

# Development of Nitric Oxide Oxidation Catalysts for the Fast SCR Reaction

Mark Crocker

Center for Applied Energy Research

University of Kentucky

2540 Research Park Drive

Lexington, KY 40511

Tel.: 859-257-0295

Fax: 859-257-0220

E-mail: [crocker@caer.uky.edu](mailto:crocker@caer.uky.edu)

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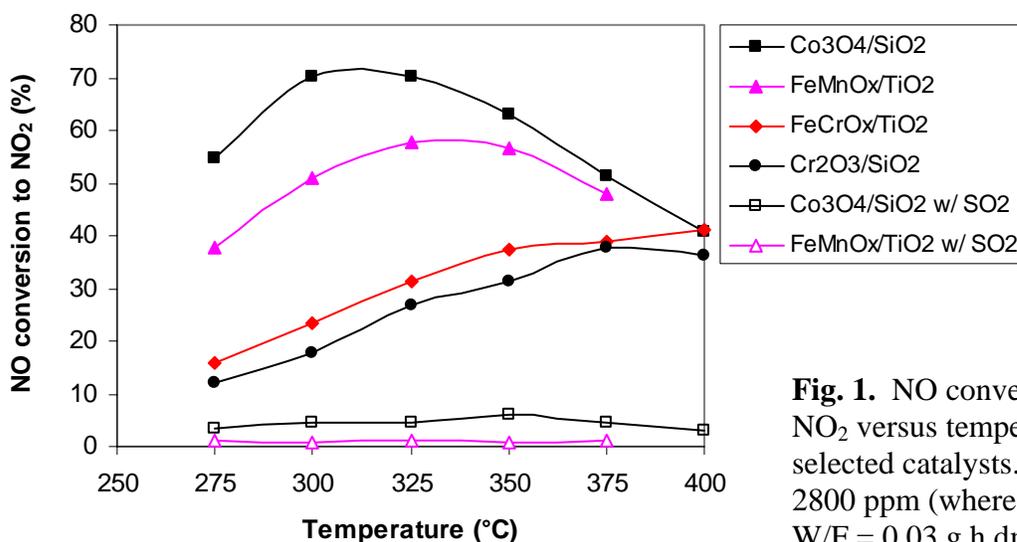
## Objective

In order to reduce catalyst costs in SCR installations, this project aims to develop catalysts which are active and selective for the oxidation of NO to NO<sub>2</sub>. Two main reactions contribute to NO<sub>x</sub> conversion over ammonia SCR catalysts:  $4\text{NH}_3 + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$  (1), and:  $2\text{NH}_3 + \text{NO} + \text{NO}_2 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O}$  (2). NO<sub>x</sub> formed in combustion processes is typically composed of >90% NO and reaction (1) therefore dominates. In the case that equimolar amounts of NO and NO<sub>2</sub> are present, NO<sub>x</sub> reduction occurs according to equation (2). This is the so-called “fast” SCR reaction. Expressed in terms of a first order rate law, the ratio of the two rate constants,  $k(2)/k(1)$ , is at least ten at  $T > 200$  °C. This implies that the rate of NO<sub>x</sub> conversion can be accelerated by use of an oxidation catalyst upstream of the SCR unit, so as to convert *ca.* 50% of the NO to NO<sub>2</sub>; this, in turn, enables the SCR catalyst volume to be reduced. Specific objectives of the project are two-fold, being firstly to identify a catalyst which is selective for the oxidation of NO to NO<sub>2</sub> under typical flue-gas conditions while possessing minimal activity for the oxidation of SO<sub>2</sub>, and which shows adequate stability with respect to long term operation in a flue-gas environment. Secondly, the activity and manufacturing cost of the catalyst should be such that a 25% saving in total SCR catalyst costs can be realized.

## Accomplishments to date

Prior to commencing experimental work, a literature study was undertaken to identify leads for the design of selective NO oxidation catalysts. Based on the outcome of this study, a number of candidate catalysts were identified for screening. Selection criteria comprised (i) proven activity for NO oxidation, (ii) low activity for SO<sub>2</sub> oxidation, and (iii) inexpensive component materials. Catalysts identified, and subsequently prepared, include (i) supported oxides of Cr, Co, Cu, Mn, Mo, Nb and Ni, (ii) Fe-Mn, Fe-Cr and Cu-Ce mixed oxides, and (iii) low loaded Pt catalysts (0.5 wt%) with added V<sub>2</sub>O<sub>5</sub> for suppression of SO<sub>2</sub> oxidation. Supported catalysts, for which the metal loading was typically 20 wt%, were prepared by incipient wetness impregnation, employing weakly sulfating supports (TiO<sub>2</sub>, SiO<sub>2</sub>). Mixed oxides were prepared via a co-precipitation procedure. The resulting materials were characterized using standard techniques, *viz.*, elemental analysis (XRF), powder X-ray diffraction (XRD) and nitrogen physisorption (BET surface area and pore volume). XRD measurements indicate that even at the high metal loadings employed, the titania support is able to stabilize the supported oxide phase in highly dispersed form. In general, use of silica as the support affords metal oxide phases with higher crystallinity.

The prepared catalysts are presently being screened for NO oxidation activity in a fixed bed reactor, under conditions chosen to be representative of the flue gas from coal-fired utility boilers:  $T = 275\text{--}375\text{ }^{\circ}\text{C}$ ,  $[\text{NO}] = 250\text{ ppm}$ ,  $[\text{SO}_2] = 2800\text{ ppm}$ ,  $[\text{H}_2\text{O}] = 7\%$ ,  $[\text{CO}_2] = 12\%$ ,  $[\text{O}_2] = 3.5\%$ , balance =  $\text{N}_2$ . Initial results indicate that while many of the catalysts show excellent NO oxidation activity when  $\text{SO}_2$  is absent from the feed gas, in the presence of  $\text{SO}_2$  the conversion of NO is greatly suppressed (Fig. 1).



**Fig. 1.** NO conversion to  $\text{NO}_2$  versus temperature for selected catalysts.  $\text{SO}_2 = 0$  or 2800 ppm (where indicated);  $W/F = 0.03\text{ g h dm}^{-3}$ .

### Future work

Work in the immediate future will focus on completion of the catalyst screening program. Based on the results, the most promising candidate will be selected for optimization. As part of this process, a kinetic analysis will be conducted to assess the dependence of nitric oxide conversion on relevant process parameters, i.e., temperature, space velocity, and gas phase concentrations of NO and  $\text{SO}_2$ . Using these data as input, the catalyst will be optimized with respect to relevant synthesis parameters, *viz.*, the active catalyst phase (loading, morphology), the use of chemical and structural promoters, and the support employed (improved resistance to sulfation and sintering). Modified catalysts will be tested according to the conditions described above.

The final experimental work will comprise a durability test. The optimized catalyst will be subjected to a test run of 1 month duration under simulated flue gas conditions in order to assess its stability.

### Students supported

One undergraduate student (Amanda Tackett) supported to date.