COMMUNICATION

Selective Catalytic Reduction of NO by Cerium-based Metal-organic Frameworks

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Cerium oxide clusters have been incorporated in a porous metal-organic framework to increase their activity for the selective catalytic reduction (SCR) of NO with NH₃. In addition, a new set of bimetallic MOFs, Ce_x/Zr-CAU-24, was synthesized to further enhance the acid properties and thus increase the SCR activity of the cerium sites.

Nitrogen oxides (NO_x, i.e. NO and NO₂, and N₂O) are major air pollutants that contribute to photochemical smog, acid rain, ozone depletion and the greenhouse effect.¹ They are mainly emitted by power plants and automobiles; increasingly stringent legislation imposes effective NO_x removal, which can be achieved via the selective catalytic reduction (SCR) with NH₃. Generally, NH₃-SCR requires a bifunctional catalyst, with both acidic and redox properties because the reaction mechanism is believed to consist of an acid cycle, in which ammonia is adsorbed, and a redox cycle that involves the oxidation of an NH₃ or NO derived species.² Finally, an intermediate with an N-N bond is formed, which decomposes to N₂ and H₂O. The catalytic cycle is closed by reoxidation of the redox site, which requires oxygen in the standard NH₃-SCR reaction (reaction 1). However, the reaction can also proceed under anoxic conditions when sufficient NO₂ is present, which is called “fast” SCR (reaction 2).³ In addition, some side reactions are known, such as the formation of N₂O, an undesired strong greenhouse gas.

Conventional SCR catalysts include transition-metal exchanged zeolites and complex mixtures of metal oxides such as the V₂O₅-

WO₃/TiO₂ catalyst.^{2,3} The toxicity of vanadium however calls for more environmentally friendly alternatives such as manganese oxide and ceria.⁴ CeO₂ is cheap and non-toxic but has been mainly investigated as SCR catalyst due to its excellent redox properties.⁵ It can easily switch between Ce⁴⁺ and Ce³⁺ resulting in very mobile oxygen atoms which can be stored and released (creating oxygen vacancies) via a redox change between the two oxidation states. Ceria is however in its pure form not a good NH₃-SCR catalyst because of its inherently weak Lewis acidity; so enhancing the number of acid sites by increasing the catalysts' surface area is an interesting strategy.⁶ High surface area ceria is however hard to synthesize and very prone to sintering; hence alternative highly dispersed ceria catalysts should be developed.⁷

Metal-organic frameworks (MOFs) are potentially porous and crystalline materials built up by metal (oxide) nodes connected through organic linkers.⁸ Their large concentration of metal nodes, exceptionally high surface area and tunable pore size and metal content makes them particularly interesting for catalysis, gas storage and separation.^{9–11} Several MOFs, such as MOF-74(M) (M = Cu, Mn, Co) and MIL-100(Fe), have already been reported for SCR but no Ce-MOFs have been studied, although they contain [Ce₆O₆]¹²⁺ clusters that can act as ceria nanoparticles.^{12–16} In addition, these Ce-MOFs are isorecticular to Zr-based frameworks with well-studied Lewis acid sites which are present either as defects (UiO-66), or as open site on an intrinsically undercoordinated cluster (NU-1000 or CAU-24).^{17–19}

Herein, we report the first NH₃-SCR reaction catalyzed by the Ce-MOFs Ce-UiO-66 and Ce-CAU-24 and their bimetallic Ce/Zr analogues. Ce-UiO-66 contains fully connected metal clusters in the ideal, defect-free framework, but the synthesized material has been reported with approximately one missing linker and thus one open site per cluster.¹² The [Ce₆O₈]⁸⁺ cluster in Ce-CAU-24 is 8-fold connected; hence four open sites per secondary building unit are expected.¹⁹ For the relatively new group of Ce-MOFs, the SCR reaction is an excellent test case to explore the reversible redox behavior of the clusters; MOFs that intactly

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survive redox changes of their metal building blocks are relatively rare.^{13,20–22}

Fig. 1. Comparison of Ce-MOFs with ceria: NO conversion (left) and NH_3 adsorption (right). The Ce-MOFs are tested up to their thermal stability limit. Reaction conditions: $[\text{NO}] = [\text{NH}_3] = 500$ ppm, $[\text{O}_2] = 10\%$; 30 ml/min (GHSV $\approx 9000 \text{ h}^{-1}$). Adsorption conditions: $[\text{NH}_3] = 500$ ppm.

Both MOFs outperform the commercially available CeO_2 catalyst and Ce-Uio-66 reaches significant NO decomposition at temperatures above 200°C (Fig. 1). Curiously, Ce-Uio-66 is more active than Ce-CAU-24, even though the latter should contain four times more open metal sites. Adsorption experiments in a 500 ppm NH_3 stream at 100°C however reveal that only $1/16^{\text{th}}$ of the open sites in Ce-CAU-24 are occupied by NH_3 , thus featuring a lower adsorption capacity than Ce-Uio-66 ($1/3^{\text{rd}}$ occupied). Both Ce-MOFs feature a much higher NH_3 adsorption than ceria, but their relative loss in NH_3 adsorption capacity with increasing temperature is larger, suggesting that Ce-MOFs contain relatively more weak acid sites. As a result, the Ce-MOFs' activities are, as for CeO_2 , very likely limited by their NH_3 adsorption capacity.⁶ Their N_2 selectivity however remains above 98% in the whole temperature range, indicating that the acidity is sufficient to avoid excessive overoxidation of NH_3 . Addition of 5% water to the gas mixture results in a reversible 30% activity drop of Ce-Uio-66 because its open metal sites render the material hydrophilic (Fig. S26).

The ammonia affinity of the Ce-MOFs could be improved by introducing the stronger Lewis acidic Zr^{4+} to the metal cluster. In addition, bimetallic Ce/Zr-MOFs can be operated in a broader temperature window because of their enhanced stability.²³ Ce/Zr-Uio-66 has already been reported but there was so far no sufficiently stable Ce/Zr-MOF with an undercoordinated secondary building unit (SBU) known. Therefore, we developed the synthesis of a new series of Ce/Zr-MOFs with scu topology: $\text{Ce}_x/\text{Zr-CAU-24}$. Four materials with Ce:Zr ratio of 10:90 ($\text{Ce}_{10}/\text{Zr-CAU-24}$), 16:84 ($\text{Ce}_{16}/\text{Zr-CAU-24}$), 29:71 ($\text{Ce}_{29}/\text{Zr-CAU-24}$) and 53:47 ($\text{Ce}_{53}/\text{Zr-CAU-24}$) were synthesized (details in SI) and their phase purity was confirmed by powder X-ray diffraction (PXRD) (Fig. 2, S2-5).

Fig. 2 PXRD patterns of the four new $\text{Ce}_x/\text{Zr-CAU-24}$ MOFs with $x = 53$ (top); 29 (top middle); 16 (bottom middle) and 10 (bottom). Right: 5-fold zoom of $5\text{--}25^\circ 2\theta$ region.

Similar to previously reported Ce/Zr-MOFs, the thermal stability of $\text{Ce}_x/\text{Zr-CAU-24}$ strongly increases when the Ce:Zr ratio drops below 16:84, i.e. one Ce atom per cluster on average, which was demonstrated by N_2 -physorption and PXRD after activation at 160°C (Fig. S7-8).²³ Furthermore, thermogravimetric analysis revealed that $\text{Ce}_x/\text{Zr-CAU-24}$ with a Ce:Zr ratio above 10:90 contains missing clusters, a defect type which, in contrast to missing linkers, decreases the number of open metal sites, and thus the SCR activity (Fig. S9-12).²⁴ Therefore, only $\text{Ce}_{10}/\text{Zr-CAU-24}$ and $\text{Ce}_{10}/\text{Zr-Uio-66}$, which contain Zr_6 and Zr_5Ce clusters, are compared to physical mixtures of Ce- and Zr-MOFs, denoted as Ce-Uio-66/Zr-Uio-66 and Ce-CAU-24/Zr-CAU-24, with the same metal ratio (Fig. 3).^{25,26}

Fig. 3 Comparison of $\text{Ce}_{10}/\text{Zr-MOFs}$ with physical Ce-MOF/Zr-MOF mixtures: NO conversion (left) and NH_3 adsorption (right). The MOFs are tested up to their thermal stability limit. The NH_3 adsorption of the all-Ce catalysts is also displayed as reference. Reaction conditions: $[\text{NO}] = [\text{NH}_3] = 500$ ppm, $[\text{O}_2] = 10\%$; 30 ml/min (GHSV $\approx 9000 \text{ h}^{-1}$). Adsorption conditions: $[\text{NH}_3] = 500$ ppm.

The mixed metal MOFs indeed feature a higher NH_3 adsorption capacity than their all-Ce analogues, demonstrating that their open sites are on average more acidic by virtue of the stronger Lewis acid zirconium. Furthermore, the nearly identical adsorption behavior of $\text{Ce}_{10}/\text{Zr-Uio-66}$ and Ce-Uio-66/Zr-Uio-66 suggests that the vicinity of the two metals does not influence the overall adsorption. However, $\text{Ce}_{10}/\text{Zr-CAU-24}$ features a lower ammonia adsorption at elevated temperatures than Ce-CAU-24/Zr-CAU-24. This can be rationalized by the

likely preferential location of the Ce atom in equatorial plane of the Zr_5Ce cluster of Ce_{10}/Zr -CAU-24, as has already been described for Ce/Zr -CAU-38 (Fig. 4).²⁶ The open metal sites of CAU-24 are situated in this equatorial plane, resulting in a higher Ce:Zr ratio in the accessible adsorption sites of Ce_{10}/Zr -CAU-24 and thus a decreased ammonia affinity.

Fig. 4 Schematic representation of Ce_{10}/Zr -UiO-66 with random missing linker defects (top) and Ce_{10}/Zr -CAU-24 (bottom) and their Zr_5Ce clusters (right). Zr = blue, Ce = yellow, O = red, C = gray, cluster μ_3 -oxygen and hydrogen atoms are omitted for clarity.

The tenfold dilution of redox active sites by zirconium results in a lower SCR activity (per mol catalyst) of Ce_{10}/Zr -UiO-66 and Ce -UiO-66/ Zr -UiO-66 compared to the all-Ce UiO-66 material. However, Ce_{10}/Zr -CAU-24 is above 150°C more active than Ce -CAU-24. This apparent discrepancy can be understood based on the need for a bifunctional catalyst: the stronger affinity of NH_3 for open Zr sites only improves the SCR activity if there is a nearby open Ce site, which is unlikely in Ce_{10}/Zr -UiO-66 because it on average contains only one open site (either Zr or Ce) per cluster. In contrast, every Ce site in Ce_{10}/Zr -CAU-24 is likely coordinatively unsaturated and has two neighboring open Zr sites which are sufficiently acidic, resulting in a greatly improved activity of the Ce ion.

The reaction orders of NO (1), NH_3 (0) and O_2 (0.07) over ceria are in accordance to literature and the absence of NO adsorption suggests an Eley-Rideal mechanism in which ammonia is first adsorbed and subsequently reacts with gaseous NO_x species to form N_2 (Fig. 5 and S23).²⁷ Similarly, the NO reaction order is 1 on Ce -UiO-66 and Ce_{10}/Zr -CAU-24 and NO adsorption is not observed (Fig. S24-25), suggesting that NO reacts from the gas phase. Remarkably, the NH_3 order is 0.25 on Ce -UiO-66 and ammonia adsorption is observed, confirming that the MOF's acidic adsorption sites are relatively weak. The ammonia order on Ce_{10}/Zr -CAU-24 is only 0.11, demonstrating the increased acidity of the bimetallic MOF. Ce-MOFs are known to solely undergo one-electron redox reactions so reoxidation

cannot occur through the conventional oxygen vacancy mechanism.¹³ Consequently, the oxygen order on Ce -UiO-66 (0.20) and Ce_{10}/Zr -CAU-24 (0.17) are slightly higher than on ceria but the exact interaction between oxygen and Ce^{3+} in the MOFs remains unclear.

Conversion in absence of one reactant can provide meaningful insights in the reaction mechanism (reaction conditions: 210°C; N_2 balance gas; 150 ml/min; 1000 mg CeO_2 or 200 mg Ce -UiO-66). When a 500 ppm NH_3 + 10% O_2 flow is sent over a ceria bed, no nitrogen oxides are formed nor is any ammonia conversion observed. Ce -UiO-66 however converts 10 ppm NH_3 but only 1 ppm NO and 0.1 ppm N_2O are observed at the reactor outlet, suggesting that NH_3 is mainly converted to N_2 by first oxidizing to NO_x , followed by reaction with another NH_3 molecule. The overoxidation of NH_3 could be rationalized by the weak acid site strength of Ce -UiO-66, meaning that the NH_3 is free to react, rather than being adsorbed on an acid site.

Under a 500 ppm NO + 500 ppm NH_3 flow in absence of O_2 , ceria converts approximately 23 ppm of NO, likely due to the stoichiometric generation of oxygen vacancies on the surface. In contrast, Ce -UiO-66 only converts 5 ppm, thereby indicating that stoichiometric reduction of Ce-MOFs is much harder, likely due to their inability to contain oxygen vacancies.

Based on literature reports and the above findings, we can suggest a simplified E-R reaction mechanism for both ceria and Ce-MOFs:

Ammonia is herein first adsorbed on an acid site and subsequently subjected to hydrogen abstraction. The oxidized NH_{2ads} species then reacts with gaseous NO and decomposes to N_2 and water. At last, the Ce^{3+} is reoxidized by oxygen. The slightly different behavior of Ce-MOFs compared to ceria can be attributed to the number and strength of the acid sites and the ability to generate oxygen vacancies in CeO_2 .

Conclusions

In conclusion, two Ce-MOFs, Ce -UiO-66 and Ce -CAU-24, were tested as NH_3 -SCR catalysts. They both outperform ceria because they feature a higher number of acid sites on which ammonia can be adsorbed. The acid strength of Ce-MOFs is believed to limit their activity; hence a new series of mixed-metal Ce/Zr-MOFs, denoted Ce_x/Zr -CAU-24, was developed. The thermally stable bimetallic Ce_{10}/Zr -CAU-24 with Zr_5Ce clusters features redox-active Ce sites surrounded by strongly acidic open Zr sites, resulting in a higher SCR activity than for Ce -CAU-24, irrespective of its much lower Ce content. Reoxidation of the MOF catalysts may however be hampered by their lack of oxygen vacancies, hence future research should focus on the synthesis of MOFs with bimetallic Ce/Zr SBUs that allow the creation of oxygen vacancies, while maintaining sufficiently acidic sites.

Fig. 5 Absolute NO and NH₃ decomposition (in ppm's) as function of a variable NO (left), NH₃ (middle) and O₂ (right) inlet concentration over ceria (top), Ce-Uio-66 (middle) and Ce₁₀/Zr-CAU-24 (bottom). Reaction conditions: 210°C; [NO] = 500 ppm, [NH₃] = 500 ppm, [O₂] = 10 %; 1000 mg CeO₂ or 200 mg MOF.

Conflicts of interest

There are no conflicts to declare.

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