Bauxite-supported Transition Metal Oxides: Promising Low-temperature and SO\textsubscript{2}-tolerant Catalysts for Selective Catalytic Reduction of NO\textsubscript{x}

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In order to develop low-temperature (below 200 °C) and SO\textsubscript{2}-tolerant catalysts for selective catalytic reduction (SCR) of NO\textsubscript{x}, a series of cheap M/bauxite (M = Mn, Ni and Cu) catalysts were prepared using bauxite as a support. Their SCR performances are much superior to typical V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2}, the addition of M into bauxite results in significant promotion of NO\textsubscript{x} removal efficiency, especially at low temperature. Among the catalysts, Cu/bauxite exhibits wide temperature window over 50–400 °C, strong resistance against SO\textsubscript{2} and H\textsubscript{2}O as well as good regeneration ability in SCR of NO\textsubscript{x}. NO\textsubscript{x} conversion is more than 80% at 50–200 °C, and N\textsubscript{2} selectivity is more than 98%. Cu/bauxite can serve as a promising catalyst in SCR of NO\textsubscript{x}.

Nitrogen oxides (NO\textsubscript{x}) are considered as one of serious air pollutants, they are mainly emitted from automobile exhaust gas and industrial combustion of fossil fuels.\textsuperscript{1–3} To meet for more and more stringent regulations of NO\textsubscript{x} emission, several promising techniques including NO\textsubscript{x} storage and reduction (NSR) and selective catalytic reduction (SCR) have been proposed for NO\textsubscript{x} post-treatment.\textsuperscript{4–9} Among these techniques, SCR of NO\textsubscript{x} with NH\textsubscript{3} is an efficient process to remove NO\textsubscript{x} from diesel vehicles and stationary sources.\textsuperscript{4–9} Titania-supported vanadia with WO\textsubscript{3} or MoO\textsubscript{3} as promoters are typical commercial catalysts for SCR of NO\textsubscript{x}.\textsuperscript{6–10} Nevertheless, these catalysts usually suffer from some problems, such as toxicity of vanadium, SO\textsubscript{2} oxidation to SO\textsubscript{3}, over-oxidation of NH\textsubscript{3} to N\textsubscript{2}O, and employment within a high and narrow temperature window of 300–400 °C.\textsuperscript{11} Due to their high operating temperature, the catalysts are always located at upstream of purification system and/or desulfurization units, resulting in deactivation in the presence of high concentrations of dust and SO\textsubscript{2}.\textsuperscript{12–13} Thus, the development of SO\textsubscript{2}-tolerant SCR catalysts working below 200 °C has attracted considerable attention.

Noble metal-based catalysts are well known to possess good catalytic activity and high selectivity in low-temperature SCR of NO\textsubscript{x},\textsuperscript{14} but high price and scarcity of noble metal source have limited their extensive application and further development. Several groups of metal oxide-based catalysts have been reported to possess the advantages of low cost, high thermal stability and good activity for NO\textsubscript{x} reduction.\textsuperscript{15} Further improvement of overall SCR performances has also been realized through the judicial combinations of different metal oxides with potential catalytic activity.\textsuperscript{15,16} Although the mixed transition metal oxides show high SCR activity below 200 °C, their catalytic activity rapidly decreases in the presence of SO\textsubscript{2}.

It is proposed that SCR performances, sulfur tolerance and thermal stability of catalysts may be adjusted through formulation modification, structure adjustment and use of complicate supports.\textsuperscript{17–18} In the context, multi-metal oxides are widely used as the supports of SCR catalysts since they can provide superior general properties through synergetic interactions of their compositions.\textsuperscript{18–20} Bauxite is composed of Al\textsubscript{2}O\textsubscript{3}, FeO\textsubscript{2}, TiO\textsubscript{2}, SiO\textsubscript{2} and trace of Pt, these compositions are well known to be advantageous in NO\textsubscript{x} removal.\textsuperscript{21} In addition, natural bauxite is cheap, readily available and non-toxic, long period of natural evolution may offer it good stability. In our continuous effort to develop highly efficient and SO\textsubscript{2}-tolerant SCR catalysts,\textsuperscript{12–23} herein, we report a series of bauxite-supported transition metal oxides, M/bauxite (M = Mn, Ni and Cu), they show superior SCR performances over typical V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2}. NO\textsubscript{x} conversion in Cu/Bauxite is more than 80% in 50–200 °C, moreover,
Cu/bauxite shows high N\textsubscript{2} selectively, strong resistance against SO\textsubscript{2} and H\textsubscript{2}O as well as good regeneration ability in SCR of NO\textsubscript{x}.

**Results**

X-ray diffraction (XRD) pattern shows that bauxite possesses the characteristic peaks of crystalline γ-Al\textsubscript{2}O\textsubscript{3} (JCPDS No. 44-1487), Fe\textsubscript{2}O\textsubscript{3} (JCPDS No. 06-0502) and mullite phase (Figure 1). X-ray Fluorescence (XRF) and Inductively Coupled Plasma (ICP) analyses show the main compositions in the modified bauxite are Al\textsubscript{2}O\textsubscript{3}, Fe\textsubscript{2}O\textsubscript{3}, and SiO\textsubscript{2} (Table S2), which are in accordance with those from XRD patterns. After the addition of 3 wt% transition metal oxides, the surface area is decreased from 194 m\textsuperscript{2}/g to 130–138 m\textsuperscript{2}/g owing to the filling or blocking of partial pore. No phases of transition metal oxides are observed, suggesting that metal oxide species are finely dispersed on bauxite or they are too small to be detected by XRD analysis.

The surface valence state and concentration of M in M/bauxite were investigated by X-ray photoelectron spectroscopy (XPS) analysis. As shown in Figure 2, the binding energy peak of Cu 2p\textsubscript{3/2} at 934.1 eV and the shake-up satellite at 942.7 eV reveal Cu\textsuperscript{2+} are the predominant species in fresh Cu/bauxite. XPS spectrum of Ni 2p\textsubscript{3/2} indicates that Ni\textsuperscript{2+} (856.2 eV) is major phase in fresh Ni/bauxite,\textsuperscript{18} while XPS spectrum of Mn 2p\textsubscript{3/2} indicates that MnO\textsubscript{2} (642.2 eV) and Mn\textsubscript{2}O\textsubscript{3} (641.2 eV) are major phases along with the third phase (643.8 eV), which is attributed to incomplete decomposition of Mn nitrate owing to relatively low calcination temperature.\textsuperscript{18} As shown in Table S1, Cu/bauxite has the highest surface concentration of MO\textsubscript{x} species (1.86 mol%), which means that more CuO\textsubscript{x} species are available to participate in SCR of NO\textsubscript{x}. The surface ratio of NiO\textsubscript{x} in Ni/bauxite and MnO\textsubscript{x} species in Mn/bauxite are 1.72 and 1.15 mol%, respectively, regardless of the same loading in the preparation of the catalysts.

SCR performances of M/bauxite were initially evaluated using NH\textsubscript{3} storage capacity and NO\textsubscript{x} conversion.\textsuperscript{13} As shown in Table S3, the storage capacities at 50 °C in Mn/bauxite, Ni/bauxite and Cu/bauxite are 0.66, 0.69 and 0.84 mmol/g, which are much higher than 0.30 mmol/g in V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2}. As the temperature is elevated, their storage capacities are gradually lowered. As expected, bauxite itself possesses catalytic activity in SCR of NO\textsubscript{x} with NH\textsubscript{3}. NO\textsubscript{x} conversion is over 40% at 50–200 °C, which is slightly higher than that of V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} (Figure 3). The superior activity in bauxite probably results from the presence of Fe\textsubscript{3}O\textsubscript{4} and trace amount of Pt. The addition of Mn, Ni and Cu leads to significant improvement of NO\textsubscript{x} conversion, especially for Cu/bauxite, which is mainly attributed to the promotion effect of MO\textsubscript{x} species in the oxidation of NO to NO\textsubscript{2}, since NO\textsubscript{2} is more reactive than NO in SCR. More than 80% of NO\textsubscript{x} conversion at 50–200 °C can be achieved in Cu/bauxite, which almost reaches two times of that in bauxite and V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2}. When temperature is increased above 200 °C, the reduction ability of NO\textsubscript{x} in Cu/bauxite and Ni/bauxite is close to each other, their NO\textsubscript{x} conversion almost reaches 90% at 200 °C, and is more than 98% after 250 °C. For V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2}, NO\textsubscript{x} conversion begins to quickly increase after 200 °C, NO\textsubscript{x} conversion at 300–400 °C is more than 96%, which is close to

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**Figure 1** | XRD patterns of bauxite and M/bauxite.

**Figure 2** | XPS spectra for Mn 2p, Ni 2p and Cu 2p.
that in Cu/bauxite and Ni/bauxite. Interestingly, the light-off temperature (the temperature where NO\textsubscript{x} conversion reaches 50%, T\textsubscript{50}) is found to be less than 50 °C in M/bauxite, while it is around 250 °C in V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2}. SCR activity of Cu/bauxite is also compared with that of the reported Cu/zeolite or Fe/zeolite,\textsuperscript{13} higher NO\textsubscript{x} conversion at low-temperature and wider temperature window are shown in Cu/bauxite. The superior SCR performances in Cu/bauxite encouraged us to further investigate its selectivity. As shown in Figure S1, N\textsubscript{2} selectivity maintains about 98% in 50–400 °C, while selectivity of N\textsubscript{2}O is less than 2%.

The effect of inlet NO\textsubscript{2}/NO\textsubscript{x} ratio on SCR activity was also investigated in Cu/bauxite. As shown in Figure S2, NO\textsubscript{x} conversion of Cu/bauxite is gradually enhanced when NO\textsubscript{2}/NO\textsubscript{x} ratio is increased from 0.25 to 0.5, and reaches the maximum at 0.5, subsequent drop of NO\textsubscript{x} conversion is observed at 0.75 and 1.0. It was reported that when NH\textsubscript{3} and NO\textsubscript{2} were fed into the reactor, NH\textsubscript{4}NO\textsubscript{3} can be formed at low conversion is observed at 0.75 and 1.0. It was reported that when NH\textsubscript{3} and NO\textsubscript{2} were fed into the reactor, NH\textsubscript{4}NO\textsubscript{3} can be formed at low temperature (the temperature where NO\textsubscript{x} conversion reaches 50%, T\textsubscript{50}) and a large amount of H\textsubscript{2}O (2–15 vol%),\textsuperscript{15} the formation of sulfates and promote the decomposition of sulfates.\textsuperscript{3} After the supply of SO\textsubscript{2} was cut off, and the sulfated catalysts were regenerated by 3.5 vol% H\textsubscript{2}, NO\textsubscript{x} conversion in Cu/bauxite and V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} is gradually restored, suggesting both Cu/bauxite and V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} possess good regeneration ability after SO\textsubscript{2} poisoning, but Cu/bauxite is highly sulfur-resistant. NO\textsubscript{x} conversion was also examined in a feed gas containing 10 vol% H\textsubscript{2}O at 200 °C. The presence of H\textsubscript{2}O results in a quick decrement of NO\textsubscript{x} conversion from 89 to 75% in Cu/bauxite (Figure S4). After cutting off the supply of H\textsubscript{2}O, NO\textsubscript{x} conversion is rapidly restored to 89% at 200 °C.

In order to clarify correlation between redox properties and SCR activities, bauxite and M/bauxite were characterized by H\textsubscript{2} temperature-programmed reduction (H\textsubscript{2}-TPR). As shown in Figure S5, bauxite presents two broad reduction peaks similar to Fe\textsubscript{2}O\textsubscript{3}.\textsuperscript{24} The peak at 420 °C corresponds to the reduction of Fe\textsubscript{2}O\textsubscript{3} to Fe\textsubscript{3}O\textsubscript{4}, and the other peak at 683 °C is assigned as the reduction of Fe\textsubscript{2}O\textsubscript{3} to FeO and subsequent reduction to Fe, suggesting Fe\textsubscript{2}O\textsubscript{3} is main active component of NO\textsubscript{x} reduction in bauxite. In M/bauxite, the two reduction peaks shift to lower temperatures, especially for the peak at 420 °C, and they are in the following order: Cu/bauxite (326 °C) < Ni/bauxite (385 °C) < Mn/bauxite (392 °C). The shift of the reduction peaks and difference in the peak area between bauxite and M/bauxite are ascribed to synergetic effect between bauxite and M. The synergetic effect through electron transfer between M and Fe ions maintains a dynamic equilibrium, and enhances the activity of low-temperature SCR in M/bauxite. For example, Fe\textsuperscript{3+} can capture an electron from Mn\textsuperscript{2+}, and they become Fe\textsuperscript{2+} and Mn\textsuperscript{3+} by the electron transfer. The formation of Fe\textsuperscript{2+} is responsible for changing NH\textsubscript{3} to NH\textsubscript{2}. The generated Fe\textsuperscript{2+} will reduce O\textsubscript{2} into O\textsuperscript{2−} by donating an electron to O\textsubscript{2}, and simultaneously changes back to Fe\textsuperscript{3+} via 2Fe\textsuperscript{2+} + 1/2 O\textsubscript{2} ↔ 2Fe\textsuperscript{3+} + O\textsuperscript{2−}.

It should be mentioned that Cu/bauxite has two additional reduction peaks at 126 and 195 °C, which may be attributed to the reduction of surface and bulk Cu\textsuperscript{2+} to Cu\textsuperscript{+}, respectively. The peak at 270 °C is assigned as the reduction of NiO\textsubscript{2}, while no obvious reductive peak is observed in Mn/bauxite, because the reduction peak of MnO\textsubscript{2}/Mn\textsubscript{2}O\textsubscript{3} to MnO (300–400 °C) is overlapped with that of Fe\textsubscript{2}O\textsubscript{3} to Fe\textsubscript{3}O\textsubscript{4}. The reduction temperature of M in Cu/bauxite is much lower than that in Ni/bauxite and Mn/bauxite,

![Figure 3](image-url) | NO\textsubscript{x} conversion of M/bauxite and V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} at different temperatures.

![Figure 4](image-url) | SO\textsubscript{2}-tolerance and regenerability of Cu/bauxite and V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} at 200 °C (a) and 350 °C (b) as function of time.
which is responsible for excellent low-temperature SCR activity in Cu/bauxite.

The adsorption behavior of catalysts is known to substantially affect SCR performances of NOx. NOx temperature-programmed desorption (NOx-TPD) experiments were carried out in order to determine the adsorption capacity of NOx in bauxite and M/bauxite. As shown in Figure S6, two NOx desorption peaks at 153 and 345 °C are observed in bauxite, which are assigned to desorption of NOx and decomposition of surface adsorbed nitrite/nitrate species, respectively. It is noteworthy that a strong desorption peak of NOx is also observed in bauxite, suggesting that bauxite is able to oxidize NOx which would be beneficial for SCR at low temperature.22,23 The addition of Cu and Ni results in the increment of desorption temperature below 200 °C to 183 and 188 °C, respectively, while the desorption temperature of NOx in Mn/bauxite is decreased to 90 °C owing to weak interaction of NOx with small MnO2/Mn2O3 particles.27 Interestingly, the peak intensity in M/bauxite is greatly increased in comparison with that of bauxite, suggesting that Mn, Ni and Cu addition is favorable for NOx adsorption at low temperature. The desorption amounts of NOx are in the order: Cu/bauxite > Ni/bauxite > Mn/bauxite > bauxite (Table S1), and this trend is in good agreement with their SCR activity. However, the relative area of desorption peak above 300 °C is decreased in M/bauxite in comparison with that of bauxite, suggesting that Mn, Ni and Cu addition has no obvious effect on desorption temperature above 300 °C.

It is well known that surface acidity plays an important role in low-temperature SCR of NOx. NH3 temperature-programmed desorption (NH3-TPD) was performed to investigate the type, amount and strength of surface acid. As shown in Figure S7, the shapes of NH3 desorption profiles in M/bauxite are very similar to that in bauxite, in which two distinct desorption processes are presented. NH3 desorption peak at low temperature contains a shoulder peak at 250–400 °C. Obviously, the addition of Cu, Ni and Mn has no significant effect on desorption temperature below 200 °C. However, NH3 desorption amounts in Cu/bauxite and Ni/bauxite are almost similar to each other at low temperature, they are much larger than that in bauxite and Mn/bauxite (Table S1). The other desorption temperature above 500 °C in Mn/bauxite is higher than that in bauxite. Because NH3 bound to Lewis acid sites is more thermally stable than NH4+ ions coordinated to Bronsted acid sites, the desorption peak at low temperature is mostly assigned to NH4+ ions on Bronsted acid sites, while the desorption peak at high temperature is associated with the adsorbed NH3 on Lewis acid sites.28–30 In comparison with bauxite, the addition of M has no obvious effect on strength of Bronsted acid sites, but it causes an obvious increment of strength of Lewis acid sites in M/bauxite. Obviously, larger Bronsted acid amount and stronger Lewis acid strength in Cu/bauxite and Ni/bauxite are favorable for facilitating adsorption and activation of NH3 in SCR of NOx.

In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of NH3 adsorption was investigated to better understand properties of acid sites in bauxite and M/bauxite. As shown in Figure 5, with the increment of temperature, the peaks gradually become weak and almost disappear above 300 °C, which is probably ascribed to unstability of the adsorbed NH3 at high temperature. As for bauxite, two bands at 1245 and 1628 cm−1 are assigned to symmetric bending vibrations of the coordinated NH3 and molecularly adsorbed NH3 on Lewis acid sites, respectively. In comparison with bauxite, such bands in Cu/bauxite are slightly blue-shifted to 1250 cm−1 and red-shifted to 1624 cm−1, respectively. The redshift is attributed to the weakening of Cu–NH3 bond, while the blue shift corresponds to the strengthening of Cu–NH3 bond.31,32 For Ni/bauxite, only the latter band is red-shifted to 1622 cm−1. Mn/bauxite shows two bands at 1236 and 1239 cm−1 owing to the coordination of NH3 on Lewis acid sites. Other two bands at 1489 and 1438 cm−1 in bauxite may be assigned to NH2 vibration and anti-symmetric bending vibration of NH4+ ions on Bronsted acid sites, respectively.33,34 In Mn/bauxite, the band at 1387 and 1498 cm−1 are assigned to symmetrical bending vibrations of the coordinated NH3 and molecularly adsorbed NH3 on Lewis acid sites, respectively. In comparison with bauxite, such bands in Cu/bauxite are slightly blue-shifted to 1250 cm−1 and red-shifted to 1624 cm−1, respectively. The redshift is attributed to the weakening of Cu–NH3 bond, while the blue shift corresponds to the strengthening of Cu–NH3 bond.35,36 For Ni/bauxite, only the latter band is red-shifted to 1622 cm−1. Mn/bauxite shows two bands at 1236 and 1239 cm−1 owing to the coordination of NH3 on Lewis acid sites. Other two bands at 1489 and 1438 cm−1 in bauxite may be assigned to -NH2 vibration and anti-symmetric bending vibration of NH4+ ions on Bronsted acid sites, respectively.37,38 In Mn/bauxite, the band at 1387 and 1498 cm−1 represent -NH2 vibration on Bronsted acid sites. Additionally, the band at 1671 cm−1 indicates anti-symmetric bending vibration of NH4+ ions. It should be mentioned that Cu/bauxite and Ni/bauxite just show one peak of NH4+ at 1408 cm−1 and one peak of -NH2 vibration on Bronsted acid sites at 1370 cm−1, respectively.

In order to clarify correlation between SCR activity and acid sites in bauxite and M/bauxite, the amounts of Bronsted and Lewis acid

Figure 5 | in situ DRIFTS of NH3 adsorption in bauxite and M/bauxite.
sites were calculated based on in situ DRIFTS at 200 °C. As shown in Figure 6, the amount of Lewis acid sites is closely associated with SCR activity, while no such correlation is observed for Brønsted acid sites. The ratios of Lewis to Brønsted acid sites are in the order: Cu/bauxite (4.83) > Ni/bauxite (3.80) > Mn/bauxite (1.49) > bauxite (0.48) (Table S1). These results clearly indicate that Lewis acidity in M/bauxite is more important than Brønsted acidity for low-temperature SCR activity.

Discussion
In our work, a series of M/bauxite catalysts were presented for low-temperature and SO2-tolerant SCR of NOx, these catalysts are cheap, non-toxic and readily available. M and FeOx in M/bauxite are confirmed to be main active species in SCR of NOx. Interestingly, Cu/bauxite shows wide temperature window over 50–400 °C in SCR of NOx. NOx conversion is more than 80% at 50–200 °C, which is more than twice than that in V2O5/TiO2, while NOx conversion at 300–400 °C reaches above 98%. N2 selectivity at 50–400 °C is more than 98%. Moreover, Cu/bauxite exhibits strong resistance against SO2 and good regenerability in SCR of NOx, while V2O5/TiO2 was greatly deactivated in the presence of SO2. The superior SCR performance in Cu/bauxite are related to better low-temperature reducibility, larger desorption amounts of NOx and NH3 as well as more Lewis acidity amount. These results have shown Cu/bauxite is a promising SCR catalyst for low-temperature removal of NOx, which provides further incentive for investigation of practical application in low-temperature NOx abatement.

Methods
M/bauxite (M = Cu, Mn and Ni) were prepared by wet deposition method, and thermal-treatment natural bauxite was used a support.21 Bauxite (1.0 g) in continuous thermal treatment at 500 °C for 2 h. The obtained samples were denoted as M/bauxite (M = Cu, Mn and Ni). 3 wt% V2O5/TiO2 was prepared according to the modified literature methods.21

XRD patterns were recorded on a RIGAKU-Miniflex II X-ray diffractometer with CuKα radiation (λ = 1.5406 Å). N2 physisorption measurement was performed on an ASAP 2020 apparatus, the sample was degassed in vacuo at 180 °C at least 6 h before the measurement. XPS analysis was performed on Physical Electronics Quantum 2000, equipped with a monochromatic Al-Kα source (1486.6 eV) and a charge neutralizer; the catalysts were calcined at 400 °C before XPS test. The components of bauxite were determined using a PANalytical Axios XRF spectrometer with a rhodium tube as the source of radiation. The results were analyzed by IQ and the concentrations were normalized to 100%. ICP analysis was performed on a JY Ultima2 spectrometer.

H2-TPR was performed on AutoChem II 2920 equipped with a TCD detector. A sample of 0.1 g was pretreated in air (30 mL/min) at 500 °C for 0.5 h, and followed by purging with Ar (30 mL/min) for 0.5 h. After cooling to room temperature, the temperature was increased at 5 °C/min up to 800 °C by a temperature-programmed controller in gas flow of 10 vol% H2/Ar (30 mL/min). H2-TPR was measured from 50 to 800 °C at 5 °C/min.

NH3-TPD was conducted on an AutoChem 2920 equipped with a TCD detector. A sample of 0.1 g pretreated at an Ar flow of 500 mL/min at 500 °C for 2 h. After pre-treatment, the sample was exposed to 5.01% NH3/Ar for 30 min, followed by flushing with Ar for 1 h. After pre-treatment, the sample was exposed to a mixture gas of 540 ppm NO and 8 vol% O2/Ar balanced by N2 (total gas flow rate: 230 mL/min) until recovery of the inlet NOx concentration, followed by flushing with 8 vol% O2/Ar to remove weakly adsorbed NOx species until the disappearance of NOx species in 8 vol% O2/Ar stream. NOx-TPD experiment was carried out from room temperature to 600 °C in a N2 flow at a rate of 3 °C/min. The outlet gas flow was continuously monitored using chemiluminescence NO-NO2-NOx detector.

in situ DRIFTS spectra were recorded on a Nicolet Nexus FT-IR spectrometer in the range of 650–4000 cm−1 with 32 scans at a resolution of 4 cm−1. Prior to each experiment, the sample was pretreated at 350 °C for 0.5 h in a flow of N2 to remove any adsorbed impurities, and then cooled down to 50 °C. The background spectrum was collected in N2 and automatically subtracted from the sample spectra. Afterward, NH3 (500 ppm balanced with He) was introduced to the cell with gas flow rate of 30 mL/min at 100 °C for 1 h to ensure complete absorption saturation. Physisorbed ammonia was removed by flushing wafer with helium at 100 °C for 3 h. DRIFTS spectra were recorded by evacuation of ammonia at successive temperatures from 50 to 400 °C.

SCR activity measurement was performed in a fixed-bed stainless steel reactor (inner diameter = 8 mm), and a thermocouple was inserted in the center of catalyst bed to measure test temperature. Before each test, a 0.5 g 20–30 mesh sample was reduced by 5 vol% H2/Ar at 500 °C for 2 h, and followed by treatment using 3 vol% O2/Ar at 500 °C for 2 h. NH3 adsorption experiment was carried out in the temperature range of 50–200 °C using 500 ppm of NH3, and 2 vol% O2 balanced by Ar. At test temperature, the catalysts were placed in the reactor until outlet NO gas reached the expected equilibrium concentration, in order to ensure that the decrement of NO concentration was caused by SCR instead of the adsorption by the catalysts. The feed gas (500 ppm NO, 500 ppm NH3, 0.67 vol% O2 and 3 vol% Ar) was introduced using mass-flow controllers at a total flow rate of 600 mL/min, and the corresponding GHSV is 72,000 h−1. The outlet gas concentrations were collected until a steady state was achieved at the given temperature for 1 h. NOx resistance was examined by introducing 10 vol% H2 into feed gas at 200 °C. NO2 poisoning experiment was performed by exposing samples to feed gas containing additional 100 ppm SO2 at 350 °C. The sulfated samples were regenerated by 3.5 vol% O2/Ar at 500 °C for 60 min. The outlet NOx concentration was measured using on-line chemiluminescence NO-NO2-NOx analyzer (model 42i-HL, Thermo Scientific). The outlet NO2 was analyzed using an FTIR spectrometer (Nicolet Nexus 6700) with a heated, multiple-path gas cell. The NH3 selectivity was analyzed using a GC7820 A. NOx conversion under steady-state conditions for 1 h was calculated according to the following equation.

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\text{NOx conversion} (%) = \frac{\text{NOx inlet} - \text{NOx outlet}}{\text{NOx inlet}} \times 100%
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Transient response method (TRM) of Cu/bauxite was carried out at 150 °C according to literature methods.21 Before each test, a 0.1 g sample was pretreated in air flow (30 mL/min) at 500 °C for 0.5 h. After cooling to 150 °C, 500 ppm NO was introduced and the reactor was maintained at steady state for 30 min, then a feed gas of 500 ppm NO, 0.05 vol% O2 and 1 vol% H2 and 500 ppm NH3 balanced by Ar were introduced in the next step. The outlet NOx concentrations were continuously monitored by a mass spectrometer and UV analyzer.

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Author contribution

X.W. and W.W. prepared the sample; X.W. and R.W. designed the experiments and wrote the paper. X.W., Z.C. and W.W. performed the measurements and analyzed the data. All authors discussed the results and commented on the manuscript.

Additional information

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