

Room temperature reduction of NO without reductants on iron Metal-Organic Frameworks

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Significance and Relevance

For the first time, using theoretical modelling, material design, state-of-the-art investigation methods and mimicking enzymes, we have found that selected porous hybrid iron(II/III) based MOF materials are able to decompose NOx, at room temperature, in the presence of water and oxygen, into N₂ and O₂ and without reducing agents. These materials, stable up to 300°C, can be easily upscaled and washcoated for possible future industrial applications. This paves the way to the development of new highly sustainable heterogeneous catalysts to improve air quality.

Preferred and 2nd choice for the topic: Air cleaning and combustion; Automotive and stationary emission control

Preferred presentation: Oral only

Introduction and Motivations

Air pollution is an epochal concern, and is linked to combustion processes, leading to the emission of nitrogen oxides (NOx), which constitutes a critical environmental problem, and it can affect severely human health.¹ At ambient temperature and pressure, NOx decomposition is thermodynamically favoured; however, this process is kinetically inhibited, owing to a high activation energy. To date, no reported heterogenous catalyst possesses the required properties to lower the activation energy of this process without the help of co-reacting agents and high temperature. Nature resolves the denitrification problem with an assortment of different iron and copper based metalloenzymes,^{2,3} that sequentially reduce nitrate to dinitrogen via nitrogen oxide intermediates, e.g., nitrate reductase, nitrite reductase (NIR), nitric oxide reductase (NOR) and nitrous oxide reductase. However, the latter ones cannot be applied directly for the purification of polluted gases, as these molecular moieties can be activated only in liquid phase. Catalysts that are intended to mimic enzyme mechanisms should therefore have a similar configuration.

Materials and Methods

MOF samples were hydro/solvothermally prepared, then characterized by XRD, BET, FTIR, SEM, HRTEM, and *in situ* XANES. The cluster model calculations were carried out based on first principles density functional theory (DFT) calculations, implemented in DMol³ and Vienna Ab initio Simulation Package (VASP). Mechanistic insights were obtained via *operando* IR investigations.

Results and Discussion

The mesoporous iron(III) trimesate MIL-100(Fe) is a hydrothermally stable MOF built up from oxocentred trimers of iron(III) octahedra interconnected by 1,3,5-benzene tricarboxylate linkers giving rise to a mesoporous zeo-type architecture (Fig. 1).⁴ IR *in situ* analyses show that, after synthesis, this material presents only accessible Fe(III) sites. After activation in Ar at 250°C for 5h, the samples show the presence of Fe(II) sites as well, in the proportion of one Fe(II) per trimer. Under a gas reaction flow



typically containing 1000 ppm NO, 10% O₂, and 1% H₂O at room temperature, the untreated sample showed a partial conversion of NO into NO₂, whereas the sample containing mixed Fe(II)/Fe(III) sites showed a steady conversion of NO into stoichiometric amounts of N₂ and O₂, depending on the space velocity (for example, 34% at GHSV = 15000 h⁻¹). Experiments using isotopically labelled ¹⁵N¹⁸O confirmed the nitrogen and oxygen yield. Additionally, it was discovered that the presence of oxygen and water vapour in the flow is a necessary condition to induce the NO decomposition. EXAFS/XANES Synchrotron analysis, using similar *operando* conditions, confirmed the presence of Fe(II)/Fe(III) mixed sites as being essential for NO conversion. Further *operando* experiments allowed to propose a reaction mechanism dealing with the partial oxidation of NO into NO₂ (and a concomitant reduction of a Fe(III) into a (Fe(II) site), the formation of a N₂O₃ intermediate, followed by its decomposition into N₂O and O₂, with the nitrogen protoxide oxidising back the Fe(II) site into Fe(III) and providing the emission of dinitrogen.

This discovery allowed to find, for the first time, a catalyst able to decompose NO at room temperature and in the presence of oxygen and water, without the assistance of a reducing species. This represents a leap forward in the comprehension of the deNOx mechanism, and allows to bridge the gap between heterogeneous and enzymatic catalysis. Moreover, different complex problems in catalysis could be solved, in perspective, using a similar approach based on enzyme mimicking via highly tailorable materials as MOFs. Finally, this kind of catalysts can be envisaged to be used for air purification in specific confined polluted ambient, such as underground parking, tunnels, factories, cockpits, in-house etc.⁵



Figure 1: Schematic representation of the iron trimesate MIL-100(Fe) and the binding of NO over the iron metal sites. (a) A mesoporous cage of MIL-100(Fe). (b) A porous cage of MIL-100(Fe). (c) View of one hydrated trimer of iron(III) octahedra. (d) One dehydrated and defluorinated trimer of iron(II, III) octahedra. (e) Coordination of one NO molecule over one Fe(II)/Fe(III) model cluster.

References

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