Exposed metal oxide active sites on mesoporous titania channels: a promising design for low-temperature selective catalytic reduction of NO with NH₃†

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A subtle catalyst design is provided with stably incorporated binary catalytically active centers of CuO and MnO₂ on the surface wall of mesoporous TiO₂. Such unique features render these mesoporous composites highly promising in the low-temperature selective catalytic reduction of NO with NH₃, including high NO conversion efficiency, and superior H₂O and SO₂ resistance.

Nitrogen oxides (NOₓ), produced mainly by the combustion of coal and fossil fuels, have been considered as the major air pollutants leading to a series of environmental issues, including acid rain, ozone depletion, etc.¹ Selective catalytic reduction (SCR) of NOₓ by NH₃ is one of the most effective technologies for the elimination of NOₓ from stationary sources.¹–³ V₂O₅–WO₃ (MoO₃)/TiO₂ composites are widely used industrial NH₃-SCR catalysts, which present high NO conversion reduction efficiency and good SO₂ tolerance.⁴,⁵ However, the commercial catalysts have several drawbacks, such as the toxicity of vanadium species, poor N₂ selectivity, and relatively high operation temperature in a narrow range (300–400°C).⁶ Therefore, it is quite desirable to develop new catalysts with high activity at reaction temperatures lower than 200°C, which could be used in add-on units located downstream of the electrostatic precipitator and even the desulfurizer, and therefore, the reheating of the effluent gases could be avoided in this procedure.⁷,⁸

Among all of the catalysts reported for the low-temperature-SCR, multi-metal oxide catalysts have been considered as the very promising candidates because of the synergetic catalysis effects of different components.⁹–¹¹ Pappas and co-authors found that TiO₂ nanotubes can act as a good support to disperse the Mn oxides and show a superior resistance to SO₂ poisoning.¹² Due to the high oxygen storage ability and outstanding redox properties, the MnO-based and CuO-containing catalysts provide a relatively high conversion of NO₂ at low temperature.¹³,¹⁴ Additionally, the SCR performance of catalysts is highly dependent on the dispersion of accessible active centres and their interaction with the matrix.⁵ In comparison with the corresponding bulk hybrid materials, transition metal oxides (MO) with meso structures and highly dispersed Cu- and/or Mn-based active centres are more attractive candidates for NO₂ elimination at low temperature. Although some previously reported SCR catalysts have mesopores, their pore connectivity is poor and the dispersion homogeneity of active components is quite low.¹⁵ Therefore, it is imperative to develop a promising approach to rationally control the mesostructure of the multi-component MO system with highly accessible pore channels and well-distributed active centres in the supporting matrix (e.g. TiO₂).¹⁶–²⁰ Great challenges still remain in the controllable soft-templating synthesis of multicomponent MO with high dispersity of different components.²¹–²⁵ The main reason is the uncontrollable hydrolysis of different MO precursors in a multi-component synthesis system, leading to the difficulty to effectively control and match the cooperative assembly with amphiphilic templates.²⁶,²⁷

In order to simultaneously retain the ordered mesostructure, high crystallinity of pore walls, homogeneous distribution of MO and promising low-temperature-SCR properties as well, an effective acetic acid-assisted one-pot synthesis approach has been demonstrated in this study to construct ordered mesoporous titania supported MO composites (CuO/MnO₂–mTiO₂). The CuO and MnO₂ nanocrystals are highly distributed on the surface of the channels of mesoporous TiO₂. These features endow CuO/MnO₂–mTiO₂ composites with excellent performance for low-temperature SCR of NO with NH₃.

HCl and acetic acid are employed to act as acidic promoters for the hydrolysis of the titania precursor and complexing agent to retard the fast nucleation and growth of Cu- and Mn-based oxides, respectively. As a typical example, mesoporous...
0.4CuO-MnO$_2$–10TiO$_2$ (CuO: MnO$_2$: TiO$_2$ with the molar ratio of 0.4: 1: 10) composites can be obtained by using titanium butoxide, copper and manganese nitrate as MO precursors, F127 as a surfactant template, HCl as the catalyst and acetic acid as the chelating agent. The small-angle X-ray scattering (SAXS) pattern of the obtained 0.4CuO-MnO$_2$–10TiO$_2$ composite presents three well-resolved scattering peaks at q values of 0.606, 1.04 and 1.23 nm$^{-1}$, respectively, which can be indexed as the 100, 110 and 200 reflections associated with the highly ordered 2D hexagonal structure ($p6mm$) (Fig. 1A). The X-ray diffraction (XRD) pattern shows eight diffraction peaks assigned to the anatase phase (JCPDS 21-1272) with high crystallinity (Fig. 1B). It should be mentioned that no crystalline phases assigned to CuO and MnO$_2$ are detected due to the highly dispersed states of the ultrafine CuO and MnO$_2$ species in the mesoporous TiO$_2$ matrix (Fig. 1B and Fig. S1, ESI†). Additionally, the ratio of Cu/Mn/Ti is detected to be about 0.4: 1: 10, which further confirms the successful incorporation of Cu and Mn in the mesoporous frameworks (Tables S2 and S3, ESI†). More importantly, the high-angle annular dark field (HAADF) image from spherical aberration corrected scanning transmission electron microscopy (Cs-STEM) and the corresponding energy-dispersive X-ray spectroscopy (EDS) elemental mapping of Cu and Mn clearly demonstrate that most of the Cu and Mn components are homogeneously distributed on the pore walls of the mesoporous TiO$_2$ matrix (Fig. 1G).

The binding energies of Ti 2p$^{3/2}$ (459.4 eV), Cu 2p$^{3/2}$ (934.1 eV) and Mn 2p$^{3/2}$ (642.8 eV) in the X-ray photoelectron spectroscopy (XPS) analysis can mainly be assigned to Ti$^{4+}$, Cu$^{2+}$ and Mn$^{4+}$, respectively (Fig. 2A-C and Fig. S4, ESI†). Raman spectrum characterization further indicates that the composite is composed of CuO, MnO$_2$ and TiO$_2$ (Fig. S5, ESI†). H$_2$-temperature programmed reduction (H$_2$-TPR) shows a peak at 146 °C associated with the reduction of Cu ions coordinated to the oxygen atoms of TiO$_2$, suggesting that Cu is in strong interaction with the TiO$_2$ matrix (Fig. 2D). The peak at 203 °C can be attributed to the reduction of CuO particles, which is favourable for SCR in low temperature regimes. These phenomena are in good agreement with previous reports. In addition, the broad peak at approximately 275 °C is ascribed to the reduction of Ti$^{4+}$ to Ti$^{3+}$ and Mn$^{4+}$ to Mn$^{3+}$, because of the interaction of MnO$_2$ and TiO$_2$, implying that the MnO$_2$ can be incorporated into the lattice of TiO$_2$. The peak at 346 °C can be associated with the reduction of MnO$_2$ and the peak at 413 °C can be attributed to the reduction of Mn$_2$O$_3$ to Mn$_3$O$_4$. Due to the good dispersion of the supported MnO$_2$, the reduction of TiO$_2$ supported Mn species can be realized at lower temperature than bulk MnO$_2$ further confirming the significance of the interaction between supports and MnO$_2$. H$_2$-TPR analyses indicate that the mesoporous 0.4CuO–MnO$_2$–10TiO$_2$ composites exhibit excellent reduction ability, which is crucial for the high performance of the catalyst in the NH$_3$-SCR process.
reaction. The desorption peaks of NH$_3$-TPD at 120 °C and 294 °C are attributed to weak and strong absorbed NH$_3$ (Fig. S6, ESI†), associated with the Lewis and Bronsted acid sites, respectively.12

Through the facile acetic acid-assisted co-assembly approach, a series of ordered mesoporous MO with different molar ratios can be straightforwardly synthesized. It is worth noting that the prepared mesoporous MO (such as 0.4CuO–MnO$_2$–20TiO$_2$ and 0.4CuO–MnO$_2$–50TiO$_2$) possess highly ordered 2D hexagonal mesostructures (Fig. S7 and S8, ESI†), only pure titania phases (Fig. S9, ESI†), high surface areas, large pore volumes and narrow pore size distributions (Fig. S10 and Table S1, ESI†). These results clearly indicate that our one-pot acetic acid-assisted co-assembly method can be used as a versatile approach to synthesize mesoporous MO with ordered mesostructures, high crystallinity and homogenous distribution of the components.

On the basis of the above results, it is speculated that the formation of the mesoporous multicomponent MO follows a chelate-assisted co-assembly process, in which acetic acid acts as the chelating agent to avoid rapid hydrolysis of the MO precursors and mediate the surfactant assembly (Fig. 3). Firstly, titanium butoxide was hydrolysed in an aqueous HCl/acetic acid/F127/Cu(NO$_3$)$_2$/Mn(NO$_3$)$_2$/ethanol solution to form titania oligomers. Sequentially, the hydrolysis and condensation can be decreased due to the replacement of hydrolyzable alkoxy oligomers. Sequentially, the hydrolysis and condensation can be decreased due to the replacement of hydrolyzable alkoxy groups by acetic acid.24 The titania oligomer can interact with the protonated and hydrophilic PEO segments of F127 via hydrogen bonding and co-assemble into an ordered mesostructure with the continuous evaporation of ethanol at 40 °C. Meanwhile, the acetic groups chelated with Cu$^{2+}$ and Mn$^{2+}$ inorganic species attach around the titania oligomer through the $^{\alpha}$H $^{\alpha}$X $^{\alpha}$I (S = surfactant, X = acetate and Cl$^{\alpha}$, I = Cu$^{2+}$ and Mn$^{2+}$) process via Columbic interactions.19 In this case, most of the Cu$^{2+}$ and Mn$^{2+}$ species chelated by acetic groups are preferentially located around the PEO domains. After removal of the F127 template, highly ordered mesoporous CuO/MnO$_2$–mTiO$_2$ composites with well-dispersed CuO and MnO$_2$ nanocrystals sitting on the surface of the pore channels were obtained. Significantly, the CuO and MnO$_2$ nanocrystals are dispersed homogeneously on the pore wall of the mesoporous TiO$_2$ channels because the acetic groups chelated with Cu$^{2+}$ and Mn$^{2+}$ inorganic species are mainly located much closer around the PEO domains than the titania oligomers. Such a striking feature of mesoporous CuO/MnO$_2$–mTiO$_2$ composites is very similar to previously reported iron oxide embedded in mesoporous carbons but partially exposed in the pore channels,33 which is extremely beneficial to catalytic applications.24,35

To explore the advantages of these mesoporous multicomponent oxides as a NO$_x$ removal catalyst, low-temperature NH$_3$-SCR reactions are carried out using mesoporous 0.4CuO–MnO$_2$–10TiO$_2$, 0.4CuO–MnO$_2$–20TiO$_2$ and 0.4CuO–MnO$_2$–50TiO$_2$. Similarly, the NO conversion increases with temperature but then decreases with further increase in temperature. It is found that mesoporous 0.4CuO–MnO$_2$–10TiO$_2$ displays the best catalytic performances for low-temperature NH$_3$-SCR, providing a superior NO conversion ability of 90% and a wide operating temperature range of 120–300 °C (Fig. 4A). The combination of CuO and MnO$_2$ within mesoporous TiO$_2$ also plays a vital role in the improvement of catalytic ability. Such synergistic effects give rise to the excellent NO conversion capability of 0.4CuO–MnO$_2$–10TiO$_2$ composites in comparison with 0.4CuO–10TiO$_2$, MnO$_2$–10TiO$_2$, and 0.4CuO–MnO$_2$/P25 catalysts (Fig. 4A and Fig. S11, ESI†).

Furthermore, the 0.4CuO–MnO$_2$–10TiO$_2$ catalyst was also tested in a wide gas hourly space velocity (GHSV) range (10 000–50 000 h$^{-1}$) at 120–160 °C. The NO conversion maintains a level over 90% even at GHSV as high as 30 000 h$^{-1}$ (Fig. 4B), which is mainly due to the high porosity and easily accessible catalytically active centres. The N$_2$ selectivity of mesoporous 0.4CuO–MnO$_2$–10TiO$_2$ is over 95% at a wide temperature range of 80–320 °C (Fig. 4C), demonstrating an effective conversion of NO$_x$ into N$_2$. The stability of the catalyst in SO$_2$ and H$_2$O was also studied, and only a slight decrease in NO conversion from 98% to 94% is observed after 1000 h of reaction (Fig. 4D).
observed when 2 vol% H2O is introduced into the stream (Fig. 4D). Notably, the NO conversion can be completely recovered to the initial value of 98%, and reach a stable conversion in the subsequent high-temperature process when the H2O stream is switched off, indicating an excellent retention behaviour for H2O. Moreover, even in the presence of SO2 and its mixture with H2O in the feed gases, the mesoporous 0.4CuO–MnO2–10TiO2 catalysts still display a NO conversion of 76% and increases to 83% when the injection of SO2 is interrupted. These outstanding catalytic performances with high NO conversion efficiency, good selectivity for N2, and excellent resistance to H2O and SO2 are ascribed to the unique structures and highly integrated mesoporous TiO2 supported by the multicomponent system with high surface areas, accessible and homogenously dispersed CuO and MnO2 with multivalent nature.36,37

In summary, a straightforward acetic acid-assisted co-assembly approach has been reported to controllably synthesize highly ordered mesoporous TiO2 with stably incorporated binary catalytically active centres of CuO and MnO2 on the pore wall. The designed mesoporous CuO/MnO2–mTiO2 composites present excellent catalytic performances with high NO conversion (> 90%) and superior H2O and SO2 resistance at low temperature (80–320 °C) for SCR of NO. It is expected that such a synthetic approach to mesoporous metal oxides with catalytically active sites located on the surface of the mesoporous channels can serve as a promising platform to design different functional mesoporous materials for various applications in adsorption, catalysts, batteries, sensors, etc.

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Conflicts of interest
The authors declare that there are no conflicts.

Notes and references
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