# Novel supported uranium oxide catalysts for $NO_x$ abatement

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**The catalytic reduction of NO has been studied over novel supported uranium oxide catalysts which exhibit comparable activity and selectivity to that of conventional supported Pt catalysts and for which *in situ* XRD identifies the active phase to be $UO_x$ ($2 < x < 2.25$).**

Emissions of NO and higher nitrogen oxides ($NO_x$) are the subject of stringent legislation as a result of their adverse environmental impact.[1] An effective method of reducing such emissions is to employ catalytic systems such as the three-way catalyst, currently installed in automotive vehicles, and selective catalytic reduction (SCR) of $NO_x$ by ammonia in stationary sources. Selectivity is a key issue since catalysts can reduce $NO_x$ to undesirable nitrous oxide ($N_2O$) instead of nitrogen. Nitrous oxide is now recognised as a contributor to the destruction of ozone in the stratosphere and has a high Greenhouse coefficient. Despite intensive research over many years few catalyst systems have been developed which exhibit both the desired levels of activity, selectivity and stability, together with high poison tolerances.

The potential of uranium oxides as catalytic materials has been reviewed by Collette *et al.*[2] Uranium is an actinide element and, with six valence electrons, is similar to chromium, molybdenum and tungsten. The ability to attain high coordination numbers makes for a promising catalytic material and indeed uranium has been used in applications such as Fischer–Tropsch synthesis, dehydrogenation and oxidation (ref. 2 and references therein). More recently, uranium oxides have been identified as candidates for the destruction of volatile organic compounds.[3,4] Uranium is reported to be a uniquely effective promoter of rhodium and platinum in three-way catalysts in the presence of high sulfur levels.[5–7] This study identifies uranium oxide derived catalysts for the selective reduction of nitric oxide.

Reactions were performed in a single-pass, fixed-bed microreactor. The reactor comprised a 10 mm i.d. silica tube located inside a Carbolite MTF furnace. Gas-flow rates were independently regulated by three mass-flow controllers (Hastings and MKS). An in-line filter (2 μm) was located downstream of the reactor to contain $UO_x$ dust particles. On-line analysis of reactant and product gas streams was performed using a Perkin-Elmer 8410 TCD gas chromatograph with a Carboxen 1000 (60/80 mesh) column. Quoted conversions are ±3% and selectivities are ±5%. The catalyst charge, of between 0.5 and 4 g (250–500 μm particle size), was supported inside the reactor on a silica wool bed. The catalyst temperature was read from an external thermocouple located adjacent to the catalyst bed. The feed gases used in this study included NO (99%), CO (99.99%) and He (99%). A constant GHSV of 2300 $h^{-1}$ (total gas flow rate of 70 ml $min^{-1}$) was employed in all experiments, using a 4% NO and 4% CO mixture with He balance. Before reaction, samples were heated to temperature under He (30 ml $min^{-1}$) before introducing reactants. *In situ* XRD spectra were acquired at BNFL Springfields using a Philips Expert MPD diffractometer and Cu-Kα radiation in conjunction with an Antonparr XRK cell equipped with Brooks mass-flow controllers. The scan range was $2\theta = 5$–50° in increments of 0.05°. Single point BET ($N_2$) surface areas were determined by standard $N_2$ adsorption for samples degassed at 200 °C.

Alumina supported catalysts were synthesised from solutions of uranium(VI) dinitrate hexahydrate, $UO_2(NO_3)_2 \cdot 6H_2O$ (Strem Chemicals 99.8%) as follows. First, $UO_2(NO_3)_2 \cdot 6H_2O$ (containing *ca.* 0.2% $^{235}U$) was dissolved in water to produce a 1.1 M solution (pH = 2). A known quantity of the support was dried and subsequently impregnated with the $UO_2(NO_3)_2 \cdot 6H_2O$ solution by the incipient wetness method. Finally, samples were dried for 24 h at 100 °C prior to calcination under flowing air for 3 h at either 450 or 800 °C. The support used was $\gamma$-$Al_2O_3$ (Alumina C, Degussa), with catalysts designated as $UO_x$(450 or 800). A third catalytic formulation, $UO_x(H_2)$, was obtained by reducing the 800 °C calcined sample under flowing hydrogen for 10 h at 523 °C as described by Madhavaram *et al.*[8] The nominal uranium oxide loadings (based on oxide stoichiometries discussed below) ranged between 26 and 29 wt%. Comparative experiments were also conducted with uranium(V,VI) oxide ($U_3O_8$ 99.8%), and a conventional 5 wt% Pt/$Al_2O_3$ Type 94 catalyst from Johnson Matthey. Before reaction, samples were heated under He (30 ml $min^{-1}$) to 450 °C for 1 h and cooled to reaction temperature. Steady-state was achieved and results obtained after > 1 h reaction.

In the absence of a reductant, the uranium-oxide catalysts, and the alumina support, were each inactive for direct NO decomposition at temperatures below 1000 °C. In contrast, following the introduction of CO the light-off curves shown in Fig. 1 were obtained. For simplicity, only results for the most active bulk $UO_x$ phase, which we have identified as $U_3O_8$, are included. The catalytic performance of the $UO_x(H_2)$ and $UO_x$(800) samples was indistinguishable, and hence only results for the $UO_x$(800) catalyst are shown.

The most striking aspect of the light-off curves is the substantial promotional effect of supporting uranium oxides on high surface area oxide supports. The temperature for 50% NO conversion ($T_{50}$) is decreased by up to 300 °C following $UO_x$

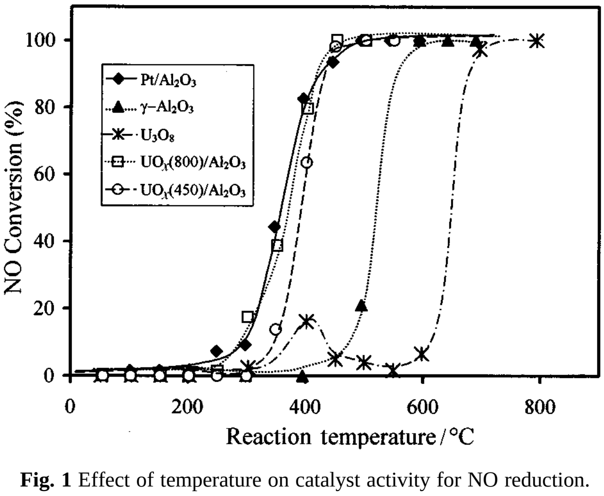

**Fig. 1** Effect of temperature on catalyst activity for NO reduction.

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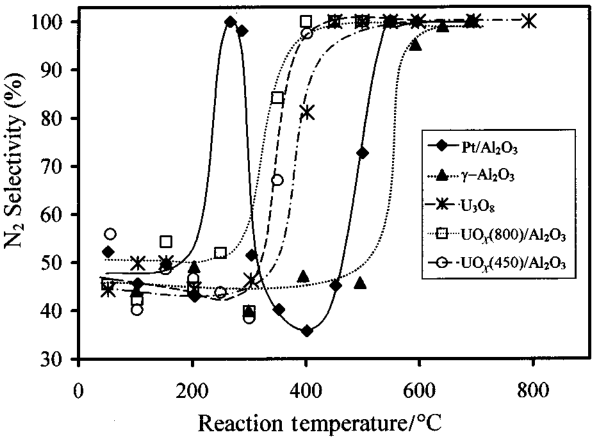

**Fig. 2** Effect of temperature on catalyst selectivity towards $N_2$.

**Table 1** BET surface areas for fresh and post light-off catalyst samples[a]

| Sample | Surface area[b]/$m^2$ $g^{-1}$ (±5 %) |
|---|---|
| 5% $Pt/Al_2O_3$ (fresh) | 144 |
| 5% $Pt/Al_2O_3$ (post reaction) | 137 |
| $UO_x$(800) (fresh) | 52 |
| $UO_x$(800) (post reaction) | 54 |
| $UO_x$(450) (fresh) | 57 |
| $UO_x$(450) (post reaction) | 57 |

[a] *Reaction conditions*: 4% NO + 4% CO, balance He; $T_{react}$ = 25–1000 °C. [b] ±5%.

dispersion on alumina; indeed bulk $U_3O_8$ is less active for NO reduction than the alumina support. $T_{50}$ values for the supported $UO_x/Al_2O_3$ catalysts appear relatively insensitive to precalcination temperature, although higher temperature calcination does produce the most active uranium catalyst. Remarkably these supported catalysts exhibit $T_{50}$ values essentially identical to those of a commercial $Pt/Al_2O_3$ $NO_x$-reduction catalyst. The best uranium-derived catalyst, $UO_x$(800) lights off at *ca.* 250 °C, attaining 100% NO conversion above 400 °C. Light-off was accompanied in all cases by small, sustained exotherms of *ca.* 5–10 °C.

Over all the uranium catalysts the initial low temperature reduction of NO produced predominantly $N_2O$ as the major product. With increasing reaction temperature and thus NO conversion, the selectivities of all bulk and supported uranium catalysts rise rapidly, with 100% selectivity towards $N_2$ achieved above 400 °C (Fig. 2). The temperature-dependent selectivity of the $Pt/Al_2O_3$ catalyst differs markedly from those of the uranium catalysts. Selectivity towards $N_2$ rises to a sharp maximum just before catalyst light off, albeit at low conversions, before gradually returning to zero at at *ca.* 400 °C. The selectivity recovers at higher temperatures with only $N_2$ formed above 500 °C, although at these temperatures the alumina support is itself active and selective for NO reduction to $N_2$.

Preliminary lifetime studies ( > 24 h on-stream) show that the supported $UO_x$ catalysts exhibit both high thermal stability and high sulfur tolerance. Indeed steady state NO conversion remains *ca.* 60% after 140 h reaction at 375 °C in the absence of $SO_2$, and at similar levels for > 17 h after the introduction of 1000 ppm $SO_2$ into the reaction stream at 550 °C, conditions which strongly poison the commercial $Pt/Al_2O_3$ catalyst. The $N_2$ BET surface areas of the fresh and spent supported $UO_x$ catalysts are *ca.* 50 $m^2$ $g^{-1}$ for reaction temperatures up to 1000 °C, above which the alumina support itself begins to sinter (Table 1).

The supported $UO_x$ catalysts underwent colour changes during use in the reactor. The $UO_x$(800) sample turned from green to brown, while the $UO_x$(450) sample changed from orange to brown. Comparison with the colours of bulk uranium oxides suggests that these changes are associated with catalyst reduction from $U_3O_8$-like and $UO_3$-like phases respectively to a $UO_2$-like phase under reaction conditions. This interpretation is supported by *in situ* XRD measurements (Fig. 3) on the $UO_x$(450) and $UO_x$(800) sample. For both catalysts a phase transformation occurs between 375 and 400 °C associated with the disappearance of reflections at $2\theta$ 21.4, 26.02 and 33.94° characteristic of stoichiometric $U_3O_8$, and the emergence of new peaks at $2\theta$ 28.37 and 32.9° characteristic of stoichiometric $UO_2$. This transformation is complete above 400 °C for the $UO_x$(800) catalyst; however, for the $UO_x$(450) catalyst calcined at lower temperature a mixture of $U_3O_8$ and $UO_2$ phases coexists even after reaction at 525 °C. The $UO_x(H_2)$ sample remained brown for the duration of the experiments and the *in situ* XRD data exhibited diffraction lines at $2\theta$ 28.37 and 32.9°, characteristic of stoichiometric $U_4O_9$, which did not change for the duration of the experiment. No such colour or phase changes are observed following identical thermal treatments under inert atmospheres for any sample. These results suggest the existence of a common active phase of stoichiometry $UO_x$ ($2 < x < 2.25$) within the supported $UO_x$ catalysts.

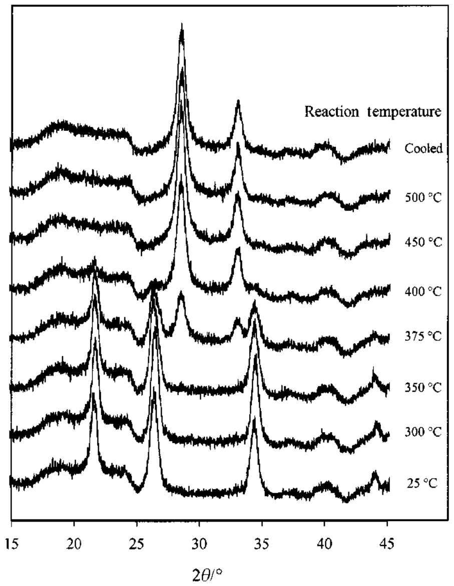

**Fig. 3** *In situ* X-ray diffractograms for $UO_x$(800) as a function of temperature under standard reaction conditions.

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