textsubscript{2} (low-temperature peak) and CeO\textsubscript{2} that is strongly interacted with ZrO\textsubscript{2} (high-temperature peak), respectively. After K poisoning, the two reduction peaks of SO\textsubscript{4}\textsuperscript{2−}/CeZr shift to lower temperatures (around 540°C), which implies K as an electron donating promoter facilitates the CeO\textsubscript{2} reduction. Compared with SO\textsubscript{4}\textsuperscript{2−}/CeZr, the two fitted reduction peaks of 1.5Fe/SO\textsubscript{4}\textsuperscript{2−}/CeZr shift to much lower temperatures (around 450°C), in which the low-temperature peak is likely related to the FeO\textsubscript{x}/CeO\textsubscript{2} reduction and the high-temperature one is attributed to the CeO\textsubscript{2} reduction (Liu and He, 2010). With increasing the amount of Fe to 3 wt % Fe and 5 wt % Fe, the reduction peaks further shift to lower temperatures of ~440°C and ~420°C, respectively (Figure S9). These results indicate that the strong interaction between Fe and Ce facilitates the reduction of CeO\textsubscript{2}. The reduction peaks of FeO\textsubscript{x}/CeO\textsubscript{2} of 1.5Fe/SO\textsubscript{4}\textsuperscript{2−}/CeZr catalysts after K poisoning shift from ~450°C to ~440°C, and the third peak reduction around 510°C appears, indicating that K poisoning improves the reduction of FeO\textsubscript{x}/CeO\textsubscript{2} species but meanwhile impairs the interaction between Fe and Ce to some extent, which restrains the reduction of CeO\textsubscript{2}. The reduction of CeO\textsubscript{2} over K poisoned 1.5Fe/SO\textsubscript{4}\textsuperscript{2−}/CeZr is still more reducible compared with K-poisoned SO\textsubscript{4}\textsuperscript{2−}/CeZr according to the highest reduction temperature of CeO\textsubscript{2} (510°C for K/1.5Fe/SO\textsubscript{4}\textsuperscript{2−}/CeZr versus 550°C for K/SO\textsubscript{4}\textsuperscript{2−}/CeZr). These indicate that the reducibility is improved over Fe-decorated SO\textsubscript{4}\textsuperscript{2−}/CeZr catalysts and K poisoning further enhances the reducibility to some extent. Via analyzing X-ray photoelectron spectroscopy (XPS) of Ce 3d, K-poisoned SO\textsubscript{4}\textsuperscript{2−}/CeZr and 1.5Fe/SO\textsubscript{4}\textsuperscript{2−}/CeZr both show higher Ce\textsuperscript{3+}/(Ce\textsuperscript{3++Ce\textsuperscript{4+}) ratio than fresh ones (Figure 2C) (Han et al., 2019b), which is attributed to that K as an electron donating promoter reduces the valence of Ce species. Although the fresh 1.5Fe/SO\textsubscript{4}\textsuperscript{2−}/CeZr has less Ce\textsuperscript{3+} fraction than SO\textsubscript{4}\textsuperscript{2−}/CeZr, the K-poisoned 1.5Fe/SO\textsubscript{4}\textsuperscript{2−}/CeZr shows the highest Ce\textsuperscript{3+} fraction of 29.2%, which indicates that the electron-donating effects of K also facilitate the electron transfer from Fe to Ce. Generally, the formation of Ce\textsuperscript{3+} species brings out more oxygen vacancies, and the higher Ce\textsuperscript{3+} ratio with more oxygen vacancies improves the oxidizability. Moreover, the surface oxygen species also deliver a different evolution after K poisoning. It is generally recognized that the surface-adsorbed oxygen species (denoted as O\textsubscript{a}) are much more reactive in SCR reactions than the lattice oxygen species (denoted as O\textsubscript{L}). As shown in Figure 2D, the O\textsubscript{a}/O\textsubscript{L} ratio of SO\textsubscript{4}\textsuperscript{2−}/CeZr significantly decreases from 87.1% to 42.6% after K poisoning, whereas the O\textsubscript{a}/(O\textsubscript{a}+O\textsubscript{L}) ratio of K-poisoned 1.5Fe/SO\textsubscript{4}\textsuperscript{2−}/CeZr keeps at 93.7% that is almost unchanged with the fresh one (94.0%). This indicates that Fe decoration maintains the surface adsorption oxygen species that are active for the oxidation process for the SCR reaction. The O\textsubscript{2}-TPD results also evidence that the chemically adsorbed oxygen molecule anion (O\textsubscript{2}−) and oxygen anion (O\textsuperscript{−}) species are notably reduced over K-poisoned SO\textsubscript{4}\textsuperscript{2−}/CeZr but almost unchanged over K-poisoned 1.5Fe/SO\textsubscript{4}\textsuperscript{2−}/CeZr (Figure S10). The electron states of Fe, Zr, and S for alkali-poisoned SO\textsubscript{4}\textsuperscript{2−}/CeZr and 1.5Fe/SO\textsubscript{4}\textsuperscript{2−}/CeZr were also investigated. As the weak Fe 2p XPS signals of 1.5Fe/SO\textsubscript{4}\textsuperscript{2−}/CeZr and K/1.5Fe/SO\textsubscript{4}\textsuperscript{2−}/CeZr (Figure S11A), the Fe 2p XPS spectra of 5Fe/SO\textsubscript{4}\textsuperscript{2−}/CeZr before/after K poisoning were analyzed (Figure S11B). The fresh 5Fe/SO\textsubscript{4}\textsuperscript{2−}/CeZr possesses more Ce\textsuperscript{3+} fraction (22.97%) than the fresh 1.5Fe/SO\textsubscript{4}\textsuperscript{2−}/CeZr (14.64%), indicating more electron transfer from Fe to Ce. Additionally, K-poisoned 5Fe/SO\textsubscript{4}\textsuperscript{2−}/CeZr possesses higher Ce\textsuperscript{3+}/(Fe\textsuperscript{3+} + Fe\textsuperscript{3+}) ratio and Ce\textsuperscript{3+} fraction than the fresh one owing to the electron-donating effects of K. 1.5Fe/SO\textsubscript{4}\textsuperscript{2−}/CeZr has higher binding energy of Zr 3d\textsubscript{52} than SO\textsubscript{4}\textsuperscript{2−}/CeZr (Figure S12), indicating Fe likely gets electron from Zr owing to the strong interaction between Fe and Zr. After K poisoning, the Zr 3d\textsubscript{52} binding energy of both catalysts shifts to a lower value due to the electron-donating effects of K. Additionally, K poisoning does not change the valence of S species, which exist in SO\textsubscript{4}\textsuperscript{2−} species on all fresh and K-poisoned catalysts (Figure S13).

Based on the above results, K-poisoned 1.5Fe/SO\textsubscript{4}\textsuperscript{2−}/CeZr improves the reducibility and maintains the high oxidative capacity because of the facilitated electron transfer between K, Fe, Ce, and Zr as well as adequate Ce\textsuperscript{3+} and active oxygen species. As a comparison, the reducibility of K-poisoned SO\textsubscript{4}\textsuperscript{2−}/CeZr is not as good as K-poisoned 1.5Fe/SO\textsubscript{4}\textsuperscript{2−}/CeZr and the oxidative capacity of K-poisoned SO\textsubscript{4}\textsuperscript{2−}/CeZr is largely impaired owing to the notable decrease of active oxygen species. Therefore, the K-poisoned 1.5Fe/SO\textsubscript{4}\textsuperscript{2−}/CeZr shows stronger redox properties than K-poisoned SO\textsubscript{4}\textsuperscript{2−}/CeZr.

It has been demonstrated that the acidity decreases but the redox properties reserve over K-poisoned 1.5Fe/SO\textsubscript{4}\textsuperscript{2−}/CeZr catalysts. Why can the K/1.5Fe/SO\textsubscript{4}\textsuperscript{2−}/CeZr catalyst maintain high activity in spite of the decreased acidity? Differences in the reactivity of adsorbed NH\textsubscript{3} and nitrate species may be the possible reason. Therefore, the adsorption and activation characteristics of NH\textsubscript{3} and NO need to be probed. From the in situ DRIFTS of NH\textsubscript{3} desorption under various temperatures (Figure S14), the NH\textsubscript{3}+ and NH\textsubscript{3} species adsorbed on both SO\textsubscript{4}\textsuperscript{2−}/CeZr and 1.5Fe/SO\textsubscript{4}\textsuperscript{2−}/CeZr catalysts are not stable and easy
to desorb above 250°C. The NH₄⁺ (1,698, 1,472, and 1,438 cm⁻¹) (Huang et al., 2016, 2017; Wei et al., 2016) and NH₃ (1,369 cm⁻¹) (Zhang et al., 2018) species still exist on K-poisoned SO₄²⁻/CeZr at 300°C (Figures 3A and 3A1), indicating that the adsorption strength of these NH₄⁺ species becomes stronger after K poisoning. By comparison, fewer NH₄⁺ and NH₃ species adsorb on K/1.5Fe/So₄²⁻/CeZr at 300°C (Figures 3B and 3B1), implying that these NH₄⁺ species are likely more reactive because of their appropriate bonding strength. Additionally, in situ DRIFTS of NO + O₂ desorption under various temperatures were studied to investigate the adsorbed strength of NOx species. It can be seen that the NO₂, bidentate nitrate, monodentate nitrite, and metal-NO₂ species adsorb on SO₄²⁻/CeZr (Figure S15A), whereas the NH₄⁺, bridged nitrate, and bidentate nitrate species adsorb on Fe-decorated SO₄²⁻/CeZr catalysts (Figure S15B). With increasing temperatures, the NOx species adsorbed on 1.5Fe/So₄²⁻/CeZr are easier to desorb than on SO₄²⁻/CeZr, implying these species could react with NH₄⁺ species more easily. After K poisoning, K/So₄²⁻/CeZr catalysts show adsorbed NOx species including N₂O₄ (1,713 cm⁻¹) (Davydov, 2003), adsorbed NO₂ (1,629 cm⁻¹) (Liu et al., 2017), bidentate nitrate (1,498 cm⁻¹) (Davydov, 2003), and metal-NO₂ (1,367 and 1,333 cm⁻¹) (Davydov, 2003) (Figures 3C and 3C1). It is notable that the bidentate nitrate and metal-NO₂ species still adsorb on K/So₄²⁻/CeZr at 300°C and the strong bonding with catalyst likely reduces their reactivity. By comparison, the NO₂ (1,707 cm⁻¹), bidentate nitrate (1,517 cm⁻¹) (Davydov, 2003), and metal-NO₂ (1,330 cm⁻¹) (Davydov, 2003) species on K-poisoned 1.5Fe/So₄²⁻/CeZr desorb more easily than those on K-poisoned SO₄²⁻/CeZr catalysts (Figures 3D and 3D1). These results indicate that the reactivities of NOx species over K-poisoned 1.5Fe/So₄²⁻/CeZr are likely higher than those over K-poisoned SO₄²⁻/CeZr. Moreover, NO-TPD-MS (Figure S16A) and NO + O₂-TPD-MS (Figure S16B) results show that the amount of nitrate species adsorbed on SO₄²⁻/CeZr reduces after K poisoning, whereas those on 1.5Fe/So₄²⁻/CeZr increases after K poisoning. This indicates that Fe decoration helps to improve the formation of nitrate species over K-poisoned catalysts, which is likely due to the improvement of reducibility properties after K poisoning.

In order to further reveal the changes in the reactivity of adsorbed NH₃ and NOx, in situ DRIFTS transient reactions of adsorbed species were investigated at 250°C. Before K poisoning, the bidentate nitrates and metal-NO₂ species adsorbed on SO₄²⁻/CeZr and the NO₂, bidentate nitrates, and metal-NO₂ species adsorbed on 1.5Fe/So₄²⁻/CeZr are all reactive upon introducing NH₃ (Figures S17A and S17B). Notably, the reactivity of nitrate species on 1.5Fe/So₄²⁻/CeZr is much higher than that on SO₄²⁻/CeZr. The adsorbed NH₄⁺ and NH₃ species on fresh SO₄²⁻/CeZr and 1.5Fe/So₄²⁻/CeZr decrease slowly upon introducing NO + O₂, indicating the reactivity of NH₃ species over both catalysts is all relatively inactive, whereas the reactivity of NH₃ species on 1.5Fe/So₄²⁻/CeZr is slightly higher than that on SO₄²⁻/CeZr (Figure S18A and S18B). These results imply that Fe decoration relatively improves the reactivities of adsorbed nitrate and NH₃ species. After K poisoning (Figures 4A and 4A1), the NO₂ (1,696 cm⁻¹), bidentate nitrates (1,562 cm⁻¹) (Liu et al., 2017), and metal-NO₂ (1,384 cm⁻¹) (Davydov, 2003) species adsorbed on K/So₄²⁻/CeZr decrease slowly and meanwhile the NH₄⁺ (1,680 and 1,423 cm⁻¹) (Ma et al., 2014) and NH₃ (1,583 cm⁻¹) (Weng et al., 2016) species gradually increase with introducing NH₃, indicating the reactivity of nitrate species largely decreases compared with the fresh one. In contrast, the adsorbed bidentate nitrate (1,573, 1,559 cm⁻¹) (Hu et al., 2015a; Liu et al., 2018) and NH₃ (1,375 cm⁻¹) (Wang et al., 2016) species on K/So₄²⁻/CeZr become more reactive after K poisoning, whereas those on 1.5Fe/So₄²⁻/CeZr become more inactive after K poisoning. This indicates that Fe decoration helps to improve the formation of nitrate species over K-poisoned catalysts, which is likely due to the improvement of reducibility properties after K poisoning.
resistance. However, K-poisoned 1.5Fe/SO4\textsubscript{2}/CeZr reserves high reactivity of adsorbed nitrate species and especially largely improves the reactivity of adsorbed NH\textsubscript{x} species. Consequently, 1.5Fe/SO4\textsubscript{2}/CeZr exhibits a satisfactory alkali resistance in spite of the decreased acidic sites.

Figure 3. In situ DRIFTS of NH\textsubscript{3}/NO\textsubscript{x} Species Desorption over Catalysts as a Function of Temperature
In situ DRIFTS of NH\textsubscript{3} desorption and the corresponding mapping results over K/SO4\textsubscript{2}/CeZr (A and A1) and K/1.5Fe/SO4\textsubscript{2}/CeZr (B and B1) catalysts after exposure to a flow of 500 ppm NH\textsubscript{3} for 1 h at 300°C; in situ DRIFTS of NO + O\textsubscript{2} desorption and the corresponding mapping results over K/SO4\textsubscript{2}/CeZr (C and C1) and K/1.5Fe/SO4\textsubscript{2}/CeZr (D and D1) catalysts after exposure to a flow of 500 ppm NO + 5% O\textsubscript{2} for 1 h at 300°C.
DISCUSSION

Nowadays, it is generally believed that the decrease in acidity is the dominant reason for the deactivation of catalysts after alkali poisoning (Hu et al., 2015b; Putluru et al., 2011; Wang et al., 2015). Additionally, the impaired redox properties resulting from alkali poisoning also lead to the decline of activity, such as the reduced reducibility for K-poisoned V₂O₅-WO₃/TiO₂ (Wang et al., 2019) and decreased oxidative capacity for K-poisoned Mn/TiO₂ (Wei et al., 2018). Besides the reduced acidity and redox properties, the absence of active NOₓ species at low temperatures and the formation of inactive nitrate species at high temperatures result in the decreased activity of alkali-poisoned V₂O₅/CeO₂ (Peng et al., 2014). In this study, we found that the redox properties rather than acidity play decisive roles in improving the alkali resistance of some specific catalyst systems. It is demonstrated that the acid amount of K-poisoned Fe/SO₄²⁻/CeZr is lower than that of K-poisoned SO₄²⁻/CeZr; however, the SCR activity of the former one is much higher than that of the latter one. The K-resistant mechanism of Fe/SO₄²⁻/CeZr is revealed as shown in Figure 5. The essential reason is that the enhanced redox properties compensate for the reduced acidity of the K-poisoned Fe/SO₄²⁻/CeZr catalysts. K-poisoned Fe/SO₄²⁻/CeZr facilitates the electron transfer between K, Fe, Ce, and Zr while reserving plenty of Ce³⁺ and active oxygen species, which improves the reducibility and reserves the high oxidative capacity. As a result, K/Fe/SO₄²⁻/CeZr maintains the high reactivity of adsorbed nitrate species and notably improves the reactivity of adsorbed NHₓ species. The higher reactivity of NHₓ species makes up for the loss in quantity of NHₓ species, which is the key for the strong K resistance of Fe/SO₄²⁻/CeZr. Consequently, Fe/SO₄²⁻/CeZr maintains the high reaction efficiency between adsorbed NHₓ species and adsorbed nitrate species (L-H mechanism). Conversely, the acidity decreases and the redox circle is locked for the decreased oxidative capacity on K/SO₄²⁻/CeZr, which largely reduces the reactivity of nitrate species and NHₓ, leading to decreased activity. This work sheds light on a novel alkali-resistant mechanism via improving redox properties and activating the reactivities of NHₓ species rather than routinely increasing acidic sites for NHₓ adsorption. This study provides a unique perspective in designing an alkali-resistant deNOₓ catalysts, which is beneficial for their commercial, environmental, and industrial applications.

Limitations of the Study

More catalyst systems should be probed that can improve their alkali resistance via improving redox properties and activating the reactivities of NHₓ and nitrate species.
Resource Availability
Lead Contact
Further information and requests for resources and reagents should be directed to and will be fulfilled by the Lead Contact, Dengsong Zhang (dszhang@shu.edu.cn).

Materials Availability
All unique/stable reagents generated in this study are available from the Lead Contact without restriction.

Data and Code Availability
All relevant data are available from the corresponding author (dszhang@shu.edu.cn) upon reasonable request.

METHODS
All methods can be found in the accompanying Transparent Methods supplemental file.

SUPPLEMENTAL INFORMATION
Supplemental Information can be found online at https://doi.org/10.1016/j.isci.2020.101173.

ACKNOWLEDGMENTS
We acknowledge the support of the National Natural Science Foundation of China (21722704; 21976117; 21906102), the National Key R&D Program of China (2017YFE0132400), the Shanghai Sailing Program (19YF1415300), and the China Postdoctoral Science Foundation (2018M630426).

AUTHOR CONTRIBUTIONS
D.Z. designed the experiments, supervised the projects, and contributed to the revision of this paper. M.N.K. and L.H. contributed equally to this work. They performed catalyst preparation and catalyst characterizations, prepared the figures, and co-wrote the manuscript. P.W. analyzed the experimental results. All authors discussed the results, drew conclusions, and commented on the manuscript.

DECLARATION OF INTERESTS
The authors declare no competing interests.

Figure 5. Schematic Diagram of the Deactivation Mechanism over K/\text{SO}_4^{2-}/\text{CeZr} and Alkali-Resistant Mechanism over K/\text{Fe}/\text{SO}_4^{2-}/\text{CeZr} Catalysts.
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Supplemental Information

Tailored Alkali Resistance of DeNO_x Catalysts
by Improving Redox Properties
and Activating Adsorbed Reactive Species

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Figure S1. NO conversion during the SCR reaction over CeZr and K-poisoned CeZr catalysts. Reaction conditions: 500 ppm NO, 500 ppm NH$_3$, 5 vol % O$_2$, N$_2$ as the balance gas, and GHSV of 100000 h$^{-1}$, Related to Figure 1.
Figure S2. NO conversion during the SCR reaction over 1.5Fe/CeZr and K-poisoned 1.5Fe/CeZr catalysts. Reaction conditions: 500 ppm NO, 500 ppm NH₃, 5 vol % O₂, N₂ as the balance gas, and GHSV of 100000 h⁻¹. Related to Figure 1.
Figure S3. NO conversion during the SCR reaction over various catalysts. Reaction conditions: 500 ppm NO, 500 ppm NH$_3$, 5 vol % O$_2$, N$_2$ as the balance gas, and GHSV of 100000 h$^{-1}$, Related to Figure 1.
Figure S4. N$_2$ selectivity during the SCR reaction over fresh and K-poisoned SO$_4^{2-}$/CeZr and Fe/SO$_4^{2-}$/CeZr catalysts. Reaction conditions: 500 ppm NO, 500 ppm NH$_3$, 5 vol % O$_2$, N$_2$ as the balance gas, and GHSV of 100000 h$^{-1}$, Related to Figure 1.
Figure S5. XRD patterns of fresh and K-poisoned $\text{SO}_4^{2-}$/CeZr and 1.5Fe/$\text{SO}_4^{2-}$/CeZr catalysts, Related to Figure 2.

XRD patterns of all catalysts show the cubic fluorite phase of CeO$_2$ (Zhang et al., 2017). No characteristic diffraction peak of ZrO$_2$ are observed likely due to the formation of Ce-Zr solid solution.
Figure S6. Raman spectra of fresh and K-poisoned SO$_4^{2-}$/CeZr and 1.5Fe/SO$_4^{2-}$/CeZr catalysts, Related to Figure 2.

All catalysts show two bands around 460 cm$^{-1}$ and 620 cm$^{-1}$. The band around 460 cm$^{-1}$ was attributed to the F2g vibration of the fluorite-type lattice, which is a symmetric breathing mode of the oxygen atoms around cerium ions. The band near 620 cm$^{-1}$ is likely attributed to a nondegenerate longitudinal optical mode of ceria (Reddy et al., 2003). No Zr-related bands are observed due to the formation of Ce-Zr solid solution.
Figure S7. SEM elemental mappings of the representative K/1.5Fe@SO₄²⁻@CeZr catalyst. Related to Figure 2.
Figure S8. The profiles of SO$_2$ ($m/z=64$) detected from the NH$_3$-TPD-MS for different catalysts, Related to Figure 2.
Figure S9. H$_2$-TPR profiles of 1.5Fe/SO$_4^{2-}$/CeZr, 3Fe/SO$_4^{2-}$/CeZr and 5Fe/SO$_4^{2-}$/CeZr catalysts, Related to Figure 2.

With increasing the amount of Fe, the reduction peaks of further shift to lower temperatures, but the FeO$_x$ reduction peak (low-temperature peak) does not increase, indicating more FeO$_x$ interacted with CeO$_x$ species and the reduction peak of FeO$_x$ may overlap with that of CeO$_x$. This results further evidence the existence of strong interaction between FeO$_x$ and CeO$_x$. 
Figure S10. \( \text{O}_2 \)-TPD profiles of different catalysts, Related to Figure 2.

All catalysts show three desorption peaks of \( \text{O}_2 \), which can be assigned to physically adsorbed oxygen \( \text{O}_2 \), chemically adsorbed oxygen \( \text{O}^{2-} \) and chemically adsorbed oxygen \( \text{O}^- \) species (Li et al., 2011).
Figure S11. (A) The XPS spectra of 1.5Fe/\text{SO}_4^{2-}/\text{CeZr} and K/1.5Fe/\text{SO}_4^{2-}/\text{CeZr}; (B) The XPS spectra of 5Fe/\text{SO}_4^{2-}/\text{CeZr} and K/5Fe/\text{SO}_4^{2-}/\text{CeZr}, Related to Figure 2.

The Fe 2p spectra of catalysts are fitted into two peaks, which correspond to Fe$^{2+}$ (712.2 eV) and Fe$^{3+}$ (709.9 eV), respectively (France et al., 2017).
Figure S12. XPS spectra of Zr 3d over different catalysts, Related to Figure 2.

The Zr 3d spectra show Zr 3d$_{5/2}$ with binding energy around 183 eV, which corresponds to the Zr$^{4+}$ state (Sun et al., 2018). Fe decorated SO$_4^{2-}$/CeZr has higher binding energy of Zr 3d$_{5/2}$ than SO$_4^{2-}$/CeZr, indicating Fe likely gets electron from Zr due to the strong interaction between Fe and Zr. After K poisoning, the Zr 3d$_{5/2}$ binding energy of both catalysts shifts to a lower value, implying K as an electron donating promoter reduces the valence of Ce species.
The S 2p spectra of catalysts are fitted into two peaks at 169.4 eV and 168.6 eV, which are both attributed to SO$_4^{2-}$ species for S 2p$_{1/2}$ and S 2p$_{3/2}$, respectively (Zhao et al., 2019).
For SO$_4^{2-}$/CeZr catalysts, NH$_4^+$ (1691, 1473, 1440 cm$^{-1}$) (Huang et al., 2017; Huang et al., 2016; Wei et al., 2016) and NH$_3$ (1357 cm$^{-1}$) (Zhang et al., 2018) species appear on SO$_4^{2-}$/CeZr catalysts after NH$_3$ adsorption, and gradually reduce with the increased temperature and only few NH$_4^+$ species are left at 250 $^\circ$C and 300 $^\circ$C. Similarly, NH$_4^+$ (1684, 1472, 1433 cm$^{-1}$) (Liang et al., 2016) and NH$_3$ (1601 cm$^{-1}$) (Zhang et al., 2018) adsorb on 1.5Fe/SO$_4^{2-}$/CeZr catalysts and gradually reduce with the increased temperature and few NH$_4^+$ and NH$_3$ species remain above 250 $^\circ$C. These results indicate that adsorbed NH$_x$ species are not stable above 250 $^\circ$C.
Figure S15. *In situ* DRIFTs of NO+O$_2$ desorption over (A) SO$_4^{2-}$/CeZr and (B) 1.5Fe/SO$_4^{2-}$/CeZr catalysts after exposure to a flow of 500 ppm NO + 5% O$_2$ for 1 h at 30 °C, Related to Figure 3.

For SO$_4^{2-}$/CeZr, N$_2$O$_4$ (1702 cm$^{-1}$) (Huang et al., 2017), bidentate nitrate (1536 cm$^{-1}$) (Hu et al., 2016), monodentate nitrite (1457 cm$^{-1}$) (Liu et al., 2018a), and metal-NO$_2$ (1398 cm$^{-1}$) (Davydov, 2003) species appear after NO+O$_2$ adsorption. These species gradually reduce with increasing the temperature. Similarly, N$_2$O$_4$ (1709 cm$^{-1}$), bridged nitrate species (1627 cm$^{-1}$) (Baltrusaitis et al., 2007) and bidentate nitrate (1520 cm$^{-1}$) (Davydov, 2003) species adsorbed on 1.5Fe/SO$_4^{2-}$/CeZr and gradually reduce with increasing the temperature. It is notable that nitrate species on 1.5Fe/SO$_4^{2-}$/CeZr desorb more easily than on SO$_4^{2-}$/CeZr, indicating the weaker adsorbed strength of the former one. This also implies the high reactivity of nitrate species on 1.5Fe/SO$_4^{2-}$/CeZr.
Figure S16. (A) NO-TPD-MS and (B) NO+O$_2$-TPD-MS profiles of fresh and K-poisoned SO$_4^{2-}$/CeZr and 1.5Fe/SO$_4^{2-}$/CeZr catalysts. NO signal ($m/z$=30) was detected during the NO$_x$-TPD process, Related to Figure 3.

For the NO-TPD-MS, fresh SO$_4^{2-}$/CeZr and 1.5Fe/SO$_4^{2-}$/CeZr catalysts show two NO$_x$ desorption peaks, and the one below 100 °C is attributed to the physically adsorbed NO and the one above 100 °C is related to chemically adsorbed NO$_x$ with higher thermal stability. The chemically adsorbed NO$_x$ obviously decreases for both K-poisoned SO$_4^{2-}$/CeZr and 1.5Fe/SO$_4^{2-}$/CeZr catalysts. It is notable that K/1.5Fe/SO$_4^{2-}$/CeZr shows one NO$_x$ desorption peak at 300 °C but no NO$_x$ desorption peak is found over K/SO$_4^{2-}$/CeZr above 200 °C, which will influence the formation of active nitrate species when O$_2$ exists.

For the NO+O$_2$-TPD-MS, the NO$_x$ desorption peaks below 150 °C could be attributed to the physically adsorbed NO$_x$ and the peaks above 150 °C were due to the chemically adsorbed monodentate nitrate, bridging nitrate or bidentate nitrate species (Lian et al., 2014). The adsorbed nitrate species over SO$_4^{2-}$/CeZr decreases after K-poisoning while those over 1.5Fe/SO$_4^{2-}$/CeZr increases after K-poisoning. This indicates that Fe decoration helps to improve the formation of nitrite species likely due to the improvement of redox properties after K-poisoning.
Figure S17. *In situ* DRIFTs of the transient reactions between NH₃ and pre-adsorbed NO+O₂ over (A) SO₄²⁻/CeZr and (B) 1.5Fe/SO₄²⁻/CeZr catalysts at 250 °C as a function of time, Related to Figure 4.

For SO₄²⁻/CeZr, bidentate nitrates (1555 cm⁻¹) (Hu et al., 2015) and M-NO₂ (1363 and 1328 cm⁻¹) (Davydov, 2003) species appear after the adsorption of NO+O₂, and these species gradually decrease and vanish after introducing NH₃ for 30 min. Meanwhile, NH₄⁺ species (1680 cm⁻¹) (Liang et al., 2016) increase with continuous introduction of NH₃. For 1.5Fe/SO₄²⁻/CeZr catalysts, N₂O₄ (1696 cm⁻¹) (Huang et al., 2017), bidentate nitrates (1559 cm⁻¹) and M-NO₂ (1376 cm⁻¹) (Davydov, 2003) species appear after the adsorption of NO+O₂, and these species gradually decrease within 5 min after introducing NH₃. Meanwhile, NH₄⁺ species (1682, 1426 and 1381 cm⁻¹) (Ma et al., 2014; Weng et al., 2016) and NH₃ (1575 cm⁻¹) (Yan et al., 2017) species gradually emerge. These results indicate that the adsorbed nitrate species are reactive over both catalysts, which can react with adsorbed NH₄⁺ or NH₃ species. Moreover, the reactivity of nitrate species over 1.5Fe/SO₄²⁻/CeZr is faster than that over SO₄²⁻/CeZr.
Figure S18. *In situ* DRIFTS of the transient reactions between NO+O₂ and pre-adsorbed NH₃ over (A) SO₄²⁻/CeZr and (B) 1.5Fe/SO₄²⁻/CeZr catalysts at 250 °C as a function of time, Related to Figure 4.

For SO₄²⁻/CeZr catalysts, NH₄⁺ (1683 and 1428 cm⁻¹) (Chen et al., 2016; Liu et al., 2014) and NH₃ (1598 and 1310 cm⁻¹) (Hu et al., 2015; Liu et al., 2018b) species appear after the adsorption of NH₃. The NH₃ species keep unchanged and NH₄⁺ species (1428 cm⁻¹) decrease slowly with introducing NO+O₂. Meanwhile, the bidentate nitrate (1541 cm⁻¹) (Hu et al., 2015) and M=NO₂ (1358 cm⁻¹) (Davydov, 2003) species gradually emerge with continuous introduction of NO+O₂. 1.5Fe/SO₄²⁻/CeZr catalysts show the adsorbed NH₄⁺ (1681 and 1430 cm⁻¹) and NH₃ (1592 cm⁻¹) species, in which the reactivity of NH₃ (1592 cm⁻¹) and NH₄⁺ species (1430 cm⁻¹) are faster than those on SO₄²⁻/CeZr. Meanwhile, bidentate nitrate (1541 cm⁻¹) and M=NO₂ (1378 cm⁻¹) species when introducing NO+O₂.
Table S1. Textural properties of fresh and K-poisoned SO$_4^{2-}$/CeZr and 1.5Fe/SO$_4^{2-}$/CeZr catalysts, Related to Figure 2.

| Catalyst               | Surface Area (m$^2$ g$^{-1}$) | Pore Volume (cm$^3$ g$^{-1}$) | Average Pore diameter (nm) |
|------------------------|-------------------------------|-------------------------------|-----------------------------|
| 1.5Fe/SO$_4^{2-}$/CeZr | 44.42                         | 0.055                         | 3.788                       |
| K/1.5Fe/SO$_4^{2-}$/CeZr | 66.29                        | 0.070                         | 3.708                       |
| SO$_4^{2-}$/CeZr       | 60.06                         | 0.064                         | 3.572                       |
| K/SO$_4^{2-}$/CeZr     | 70.37                         | 0.070                         | 3.497                       |

The Brunauer–Emmett–Teller (BET) surface area of SO$_4^{2-}$/CeZr and Fe/SO$_4^{2-}$/CeZr after K-poisoning both increases to some extent likely due to the contribution of K$_2$O nanoparticle on catalyst surface. The pore volume increases and the pore size decreases a little for both K-poisoned SO$_4^{2-}$/CeZr and Fe/SO$_4^{2-}$/CeZr because of the formation of micropore resulting from K$_2$O coverage.
Transparent Methods

Catalyst Preparation

CeZr mixed oxides were prepared by a co-precipitation method. Firstly, 3.25 g of Ce(NO$_3$)$_3$·6H$_2$O and 1.07 g of ZrOCl$_2$·8H$_2$O were dissolution in 100 mL of deionized water. Then ammonia solution was added till the pH reached to 10 and stirred the solution for 1h and then filtered and washed till pH became 7. The precipitate was then dried at 60 °C for 18 h and calcinated at 500 °C for 2 h.

SO$_4^{2-}$/CeZr was prepared by pretreating CeZr mixed oxides with H$_2$SO$_4$. 2 g of CeZr oxide powder was stirred in 0.5 M H$_2$SO$_4$ solution for 3 h and then filtered and dried for 12 h at 60 °C. Via analyzing the atom ratio from XPS results of SO$_4^{2-}$/CeZr, the molar ratio of SO$_4^{2-}$/Ce/Zr is 1/2/1.

xFe/SO$_4^{2-}$/CeZr was prepared by a wet impregnation method by dissolving x wt% of Fe(NO$_3$)$_3$·9H$_2$O (x= 0.75, 1.5, 3, 5 wt% ) in 20 ml of deionized water and then 2 g of SO$_4^{2-}$/CeZr was added. The catalyst was then dried at 60 °C and calcined for 500 °C for 2 h.

1 wt% of K$_2$O poisoned catalysts were prepared by a wet impregnation method. SO$_4^{2-}$/CeZr and xFe/SO$_4^{2-}$/CeZr were impregnated with a specific amount of potassium nitrate aqueous solutions followed by drying at 60 °C and then calcination at 500 °C for 2 h. The catalysts are named as K-SO$_4^{2-}$/CeZr and K-xFe/SO$_4^{2-}$/CeZr, respectively.

Characterization

The X-ray diffraction (XRD) experiments were carried out on a Rigaku D/MAS-RB X-ray diffractometer with Cu Kα (40 kV, 40 mA) radiation, and the XRD patterns were recorded in the 2θ range of 10° to 90° with a scan rate of 8 °/min.

The Raman spectra were recorded on the LabRAM HR Evolution. The Raman spectra were acquired in the range of 100~900cm$^{-1}$ using a laser with a wavelength of 532 nm and the spectral resolution employed was 4 cm$^{-1}$.

The scanning electron microscope mapping was conducted on the scanning electron microscope (ZEISS SIGMA300) with an energy dispersive detector (Oxford AZtecX-MaxN 50).

The nitrogen adsorption-desorption isotherm of the samples was measured at -196 °C using an automatic surface and pore size analyzer (Autosorb-IQ2, Quantachrome Corporation)

The acid amount of the catalysts was measured by ammonia temperature-programmed desorption-mass spectrum (NH$_3$-TPD-MS) using a chemisorption analyzer (TP-5080, Xianquan Industrial and Trading Co., Ltd) and an online mass spectrometer (OMNISTAR, Pfeiffer). Prior to the TPD experiments, 100 mg catalysts were outgassed under He protection (30 ml/min) at 300 °C for 30 min and then cooled to room temperature. Samples were exposed to 10% NH$_3$/N$_2$ for one hour at room temperature, the physical adsorption of ammonia was removed by He purging for 1 h at the same temperature. Finally, the temperature was raised to 800 °C with a ramping rate of 10 °C/min. The acid amount was quantitated based on the intensity of desorbed NH$_3$ signal (m/z=17) from NH$_3$-TPD-MS and the pulse of specific amounts of NH$_3$. 
The X-ray photoelectron spectroscopy (XPS) systems (PHI-5300) 48 with Mg-Kα radiation were used to detect the surface atomic valence. The binding energies Ce and O were referenced to the adventitious C 1s line at 284.6 eV and the peaks were fitted by Avantage Software.

The reducibility of catalysts was measured by hydrogen temperature-programmed reduction (H₂-TPR) by using Micromeritics AutoChem II Chemisorption Analyzer, 2920.

O₂-TPD, NO-TPD and NO+O₂-TPD were measured by a chemisorption analyzer (TP-5080, Xianquan Industrial and Trading Co., Ltd) and an online mass spectrometer (OMNISTAR, Pfeiffer). Prior to the TPD experiments, 100 mg catalysts were outgassed under He protection (30 ml/min) at 300 °C for 30 min and then cooled to room temperature. Samples were exposed to 5% O₂/N₂, 500 ppm NO/N₂ or 5% O₂/N₂ + 500 ppm NO/N₂ for one hour at room temperature, the physical adsorption of ammonia was removed by He purging for 1 h at the same temperature. Finally, the temperature was raised to 800 °C with a ramping rate of 10 °C/min.

In situ diffuse reflectance infrared Fourier transform spectroscopy (In situ DRIFTS) experiments was carried out on a Nicolet 6700 spectrometer equipped with a Harrick Scientific DRIFTs cell and with a liquid nitrogen cooled mercury cadmium telluride (MCT) detector. The DRIFTs spectra were collected in the range of 1000-2000 cm⁻¹ in Kubelka-Munk format, accumulating scans at 4 cm⁻¹ resolution. Prior to each test, each sample was pretreated at 300 °C for 30 min under a 50 mL/min N₂ flow. The background spectrum at the desired temperature is collected after pretreatment, which be deducted from the sample spectra for each measurement. For the transient reactions, the catalysts were exposed to 500 ppm of NH₃ (or NO+O₂) at 250 °C for the adsorption. One hour later, the samples were switched to a flow of NO+O₂ (or NH₃), and meanwhile the reaction proceeded with time recorded. The test conditions: NO 500ppm, NH₃ 500ppm, O₂ 5 vol%, N₂ as the carrier gas.

Reactivity Tests
The SCR activity was conducted by using 0.3 mL of catalysts of 40-60 mesh. The condition of the gases for the reaction was adjusted as 500 ppm NO, 500 ppm NH₃, 5 vol% O₂, and N₂ as a balance gas where VM 4000 flue gas analyzer was used for the analysis of NOₓ concentration. The N₂ selectivity was measured by using FTIR, Antairs by Thermo Fisher. The sum of all the gases rate of flow was 500 mL/min and gas hourly space velocity (GHSV) was 100000 h⁻¹. The NO conversion percentage, N₂ selectivity and GHSV was calculated by using the following formula:

\[
\text{NO conversion (\%) = } \frac{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}}{[\text{NO}]_{\text{in}}} \times 100 \%
\]

\[
\text{N₂ selectivity (\%) = } \left(1 - \frac{2[\text{N₂O}]_{\text{out}}}{[\text{NO}]_{\text{in}} + [\text{NH₃}]_{\text{in}} - [\text{N₂O}]_{\text{out}} - [\text{NH₃}]_{\text{out}}} \right) \times 100 \%
\]

Where NOₓ stood for the total concentration of NO and NO₂. [NO]ₙᵢₙ, [NO]ₜₐₜ, [N₂O]ₜₐₜ, [NOₓ]ₙᵢₙ, [NOₓ]ₜₐₜ, [NH₃]ₙᵢₙ, and [NH₃]ₜₐₜ indicated the corresponding the inlet and outlet gas concentrations, respectively.

The GHSV was obtained by the following formula:

\[
\text{GHSV = } \frac{q_v}{vh^2}
\]

qᵥ corresponded to the total flow rate; h meant the height of the catalyst in the reactor; and r represented the inner radius of the reactor.
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