prospect of NO_xRR will become increasingly important and more adoption of NH_3 within the energy mix will inevitably lead to more production of NO_x (specifically through combustion).

A range of materials and strategies have been employed to deliver high yields during NO_xRR. For instance, pristine Cu foam was reported generate NH_3 with a large yield of 517 $\mu molcm^{-2}h^{-1}$, albeit at a very high operating potential of -0.9 V vs reversible hydrogen electrode (RHE) in NO saturated 0.25M Li_2SO_4. Similarly, Cu centres within organic molecular complex exhibits an NH_3 production rate of $436 \pm 85\ \mu gh^{-1}cm^{-2}$ at a low potential of -0.4 V vs RHE. Very recently, defects such as oxygen vacancies are being reported to be beneficial for NO_xRR, owing to the improved binding of NO_3^- ions within the vacancies and as a result, defective TiO_2 catalyst, can generate ammonia with a yield of $0.05mmolh^{-1}mg^{-1}$. Despite this progress, there remains gaps in our understanding of the active sites that are responsible for nitrate reduction to ammonia, in place of the competing hydrogen evolution reaction(HER), that can also take place in the same reaction environment. Specifically, to the best of our knowledge, there remains no systematic investigation into the tuning of defects and coordination and correlating their performance for NO_xRR.

Summary

The disclosure provides a metal oxide catalyst in the form of nanoparticles, said metal oxide catalyst having engineered surface defects in the form of oxygen vacancy defects.

According to a first aspect, the disclosure provides a metal oxide catalyst comprising a metal oxide having engineered surface defects in the form of oxygen vacancy defects, wherein the catalyst is prepared by a process including a step of flame spray pyrolysis.

The metal may be any suitable metal, such as for example, a transition metal, a lanthanide metal or a post-transition metal. For preference, the metal is a transition metal such copper, or a lanthanide metal such as cerium, or a post-transition metal such as tin and bismuth. The disclosure will be disclosed and discussed herein with respect to copper as the metal, but it will be appreciated that it is equally applicable to other metals.

In some examples, the metal may be selected from copper, cerium, tin or bismuth. Alternatively, the metal may be selected from copper, cerium, or bismuth; or the metal may be selected from copper, cerium, or tin; or the metal may be selected from copper, tin or bismuth; or the metal may be selected from cerium, tin or bismuth. Alternatively, the metal may be selected from copper or cerium, or the metal may be selected from copper or tin; or the metal may be selected from copper, or bismuth; or the metal may be selected from cerium, or tin; or the metal may be selected from cerium or bismuth; or the metal may be selected from tin or bismuth.

When the metal is copper, the catalyst is CuO with oxygen vacancy defects. When the metal is cerium, the catalyst is CeO_2 with oxygen vacancy defects and when the metal is bismuth, the catalyst is Bi_2O_3

with oxygen vacancy defects.

If desired the metal oxide catalyst may be supported on a substrate, for example a carbon substrate, such as a carbon fibre paper substrate and carbon cloth.

The metal oxide catalyst of the present disclosure is broadly prepared by a two stage process, firstly,

preparation of a high surface area metal oxide in the metal's native oxidation state, and secondly plasma surface modification of the high surface area metal oxide to produce regions of oxygen deficiency (oxygen vacancy defects) at the metal oxide catalyst surface.

The metal oxide may be prepared by any conventional process for forming high surface area metal oxides. Examples include flame spray pyrolysis, electrodeposition, hydrothermal synthesis, precipitation etc. The disclosure will be disclosed herein with reference to flame spray pyrolysis, but it will be appreciated that any technique can be utilised to produce a high surface area catalyst.

The plasma surface modification can be conducted by any suitable plasma that can remove surface oxygen from the metal surface. For instance, the plasma may be a helium plasma, an argon plasma, a hydrogen plasma, a nitrogen plasma, an air plasma or mixtures thereof. For preference, the plasma is a helium plasma, argon plasma or a mixed plasma.

A high surface area refers to a catalyst having a high electrochemical surface area (ECSA). Those skilled in the art will be aware that the higher the ECSA the better. A high surface area catalyst would for instance have an ECSA greater than $10m^2/g$, preferably greater than $50m^2/g$ and more preferably greater than $100m^2/g$

Any suitable level of surface oxygen defect will catalyse the conversion of NOx to Ammonium.

The plasma treatment is applied for a time sufficient to create defects while maintaining morphology and crystallinity without inducing surface amorphization. Those skilled in the art will appreciate that a variety of experimental parameters, including the initial morphology of the metal oxide, will affect the exact etching time required to achieve and an optimal combination of oxygen defective sites without leading to surface amorphization or decreasing crystallinity or gelling, which removes accessible reduction sites on the catalyst surface. For a given metal oxide and prepared and etched under the same experimental regime, controlled variation of the etching time will enable the optimal surface vacancy to be determined.

For example, in the case of a CuO catalyst prepared by flame spray pyrolysis, the plasma treatment is optimally applied for 3-7 minutes, and more preferably, the plasma treatment is applied for 5 minutes.

The disclosure provides a method of producing a metal oxide catalyst for NOx reduction, the method comprising:

preparing a high surface metal oxide catalyst; and

plasma treating the metal oxide particle to induce a controlled level of defects.

According to another aspect, the disclosure provides a method of producing a metal oxide catalyst for NOx reduction, the method comprising:

preparing a metal oxide catalyst having engineered surface defects in the form of oxygen vacancy defects by a process including a step of flame spray pyrolysis.

According to another aspect, the disclosure provides a method of producing a metal oxide catalyst for NOx reduction, the method comprising:

preparing a metal oxide catalyst having engineered surface defects in the form of oxygen vacancy defects by a process including a step of flame spray pyrolysis; and

plasma treating the metal oxide particle to induce a controlled level of defects.

For instance, the disclosure provides a method of producing a CuO catalyst for NOx reduction, the method comprising:

preparing CuO nanoparticles by flame-spray pyrolysis; and

plasma treating the CuO nanoparticles to induce a controlled level of defects.

Preferably the flame spray pyrolysis for preparing CuO catalysts utilises an organochelated copper compound in a combustible solvent, for example, the organochelated copper compound is copper 2-ethylhexonate. The combustible solvent may be an aromatic hydrocarbon, such as xylene. Preferably, the organochelated copper compound has a concentration in the range of 0.1 – 1.0M, for example, the organochelated copper compound has a concentration in the range of 0.5M.

In one example, the flame spray pyrolysis deposits the CuO nanomaterial on a glass fibre filter.

According to another aspect the disclosure provides a metal oxide catalyst prepared by the method as described herein.

The disclosure provides a method of producing NH_4^+ from NOx comprising depositing a metal oxide catalyst as described herein, or a metal oxide catalyst prepared according to the method as described herein onto a substrate to provide an electrode, or a metal coordinated with nitrogen doped carbon, contacting the electrode with an aqueous solution containing NOx species and applying a current to the electrode to reduce NOx species to NH_4^+.

According to another aspect the disclosure provides a method of producing NH_4^+ from NOx comprising depositing a metal oxide catalyst as described herein, or a metal oxide catalyst prepared according to the method as described herein, onto a substrate to provide an electrode, or a metal coordinated with nitrogen doped carbon, contacting the electrode with an aqueous solution containing NOx species and applying a current to the electrode to reduce NOx species to NH_4^+/NH_3.

The nitrogen doped carbon may have any coordination structure, including but not limited to Cu-N4, Cu-N3-C1, Cu-N2-C2, Cu-N3-V1, Cu-N2-V2.

The method may further comprise the step of monitoring NOX reduction by analysis of NH_4^+ production in the aqueous solution.

According to another aspect the disclosure provides a method of producing NH_3 from NOx comprising depositing a metal oxide catalyst as described herein, or a metal oxide catalyst prepared according to the method as described herein onto a substrate to provide an electrode, contacting the electrode with an aqueous basic solution containing NOx species and applying a current to the electrode to reduce NOx species to NH_3.

The method may further comprise the step of monitoring NO_X reduction by analysis of NH_3 production in the aqueous basic solution.

The process may also be carried out in the gas phase, where NOx species and a hydrogen donor in gas form are passed over the catalyst of the present disclosure.

The NOx may be part of a waste stream.

Description of the Drawings

Figure 1. (a) Schematic displaying the closed loop nitrate reduction reaction pathway that can be used to convert waste NO_x (from powerplant, industry and wastewater) to NH_4^+ (which can be used as fertilizer or converted to NH_3 for use as feedstock). **(b)** Benchmarking ammonia production yield with our defective CuO with Li intermediary, eNRR systems and NO_xRR catalysts. **(c)** Economic modelling showing the importance of reducing cell voltage and increasing current density to lower the levelized cost of ammonia generation. **(d-f)** Theoretical results assessing the role of defects in catalyzing nitrate to ammonia and HER. **(d)** The pristine CuO (111) slab model used in DFT calculations and top view of the relaxed structures of CuO (111) surface with 1, 2 and 3 OVs, with the circles highlighting the missing