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# Noble metal free $NO_x$ storage catalysts using cobalt discovered via high-throughput experimentation

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**Abstract**

The addition of manganese, iron, and cobalt to $NO_x$ storage and reduction (NSR) catalysts containing 1% w/w platinum and 15% w/w barium (1Pt/15Ba) on $\gamma$-$Al_2O_3$ has been studied. Under fuel lean conditions, the addition of Mn or Fe slightly improved the $NO_x$ storage, while the addition of Co more than doubled the $NO_x$ storage. In addition, a noble metal free 5Co/15Ba catalyst was found to store $NO_x$ as efficiently as a 1Pt/15Ba NSR catalyst. This increase in efficiency is associated with the strong oxidizing effect of Co, providing nitric oxide oxidation sites and contact area for $NO_2$ spillover to the Ba $NO_x$ storage sites. By utilizing Co as an oxidizing metal instead of Pt, the storage capacity of NSR catalysts can be improved without the need for an expensive noble metal oxidizing catalyst.


*Keywords:* Combinatorial catalysis; NSR catalysts; FTIR imaging; $NO_x$ storage and reduction; High-throughput screening

## 1. Introduction

Lean burn gasoline and diesel engines will improve the fuel efficiency of automobiles, resulting in decreased dependence on non-renewable petroleum and a reduction in the emission of greenhouse gases. Impeding the widespread implementation of lean burn engines is the inability of current three-way catalytic converters (TWC) to reduce nitrogen oxides ($NO_x$) under net-oxidizing conditions. Extensive research has been performed in search of alternative catalysts that will reduce $NO_x$ in oxygen rich environments under steady-state conditions, but an acceptable catalyst has not yet been discovered [1–3].

To address the apparent conflict of high engine efficiency and low $NO_x$ emissions, $NO_x$ storage and reduction (NSR) catalysts have been developed to store $NO_x$ during a fuel lean cycle and reduce the stored $NO_x$ during a subsequent fuel rich cycle [4–7]. Extensive research has been performed over the past decade examining the performance of NSR catalysts containing platinum as an oxidative and reductive catalyst and barium as a $NO_x$ storage material [8–11]. In addition, the use of other noble metals in place of, or in addition to, Pt [12,13] and other $NO_x$ storage components in place of Ba [5,14] have been researched. The use of transition metals to improve resistance to sulfur poisoning has also been investigated [15]. However, to the best of our

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knowledge, there have been no published reports detailing the use of noble metal free catalysts for $NO_x$ storage. This communication reports the results of a high-throughput study on the use of transition metals to improve lean $NO_x$ storage for NSR catalysts and the discovery of a noble metal free $NO_x$ storage catalyst.

## 2. Experimental

### 2.1. High-throughput experimental set-up and testing procedure

All catalytic tests were performed using a 16-channel parallel reactor. Details concerning the reactor have been described previously [16]. The reaction products from all 16 channels were analyzed simultaneously using Fourier transform infrared (FT-IR) imaging [17–20]. The optical set-up consists of a Bruker Equinox 55 FT-IR spectrometer interfaced with a $64 \times 64$ pixel mercury cadmium telluride FPA detector (Santa Barbara Focalplane, Goleta, CA, USA) capable of collecting IR spectra of the effluents from all 16 reactors in less than 2 s [21]. Details of the optical set-up and analytical methods can be found in previous publications [17,22,23].

A typical data set collected during a switch from fuel rich to fuel lean conditions for three different catalysts is shown in Fig. 1. The outlet $NO_x$ concentration profiles are shown as functions of time, with the dotted lines representing the inlet $NO_x$ concentration and 300 ppm $NO_x$. The performance of each catalyst was based on the $NO_x$ storage, defined as the integrated area between the inlet $NO_x$ concentration and outlet $NO_x$ concentration, in the fuel lean state, from time zero to the time when the outlet $NO_x$ concentration reached 300 ppm. Catalytic performance was evaluated when the $NO_x$ storage behavior became reproducible over several cycles. The feed gas consisted of 0.14% v/v NO, 6% v/v $O_2$, 0.9% v/v CO, 0.15% v/v $C_2H_4$ in helium for the fuel lean phase at a space velocity of 42,000 mL/h/gm catalyst. The fuel rich phase was simulated by replacing the oxygen with an equal volume of helium while maintaining the other flow rates constant at the fuel lean conditions. The catalysts were cycled multiple times between 15 min of fuel rich phase and 30 min of fuel lean phase. For all results reported, 150 mg of catalyst was loaded into each reactor, and all reactions were performed at $T = 648$ K.

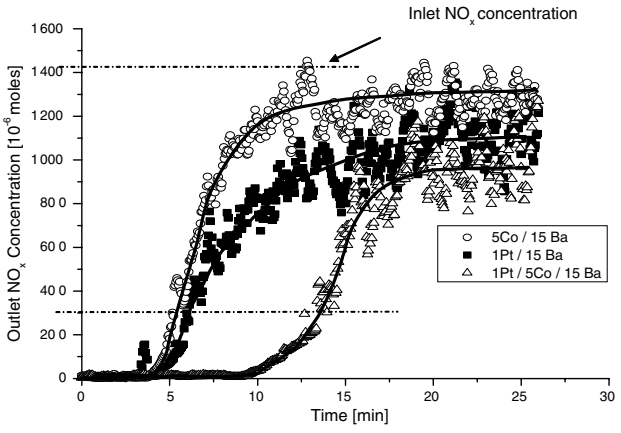


Fig. 1. $NO_x$ concentration profile for different catalyst under fuel lean conditions.

### 2.2. Catalyst preparation

The catalysts were synthesized via incipient wetness on $\gamma$-$Al_2O_3$ (Catalox® Sba-200, 200 $m^2/g$). A list of Pt/Co catalysts tested in this study is shown in Table 1. The naming convention for each catalyst throughout the paper is based on the nominal weight loading. Thus, a catalyst with a nominal weight loading of 1% w/w Pt and 15% w/w Ba is referred to as 1Pt/15Ba. Chloroplatinic acid hexahydrate, barium nitrate, cobalt nitrate, iron (III) nitrate nonahydrate, and magnesium nitrate precursors (Strem Chemicals) were dissolved in distilled water prior to impregnation. Details concerning the impregnation procedure can be found elsewhere [24]. All catalysts were calcined by heating to 473 K over 2 h, holding the temperature at 473 K for 1 h, further heating to 823 K over 3 h, holding at 823 K for 2 h, and then cooling to 298 K. In addition, all catalysts were reduced in the high-throughput reactor for 1 h in 10% v/v $H_2$/He at 773 K before performing the reaction studies.

### 2.3. Characterization procedures

The weight loadings of all Pt/Co catalysts were verified by atomic absorption spectroscopy (S series atomic absorption spectrometer, Thermo Electron). The details of this procedure can be found elsewhere [25] and will not be discussed here. X-ray diffraction patterns were acquired under atmospheric conditions with a Philips X'Pert diffractometer using Cu K$\alpha$ radiation at 40 kV and 40 mA.

## 3. Results

Fig. 2 shows the effect of different transition metals as promoters on lean $NO_x$ storage of Pt/Ba based NSR catalysts. The addition of either Fe or Mn shows an increase in the $NO_x$ storage by 25–30%. Co, however, has a considerably higher promotional effect, increasing the lean $NO_x$ storage by more than 100%. Due to the significant increase in performance shown by the Co-containing NSR catalyst, a detailed study was per-