J|A|C|S
ARTICLES

Application of a New Color Detection Based Method for the Fast Parallel Screening of DeNO$_x$ Catalysts

Oliver M. Busch,† Christian Hoffmann,† Thorsten R. F. Johann,†
Hans-Werner Schmidt,† Wolfgang Strehlau,‡ and Ferdi Schüth*,†

Contribution from the Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr, Germany, and hte AG, Heidelberg, Germany

Received May 1, 2002

Abstract: A new fast parallel detection method for stage I screening of solid catalysts has been developed. This method is based on the color change of organic dyes in the presence of either educts or reaction products in a reaction gas flow. As an example, NO decomposition and NO reduction with propylene under lean or rich conditions were studied. The presence of NO in a gas stream was detected by the color change from colorless to blue-green of filter paper impregnated with an organic dye, 2,2′-azinobis(3-ethylbenzthiazoline-6-sulfonic acid) (ABTS), which was placed in the gas stream after the catalyst bed. The catalyst library was made up of mixed metal oxides, synthesized by impregnation of activated carbon with metal oxide precursor solutions and subsequent combustion of the carbon matrix. Catalytic activity of these metal oxides was compared to platinum on γ-alumina as a reference catalyst. The most active compounds were then studied in detail for their DeNO$_x$ properties in a high precision parallel flow test rig under a stationary and cyclic lean/reach operation. A new promising NO$_x$ storage catalyst was discovered.

1. Introduction

High throughput experimentation has emerged as a promising methodology to discover materials, especially catalysts, in past years. In the pharmaceutical industry, the use of combinatorial methods was introduced about 15 years ago to speed up the discovery process,[1] while in materials science and catalysis research, it took some years to adapt those methods to the requirements necessary in these fields. These approaches have been extensively reviewed over the last years.[1−5] High throughput approaches in heterogeneous catalysis consist of four components that are closely connected: automated synthesis of catalyst libraries,[6−8] testing in multipath flow reactors[9,10] or parallelized multiphase batch reactors,[11−13] analysis in high-speed systems that are linked to the reactor, which are discussed in more detail in the following, and data management of the results.[14,15]

With regard to the analysis of the products from catalytic reactions, there are now two different principal possibilities: sequential or real time parallel detection. Sequential detection is the most common technique for stage II screening of solid catalyst libraries (i.e., further development of known materials), but it is also used for stage I screening (i.e., discovery of new materials). Either multiport valves are used to switch the outlet from the catalysts sequentially to the analytical system and vent the exhaust from the other catalysts[9,10] or positioning devices are integrated in the system to sample the exhaust from the catalysts sequentially with the inlet capillary of a mass spectrometer.[16−20] Although quite impressive speeds of analysis can be achieved with these methods, switching times between channels can still be significant on the order of minutes.

For stage I screening, several other, truly parallel analysis techniques have been reported. Moates et al. used infrared thermography to monitor simultaneously an array of 16 different catalysts for the hydrogen/oxygen reaction.[21] Maier et al.

---

* To whom correspondence should be addressed. E-mail: schueth@mpi-muelheim.mpg.de.

† Max-Planck-Institut.

‡ hte AG.

(1) Jandeleit, B.; Schaefer, D. J.; Powers, T. S.; Turner, H. W.; Weinberg, W. H. *Angew. Chem., Int. Ed.* **1999**, *38*, 2494−2532.
(2) Senkan, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 312−329.
(3) Reetz, M. T. *Angew. Chem., Int. Ed.* **2001**, *40*, 284−310.
(4) Newsam, J. M.; Schüth, F. *Biotechnol. Bioeng.* **1999**, *61*, 203−216.
(5) Gennari, F.; Seneci, P.; Miertus, S. *Catal. Rev.-Sci. Eng.* **2000**, *42*, 385−402.
(6) Akporiaye, D. E.; Dahl, I. M.; Karlsson, A.; Wendelbo, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 609−611.
(7) Lai, R.; Kang, B. S.; Gavalas, G. R. *Angew. Chem., Int. Ed.* **2001**, *40*, 408−411.
(8) Newsam, J. M.; Bein, T.; Klein, J.; Maier, W. F.; Stichert, W. *Microporous Mesoporous Mater.* **2001**, *48*, 355−365.
(9) Hoffmann, C.; Wolf, A.; Schüth, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 2800−2803.
(10) Hoffmann, C.; Schmidt, H.-W.; Schüth, F. *J. Catal.* **2001**, *198*, 348−354.
(11) Desrosiers, P.; Guram, A.; Hagemeyer, A.; Jandeleit, B.; Poojary, D. M.; Turner, H.; Weinberg, H. *Catal. Today* **2001**, *67*, 397−402.
(12) Lucas, M.; Claus, P. *Chem. Eng. Technol.* **2001**, *73*, 252−257.
(13) Thomson, S.; Hoffmann, C.; Ruthe, S.; Schmidt, H.-W.; Schüth, F. *Appl. Catal., A* **2001**, *220*, 253−264.
(14) Wolf, D.; Buyevskaya, O. V.; Baerns, M. *Appl. Catal., A* **2000**, *200*, 63−77.
(15) Holzwarth, A.; Denton, P.; Zanthoff, H.; Mirodatos, C. *Catal. Today* **2001**, *67*, 309−318.
(16) Cong, P.; Doolen, R. D.; Fan, Q.; Giaquinta, D. M.; Guan, S.; McFarland, E. W.; Pooray, D. M.; Self, K.; Turner, H. W.; Weinberg, W. H. *Angew. Chem., Int. Ed.* **1999**, *38*, 483−488.
(17) Senkan, S.; Ozturk, S. *Angew. Chem., Int. Ed.* **1999**, *38*, 791−795.
(18) Orschel, M.; Klein, J.; Schmidt, H.-W.; Maier, W. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 2791−2794.
(19) Claus, P.; Hönicke, D.; Zech, T. *Catal. Today* **2001**, *67*, 319−339.
(20) Rodemerck, U.; Wolf, D.; Buyevskaya, O. V.; Claus, P.; Senkan, S.; Baerns, M. *Chem. Eng. J.* **2001**, *82*, 3−11.

10.1021/ja020629x CCC: $22.00 © 2002 American Chemical Society

reported the application of a more sensitive, background-corrected infrared thermography for exothermic reactions such as the oxidation of hydrocarbons as a real time parallel measurement of catalytic activity.[22] However, although thermography is excellently suited to detect activity, selectivity information can hardly be obtained, due to the fact that most chemical conversions are accompanied by enthalpic effects and thus any reactivity would show up as a signature in a thermography experiment.

There are also methods allowing the analysis of specific products in a parallel setup. Senkan used resonance enhanced multiphoton ionization (REMPI) combined with detection of the charge carriers generated by an electrode array to monitor the benzene formed in cyclohexane dehydrogenation over an array of catalysts.[23] Su et al. utilized the fluorescence of naphthoquinone after excitation by laser (so-called LIFI = laser-induced fluorescence imaging) for real time parallel measurements of the oxidation of naphthalene on V_2O_5 surfaces. They observed the catalytic activity via a CCD imaging system that is suitable for the detection of the fluorescence emission at 515–545 nm.[24] Both techniques are very elegant, but they can only be used if the target product has a detectable fluorescence emission which can be detected among other possible products in the case of LIFI, or suitable electronic states allowing the ionization via REMPI.

Yet another real parallelized analytical technique would be the use of a selective color or fluorescence reaction of the product or the educt of a reaction with a dye molecule, where the color or luminescence would be altered by the reaction. This method is frequently used in homogeneous catalysis to accelerate the discovery and development of catalysts.[25,26] A first description of a related approach in heterogeneous catalysis has been given by Reddington et al.[27] and Chen et al.,[28] who applied a pH sensitive fluorescence dye to discover novel fuel cell catalysts. However, there seem to be no reports for related techniques applied to gas-phase reactions with the exception of a patent application by Schüth et al.[29] and a related technique reported by the Symyx group.[30,31]

In the following, we describe in more detail the application of a simple color detection scheme for the parallelized semi-quantitative analysis of NO. To be useful in such applications, the dyes have to meet several requirements: (i) it must be possible to impregnate them onto a support that can be placed in a gas flow, (ii) the change of color must occur even in dry atmosphere, and (iii) the intensity of the color must be dependent on the concentration of the product in the gas flow. Advantages of dye detection methods are obvious: (i) it is, in principle, possible to measure a very high number of solid catalysts at the same time in a truly parallelized fashion, and (ii) costs are very low in comparison to gas chromatography or mass spectrometry. Disadvantages are (i) the requirement to develop a specific dye for each reaction to be investigated, (ii) possible cross-sensitivity against byproducts, and (iii) the fact that this test will normally be semiquantitative only. In addition, for some reactions, no suitable dye may be available at all.

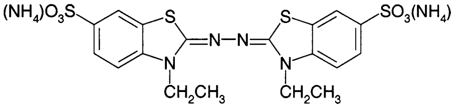

Figure 1. 2,2′-Azinobis(3-ethylbenzthiazoline-6-sulfonic acid) (ABTS) forms a green color in the presence of NO and a deep blue-green color in the presence of NO_2.

Several dyes are known to react with NO_x. The first publication about the application of an organic dye for this purpose is from the 1950s. Saltzman presented a system that is able to detect NO_x quantitatively, when the components are dissolved in water.[32] Unfortunately, this method does not work if the components are supported, because the formation of the azo dye takes place after some equilibration steps that cannot occur without solvent.

We have found that 2,2′-azinobis(3-ethylbenzthiazoline-6-sulfonic acid) (ABTS), Figure 1, a dye that is used in biochemistry to detect cell regions with high nitric oxide concentration,[33] is a suitable probe that reacts with NO and fulfills the foresaid requirements. The color turns from colorless to blue-green. NO_2 also leads to some coloration, which can, however, be discriminated from the color caused by NO.

The goal of the present study was to demonstrate the usefulness of the detection scheme and apply it to analyze high surface area metal oxide libraries created by the combustion of activated carbons, which had previously been impregnated with mixed metal nitrate solutions, for their activity in NO removal from gas streams. The general synthesis pathway and the properties of the mixed metal oxides have been reported before.[34]

2. Experimental Section

2.1. Samples and Reagents. The 5 wt % platinum on γ-alumina used as a reference was a commercial Merck sample. ABTS used as dye was supplied by Fluka. The activated carbon used for impregnation was Darco KB-B, −100 supplied by Aldrich. Fe, Co, Cr, Cu, Mn, Ni, Zn, La, and Pb were hydrates of nitrate salts supplied by Fluka and were used as metal salt precursors. All of these precursor solutions were saturated. 589^1 black ribbon ashless Filter Paper Circles ∅ 150 mm from Schleicher and Schuell were used as dye support.

2.2. Methods. Dye impregnated filter paper: A filter paper is impregnated with 5 mL of ABTS solution (20 mmol/L of ABTS in methanol) that is imbibed completely and dried in air subsequently. Every filter paper was impregnated freshly just before measurement. To evaluate the quantitative accuracy of the measurement with impregnated filter papers, ABTS was redissolved again in methanol

---

(21) Moates, F. C.; Somani, M.; Annamalai, J.; Richardson, J. T.; Luss, D.; Willson, R. C. *Ind. Eng. Chem. Res.* **1996**, *35*, 4801–4803.
(22) Holzwarth, A.; Schmidt, H.-W.; Maier, W. F. *Angew. Chem., Int. Ed.* **1998**, *37*, 2644–2647.
(23) Senkan, S. M. *Nature* **1998**, *394*, 350–353.
(24) Su, H.; Yeung, E. S. *J. Am. Chem. Soc.* **2000**, *122*, 7422–7423.
(25) Crabtree, R. H. *CHEMTECH* **1999**, 21–26.
(26) Cooper, A. C.; McAlexander, L. H.; Lee, D.-H.; Torres, M. T.; Crabtree, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 9971–9972.
(27) Reddington, E.; Sapienza, A.; Gurau, B.; Viswanathan, R.; Sarangapani, S.; Smotkin, E. S.; Mallouk, T. E. *Science* **1998**, *280*, 1735–1737.
(28) Chen, G.; Delafuente, D. A.; Sarangapani, S.; Mallouk, T. E. *Catal. Today* **2001**, *67*, 341–355.
(29) Brenner, A.; Lange de Oliveira, A.; Schüth, F.; Schunk, S.; Stichert, W.; Unger, K. Offenlegungsschrift DE 198 30 607 A1, 1998.
(30) Bergh, H. S.; Guan, S. WO 00/51720, 2000.
(31) Hagemeyer, A.; Borade, R.; Desrosiers, P.; Guan, S. H.; Lowe, D. M.; Poojary, D. M.; Turner, H.; Weinberg, H.; Zhou, X. P.; Armbrust, R.; Fengler, G.; Notheis, U. *Appl. Catal., A* **2002**, *227*, 43–61.
(32) Saltzman, B. E. *Anal. Chem.* **1954**, *26*, 1949–1955.
(33) Nims, R. W.; Darbyshire, J. F.; Saavedra, J. E.; Christodoulou, D.; Hanbauer, I.; Cox, G. W.; Grisham, M. B.; Laval, F.; Cook, J. A.; Krishna, M. C.; Wink, D. A. *Methods: A Companion to Methods in Enzymology*; Academic Press: New York, 1995; Vol. 7, pp 48–54.
(34) Johann, T.; Brenner, A.; Busch, O.; Marlow, F.; Schunk, S.; Schüth, F. *Angew. Chem., Int. Ed.* **2002**, *41*, 2966–2968. Schwickardi, M.; Johann, T.; Schmidt, W.; Schüth, F. *Chem. Mater.* **2002**, *14*, 3913–3919.

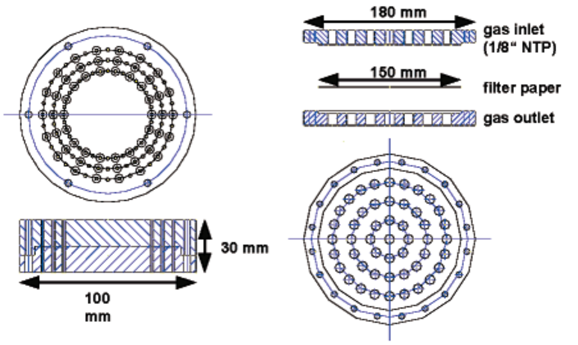

Figure 2. Left side: schematic assembly of the gas switch. It consists of two parts that can be turned against each other by 10° to direct the gas flow to the filter paper or to the exhaust. Right side: schematic assembly of the analytical device. Side view (top) shows the two plexiglass disks with the filter paper placed between them; front view (bottom) shows the arrangement of bores in the plexiglass device which corresponds to the arrangement of the channels in the reactor. The reaction gas passes through the bores and contacts the paper, where the formation of the dye can be observed.

after reaction with nitric oxide. These solutions were analyzed with a VARIAN CARY 5G UV−vis−NIR spectrophotometer.

Catalysts: Catalyst preparation was automated by use of a commercial pipet system (Gilson XL 232) which distributed the metal salt precursors to preweight activated carbon. Activated carbon (230 mg) was impregnated with 450 μL of highly concentrated metal nitrate precursor solutions.[34] The composition of the 450 μL of mixed precursor solutions is based on a random algorithm, which determines whether a precursor is chosen or not and, if a precursor is chosen, in which quantity it contributes to the total volume. The impregnated samples were then calcined on a 77 well plate which had been covered with gauze to avoid oxide particles from being expelled during carbon combustion. Samples were dried overnight at 90 °C, and calcination took place at 500 °C for 2 h which led to the combustion of the carbon and to formation of oxides. As-calcined samples were used for the catalytic reaction. The amount of catalyst varied between 40 and 50 mg per position. One hundred milligrams of 5 wt % platinum on γ-alumina (sieve fraction 500−1000 μm) was used as a reference catalyst.

Catalytic experiments: All experiments were carried out in a 49 parallel path flow reactor that is described elsewhere.[10] Prior to each experiment, the catalysts were heated in a nitrogen gas flow at 180 °C and then exposed to the reaction gas. Three different compositions were tested: (i) 1000 ppm nitric oxide, 1000 ppm propylene, 5 vol % oxygen and nitrogen as balance; (ii) 1000 ppm nitric oxide, 1000 ppm propylene and nitrogen as balance; and (iii) 1000 ppm nitric oxide and nitrogen as balance. The total flow rate entering the reactor was 490 mL/min. Reactant gases were fed from independent mass flow controllers (Bronkhorst Hi-Tec). The feed gas containing the nitric oxide was a mixture from Messer with 3000 ppm nitric oxide in nitrogen as balance. Reactions were carried out at different temperature levels, mostly 200, 250, 300, and 350 °C. As catalysts might deactivate over the time needed for a full analytical cycle over all temperatures, typically two or three cycles were performed to detect changes of catalyst activity with time. The stainless steel of the reactor had no blank activity for the DeNO$_x$ reaction.

Analytics: Schematic drawings of the analytical gas outlet and of the 54 path gas switch are given in Figure 2. The gas switch is necessary to define $t = 0$ for the analysis. For the analysis, the catalysts are first equilibrated under reaction gas flow, and the effluent from the reactor is passed to the exhaust. After equilibration, the gas is switched to the impregnated filter device, and analysis starts for a predetermined time, after which the gas is switched to the exhaust again.

The gas switch is connected to the 49 path flow reactor by capillaries with a diameter of 1.6 mm and a length of 500 mm. This length is necessary to avoid heat transfer from the reactor to the analytical device. The gas switch is wrought from plexiglass and has a diameter of 100 mm. It consists of two parts: the gas inlet side has three circles of 36 bores, and the gas outlet side has three circles of 18 bores (allowing a total of 54 positions; i.e., five positions are left blank, if the switch is connected to the 49 path flow reactor) which are sealed with Viton O-rings to avoid gas exchange between the capillaries. By turning the gas outlet side of the switch by 10°, the gas flow can either be directed to the exhaust or to the impregnated filter paper. The outlet of the multipath gas switch is connected to the unit with the filter paper via capillaries with a diameter of 1.6 mm and a length of 500 mm. This length is required to have a capillary bundle that is flexible enough for the 10° turn of the switch. The analytical unit is made from plexiglass and has a diameter of 180 mm. The filter paper is placed between two plexiglass plates, and the flow from the reactor is passed through the filter paper, replicating the channel arrangement in the reactor on the filter paper.

Characterization of materials: XRD measurements were carried out using a Stoe STADI-P θ/θ reflection diffractometer employing Cu Kα radiation ($\lambda = 1.5418$ Å). The specific surface area of the solids was checked by N_2 adsorption (BET) using a Fisons Sorptomatic 1990 system. Infrared spectra were measured with a Nicolet Magna-IR 750 spectrometer.

3. Results and Discussion

Many systems are known which allow the detection of NO via a color reaction. However, some of them could be excluded a priori, because they require oxidation of the NO under conditions which make the presence of a solvent necessary or need oxidants, such as CrO_3/H_2SO_4, which destroy the filter paper. Some systems are described in the literature which could be used supported on silica and thus seemed to be transferable to filter paper. The dyes were the Saltzman reagent,[32] *o*-dianisidine,[35] and ABTS.[33] The transfer was only successful in the case of ABTS which turns from colorless to blue-green in the presence of NO also if impregnated on a filter paper.

Thus, all of the following experiments were carried out only with ABTS. To check whether the color intensity scales reproducibly with the amount of NO passed through the filter, a series of experiments with calibrated model gases was carried out. The reaction was carried out with 500, 1000, 1500, 2000, 2500, and 3000 ppm nitric oxide in nitrogen and an exposure time of 300 s. Nine spots showing the coloration brought about by exposure to NO were cut out of an impregnated filter paper for each concentration, three sets of three cuts were extracted in 5 mL of methanol, and the extracted solutions were analyzed in a UV/vis spectrophotometer in quartz cuvettes.

The results for the three sets were averaged and plotted versus the NO concentration in the gas (Figure 3). As the figure shows, there is a certain threshold amount of nitric oxide needed to start the reaction with ABTS. Beyond that threshold value, the absorbance is proportional to the concentration of the NO. Because no fully quantitative analysis is expected, but the technique shall rather be used as a semiquantitative prescreening method, the existence of the threshold can be neglected for sufficiently long exposure times, and the method is suitable as a prescreening technique for the preevaluation of DeNO$_x$ catalysts.

The parallelized color detection system was adapted to a 49 path flow reactor (Figure 4) that was designed in our institute.[10]

---

(35) Dräger-Röhrchen Handbuch of the company Dräger, 11th ed.; Dräger Aktiengesellschaft: Lübeck, 1997.

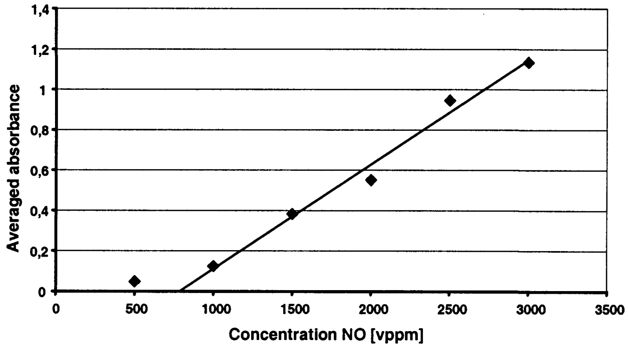

Figure 3. Averaged absorbance of ABTS at 412 nm depending on nitric oxide concentration. Nine spots showing the coloration brought about by exposure to NO for five min were cut out of an impregnated filter paper for each concentration, three sets of three cuts were extracted in 5 mL of methanol, and the extracted solutions were analyzed in a UV/vis spectrophotometer in quartz cuvettes. Because of the existence of a threshold, low concentrations were disregarded for the regression line.

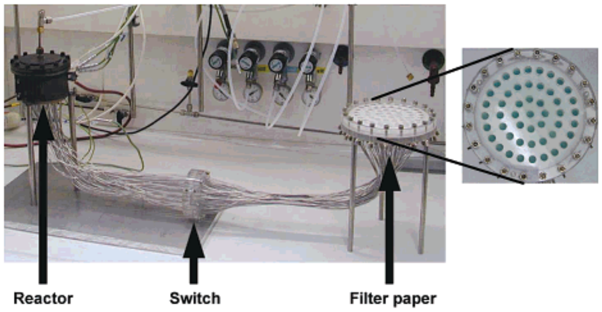

Figure 4. Setup of 49 path flow reactor, gas switch, and analytical device in our lab.

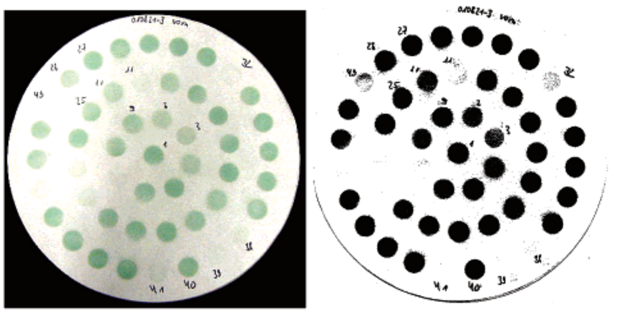

Figure 5. Color reaction with reference catalyst (5 wt % platinum on γ-alumina); flow contains 1000 ppm nitric oxide, 1000 ppm propylene, and nitrogen as balance, reaction temperature: 250 °C. Positions corresponding to the reference catalyst remained (almost) white; positions without catalytic material turned blue-green.

It had previously been shown that the flows between the individual channels did not deviate by more than about 5% from each other, even without additional flow control elements. This was confirmed also using the color detection scheme. For the reactor without catalyst, the coloration of the filter paper was identical in all 49 positions. Different concentrations of nitric oxide in the gas flow resulted in different intensities of the color spots, as had already been observed in nonparallel measurements.

In principle, DeNO$_x$ reactions via four different pathways can occur under the conditions used in our experiments: (i) The most elegant method would be the thermodynamically possible decomposition of NO to the elements. This, however, is also the least likely pathway. (ii) The second method is NO reduction in the absence of oxygen (only NO and propene in feed). The rate of this reaction is expected to increase with increasing temperature. (iii) The third method is NO reduction in lean gases (NO, propene, and oxygen in feed). For this reaction, catalysts are available which, however, often have a rather narrow temperature window for operation, because at high temperatures the overall process is dominated by combustion of the hydrocarbon with the excess of oxygen. (iv) The final method is NO storage in the form of nitrates or nitrites. This typically involves first oxidation of NO to NO$_2$ which is converted to a surface nitrate or even a bulk nitrate on the material and thus stored. After the storage capacity of the material is exceeded, NO breakthrough occurs. For a technical solution, a storage material is combined with a reduction catalyst. Under lean conditions, NO is stored in the form of nitrate. Periodically, then, a rich gas is fed, which leads to decomposition of the nitrate and reduction of the released NO$_x$ by a reduction catalyst, such as platinum. Our experiments were carried out without targeting one particular of these four reactions, because the material class we wanted to investigate is quite diverse and novel.

For testing the system, under catalysis conditions, initially platinum on γ-alumina was tested as a reference catalyst for the DeNO$_x$ reaction. Several positions of the reactor were filled with the reference catalyst (5 wt % Pt on γ-Al$_2$O$_3$); the remaining positions were filled with the same amount of pure γ-Al$_2$O$_3$.

Catalytic tests in the presence of propylene and the absence of oxygen in the gas flow demonstrated the activity of the catalyst for the DeNO$_x$ reaction under these conditions and at temperatures between 200 and 250 °C (Figure 5), corresponding to literature data on these systems. It has been found to be advantageous to use a black and white scan of the filter paper after measurement to amplify the differences between different spots. Those positions that remained (almost) white had no contact with nitric oxide and, as expected, correspond to the positions in which the reference catalyst had been placed and where the NO had been fully converted. The positions that changed color to blue-green corresponded to blank positions of the reactor. After oxygen addition to the feed to create a lean gas, the platinum catalysts oxidized the nitric oxide to nitrogen dioxide. From pretests, it was known that NO$_2$ causes a color change of ABTS which has stronger intensity than that obtained by reaction with NO. The test positions with platinum catalysts accordingly showed a deeper blue-green than the blank positions. The performance of the reference catalyst as evaluated with the color detection system thus corresponded to the expectations based on literature data. This increased our confidence to embark on a discovery program using solids with unknown catalytic properties as possible catalysts.

These solids are obtained by a new pathway to obtain metal oxides with high specific surface areas which was developed in our group.[34] Activated carbon was impregnated with a certain volume of mixed metal precursor solutions, containing the desired elements (mostly in the form of their nitrates) in the desired proportions. After impregnation, the activated carbon was removed by calcination, and the mixed metal oxide remained, typically having rather high surface area between 50 and above 100 m^2/g. This method was further developed to allow parallel synthesis of many mixed metal oxides with high surface area. These mixed metal oxides contained arbitrary ratios of iron, cobalt, chromium, copper, manganese, nickel, zinc,

Table 1. Composition of Active Compounds and Conditions for Their Catalytic Activity

cat. no. (library)	Fe (mol %)	Co (mol %)	Cr (mol %)	Cu (mol %)	Mn (mol %)	Ni (mol %)	Zn (mol %)	La (mol %)	Pb (mol %)	shows activity in	temperature (°C)
38	9	12	10	19	16	15	14	0	5	reductive atmosphere	250−350
46	0	0	55	0	45	0	0	0	0	reductive atmosphere	300−400
49	12	12	14	21	0	17	17	0	7	reductive atmosphere	200−350
68	15	17	16	29	0	0	23	0	0	reductive atmosphere	350−400
20	23	0	0	0	27	27	0	13	10	oxidative atmosphere	200−300
41	18	0	0	30	29	0	0	12	11	oxidative atmosphere	200−300
42	0	47	0	0	0	0	0	28	25	oxidative atmosphere	250−350

lanthanum, and lead. The mixing of the precursors was performed according to an algorithm, which randomly selected the identity and relative amount of each precursor species. These oxides so prepared were then tested for their catalytic properties in the DeNO$_x$ reaction. In all of the following measurements, platinum on alumina was used as the reference catalyst; one other well was filled with pure alumina support and was used as the blank.

Catalysts were evaluated under reducing conditions (propene as reducing agent), oxidizing conditions (propene and an excess of oxygen), and conditions where only decomposition was possible (no propene). The compositions and conditions for which activity was observed are summarized in Table 1. No decomposition catalyst was identified, but several compositions were active under either net oxidizing or net reducing conditions; none, though, were found to be active under both conditions. Some compounds showed initial activity in net reducing atmosphere which disappeared in a second run. This could be attributed to a stoichiometric reaction with reduced oxides formed via the activated carbon route. Under oxidizing conditions at higher temperatures exceeding 300 °C, most catalysts oxidized NO to NO_2, as indicated by the deep green-blue coloration of the corresponding spots.

After analysis of all samples at different temperatures, four members of a library of 77 compounds were sufficiently active under net reducing conditions, and three compositions were identified to be promising under net oxidizing conditions, to justify a more detailed investigation to see if the results from this simple color reaction can be reproduced in a more accurate test (see below). All samples with activity under net oxidizing conditions contain lanthanum, which suggests its important role for the DeNO$_x$ activity.

All catalysts given in Table 1 were then tested in a close-to-conventional stage II screening setup at hte AG under more realistic reaction conditions. The system is also a parallel reactor, but it only comprises 16 parallel channels and is equipped with an analytical system allowing one to analyze the full product range. The rig had been carefully evaluated and was found to give data of a quality as a conventional single pass reactor setup.[36] The gas composition of this test rig simulates the exhaust of an engine running with rich lean cycles that start with 380 s of lean gas mixture (consisting of 380 ppm nitric oxide, 850 ppm carbon monoxide, 5.2 vol % oxygen, and nitrogen as balance) followed by a cycle of a two second pulse of rich gas mixture (consisting of 6 vol % carbon monoxide and 2 vol % hydrogen and nitrogen as balance) and 80 s of lean gas mixture; this cycle is repeated three times. The analytical device of the rig can detect separately NO, NO_2, N_2O, CO, CO_2, and hydrocarbons. Nitric oxide and nitrogen dioxide were detected via time-resolved chemoluminescence. In general, the results obtained in this system confirmed the results from the color detection analysis. The materials found to remove NO in the preliminary tests also showed activity for the DeNO$_x$ reaction under the above given conditions. However, while the color detection scheme is not able to discriminate easily between the different DeNO$_x$ pathways, this question could be answered by the full analysis of the reaction.

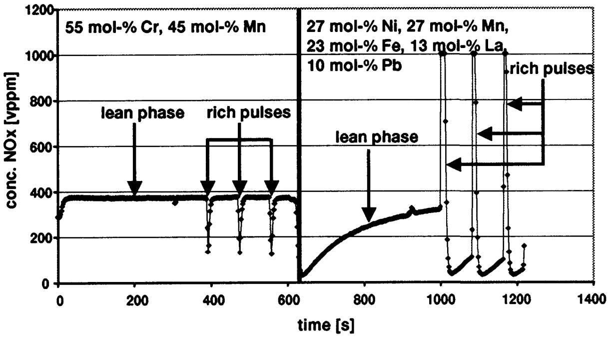

Figure 6. NO outlet concentration for two different catalysts. Each material is first exposed for 380 s to a lean gas (380 ppm NO, 850 ppm CO, 5.2 vol % O_2, nitrogen as balance) followed by three cycles of two seconds rich pulses (6 vol % CO and 2 vol % H_2) and 80 s lean periods (conditions as above). Left side: active material for catalytic NO reduction. Right side: active material for NO$_x$ storage.

As expected, none of the compositions was active in the decomposition of NO. However, reduction of NO under rich conditions and substantial NO storage were both observed for some of the compositions identified in the stage I screening. In the following, we will focus on two prototypical examples, one for the reduction and one for the storage pathway.

The example for a reduction catalyst is the material consisting of 55 mol % chromium and 45 mol % manganese (Figure 6). Only during the rich pulse is about 65% of the nitric oxide reduced. After switching to the lean mixture again, the reduction of nitric oxide stops. A similar material for the selective catalytic reduction of nitric oxide with ammonia, based on chromium manganese spinels, was recently reported by Słoczyński et al.[37] XRD analysis of our material revealed that a chromium manganese spinel had formed during the combustion of the carbon, accompanied by traces of manganese oxide (Mn_3O_4) and chromium oxide (Cr_2O_3). The specific surface area (BET) of the substance was 46 m^2/g.

A compound consisting of 27 mol % nickel, 27 mol % manganese, 23 mol % iron, 13 mol % lanthanum, and 10 mol % lead was found to be active under lean conditions in the color

---

(36) Bechtel, J.; Demuth, D.; Finger, K. E.; Schunk, S.; Stichert, W.; Strehlau, W.; Newsam, J. M. Presentation at the North American Catalysis Society Meeting 2001, Toronto, June 6th, 2001.

(37) Słoczyński, J.; Janas, J.; Machej, T.; Rynkowski, J.; Stoch, J. *Appl. Catal., B* **2000**, *24*, 45−60.

detection experiment (Figure 6). The performance of this material during the lean rich cycles is completely different as compared to the spinel compound described above. At the beginning of the cycle under lean conditions, almost full removal of NO is observed, the exit concentration being close to 0 ppm. The outlet NO concentration then increases continuously until the first rich pulse is admitted. During the rich pulse, the nitric oxide concentration shoots up beyond the detection limit of the NO_x sensor, and after the rich pulse the nitric oxide concentration drops again to almost 0 ppm. The same performance is observed during repetition of lean rich cycles. Such a behavior is typical for NO storage materials.

During the first 45 s, 80% of the nitric oxide offered in the gas mixture is stored on the catalyst. Using a different range of the nitric oxide sensor, we quantified the amount desorbed during the rich cycle. It was found that the total amount stored during the lean cycle is higher than the amount desorbed during the rich cycle. This means that the material also has some activity for reduction. This is not totally unexpected, because a material with a related composition, a perovskite containing lanthanum, strontium, iron, and manganese, was found to be active for the reduction of NO with propene under lean conditions.[38]

Evidence for the NO storage of the material is obtained from comparing the infrared spectra of the samples before and after exposure to the NO-containing gas mixture, where an intense band appears at 1380 cm^{-1} in the used sample, indicative for the formation of nitrate during exposure to NO. Further structural characterization of the material proved to be difficult, because it is completely amorphous. The specific surface area (BET) of the substance, however, was 71 m^2/g and thus substantially higher than that of the reported (La,Sr)(Fe,Mn) perovskites with a maximum of 20 m^2/g.[38]

Lead as a component of a commercial car exhaust catalyst would certainly be intolerable. The same holds for nickel due to the danger of carbonyl formation. These elements were introduced in the catalyst mixture by the random algorithm, which was not biased towards certain elements. Thus, the promising compositions were resynthesized separately, but without lead and nickel. In addition, platinum was added separately, corresponding to a concentration of 1 wt % in the final catalyst prior to carbon combustion, to provide a better reduction functionality during the rich cycle. First experiments with this catalyst proved that the storage ability is maintained also with the lead-free material and that the addition of the platinum catalyst leads to increased NO_2 reduction during the rich pulse (Figure 7). In this figure, averaged NO removal over the lean/rich cycle is plotted over the temperature.

The average NO conversion is above 70% in a rather wide temperature range for both the lead- and nickel-containing and the lead- and nickel-free compositions, if platinum is added to improve the NO reduction performance during the rich phase.

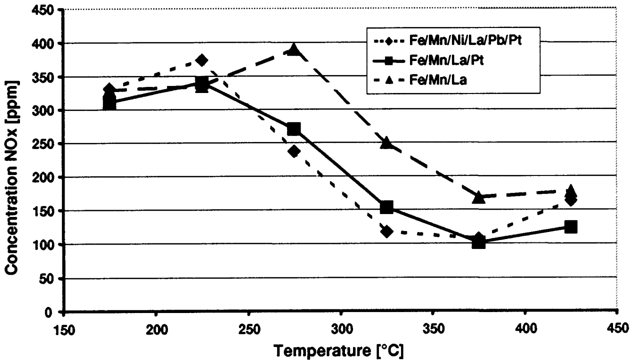

Figure 7. NO conversion averaged over full lean/rich cycle versus temperature for three different catalyst compositions. Conditions are as in Figure 6.

Yet even without platinum, an average NO conversion above 50% can be achieved at higher temperatures. These results are encouraging with respect to further development of such catalyst systems, which are targeted at improved low-temperature activity and tests with respect to deactivation behavior in sulfur-containing exhaust streams. It is, however, expected that the sulfur tolerance would be better than that of the best NO storage catalyst system known so far, which is based on alkaline earth compounds, such as barium.

4. Conclusions

We have developed a truly parallelized stage I screening technique for the detection of NO in the product gas from an array of catalysts. This is based on the color reaction of a reagent with the dye ABTS impregnated on a filter paper. The results are semiquantitative, and the method can thus be used for a preselection of catalyst compositions for a more detailed evaluation. In a first exploratory study, we have used the method to rapidly screen possible $DeNO_x$ catalysts prepared by a route involving impregnation of activated carbon with metal oxide precursors and subsequent combustion of the carbon. Several active compositions have been identified, some of which were more extensively evaluated using a stage II screening system for detailed evaluation of catalyst performance. The results of the stage I screening could be confirmed, and a promising NO storage material was identified which could become useful as a component of a diesel $DeNO_x$ catalyst system. The potential of these systems is being explored further in our laboratories.

The screening method described can be extended toward more massive parallelization to speed up preevaluation of catalysts further, which is underway in our laboratory, and toward other reactions, if suitable dyes are found. For instance, we have also used the technique to detect maleic anhydride as a target product, which reacts with many different dyes having conjugated π-systems via a Diels−Alder reaction, leading to discoloration of the dye on a filter paper and thus indicating formation of maleic anhydride over a catalyst. This method could thus become a very efficient, fast, and cheap stage I screening technique.

JA020629X

---

(38) Kammer Hansen, K.; Skou, E. M.; Christensen, H.; Turek, J. *J. Catal.* **2001**, *199*, 132−140.

(39) Fridell, E.; Persson, H.; Westerberg, B.; Olsson, L.; Skoglundh, M. *Catal. Lett.* **2000**, *66*, 71−74.