Letter

Discovery of new fuel-lean NO reduction catalyst leads using combinatorial methodologies

Sukru Ozturk, Selim Senkan[*]

Department of Chemical Engineering, University of California, Box 951592, Los Angeles, CA 90095-1592, USA

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Abstract

Tools of combinatorial heterogeneous catalysis have been applied for the discovery of new leads of catalytic materials for the hydrocarbon (HC) selective reduction of NO under fuel lean conditions. In a period of 3 months, over 1500 different catalytic materials were explored that contained most of the single component and binary, and some of the ternary and quaternary combinations of metals from the periodic table over γ-Al_2O_3, CeO_2, 13X, Y, ZSM-5, Mordenite and beta zeolites. Diverse libraries were synthesized by the solution-based impregnation and ion-exchange methods for the oxide-based and for the zeolite-based supports, respectively. Catalyst screening was accomplished using array channel micro-reactors and mass spectrometry. A combination of Cu (10 wt.%) and Os (1%) ion exchanged 13X zeolitic material was determined to be an effective NO reduction catalyst lead with C_3H_6 in the temperature range of 250–600 °C. This catalyst also successfully passed a 36 h aging test at 450 °C in the presence of 12% steam and excess oxygen. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Recent developments in automotive engineering have made possible the production of more fuel efficient up to 25%—gasoline engines that operate under excess air conditions [1]. However, the lack of appropriate catalytic technology to reduce NO_x emissions under lean burn conditions is slowing the commercialization of such engines. Lean-burn NO_x reduction catalysts will also be useful to control pollutant emissions from diesel engines [2,3] as well as from gas boilers [4].

Selective catalytic reduction (SCR) of NO_x using on-board hydrocarbons (HC) is one of the most widely investigated areas of automotive NO_x control [5–21]. In spite of decades long research, Pt [10] and Cu [11] exchanged ZSM-5 remain the most significant discoveries. However, Cu/ZSM-5 suffer from the lack of stability under humid exhaust conditions, and Pt supported formulations are active only between 200 and 300 °C, and even then with significant N_2O formation. The lack of progress and the need to consider a vast number of combinations of catalytic materials, both with respect to active elements and supports have been discouraging [22]. In our opinion, this pessimism is partly due to the slow pace inherent with traditional catalysis research methods, compounded by the differences in preparation and testing procedures used in different laboratories which impeded the determination of useful insights regarding the reactivity trends of materials. In addition, the absence of realistic

* Corresponding author. Fax: +1-310-267-0177.
E-mail address: senkan@ucla.edu (S. Senkan).

operating conditions employed by some of the earlier investigators rendered these studies of limited utility for the development of practical automotive catalysts. However, the emergence of combinatorial catalysis promises rapid advances to be made through the systematic exploration of large diversities of catalytic materials in a short period of time.

In order to realize the potential of combinatorial approaches in catalysis, we have been developing high-throughput methodologies to prepare, process and screen libraries of solid-state catalytic materials [23–25]. Specifically, we miniaturized and automated the impregnation and ion-exchange methods of catalyst preparation [24,26]. In addition, we developed array channel microreactors as library structures to simultaneously screen and time-test catalytic materials for the discovery and optimization of practical catalysts [24,25]. In this communication, we now report the first successful application of combinatorial catalysis for the discovery of new lean-burn NO_x reduction catalysts. The significance of our work is to show how combinatorial methods can dramatically accelerate the pace of catalysis research and produce practical leads in an extremely short period of time compared to traditional methods, even when applied to catalysis problems encountered under very harsh operating conditions.

2. Experimental

In our experimental program, we did not bias our library preparation strategy towards formulations that were studied before. Instead, our objective was to systematically create and screen large libraries of new catalytic materials using highly reproducible preparation methods and to generate leads, and to develop a standardized data base for future mining applications. The optimization and characterization of the leads with regard to composition and structure also were not the focus of our studies.

Forty-one active elements and 13 support materials, as shown in TBL1, are presently being considered in our lean-burn NO_x reduction catalysis exploration program. Although we have not completed investigating most of the parameter space, our efforts to date generated exciting new leads for catalytic materials, one of which is reported here.

Table 1

Active component/promotor			Support materials
Ag	Mn	In	13X
Au	Cr	Tl	Y
Pd	V	Ge	Beta zeolites
Pt	Mo	Sn	Mordenite
Rh	Nb	Sb	Ferrierite
Ir	Y	Bi	ZSM-5
Ru	W	Li	ALPO
Os	Ta	K	SAPO
Re	La	Na	Al_2O_3
Zn	Ce	Mg	SiO_2
Cu	Nd	Ca	TiO_2
Ni	Sm	Sr	CeO_2
Co	Sn	Ba	ZrO_2
Fe	Ga		

2.1. Catalyst preparation

In a period of 3 months, we have explored over 1500 different catalytic materials that contained most of the single component, binary, ternary and quaternary combinations of active components (elements) from Table 1 over γ-Al_2O_3, CeO_2, 13X, Y, ZSM-5, Mordenite and beta zeolites. Diverse libraries were synthesized by the solution-based impregnation and ion-exchange methods for the oxide-based and for the zeolite-based supports, respectively. First, solution libraries of precursors were prepared in a 300-site well-plate using a computer-controlled liquid dispensation system [26]. Predetermined volumes of standard stock solutions, each containing an appropriate concentration of metal salts (mostly chlorides and nitrates) were dispensed into the wells. Relative concentrations of each component in the solution were adjusted so that the target metal loadings (wt.%) in the final catalyst pellets or powders were in the range 0–10% for all metals, except noble metals for which the loading ranges were 0–1%. After dispensing appropriate amounts of precursor solutions to the solution library well plate, each site was diluted to 50 μl with deionized water, after which 20–30 mg pellets (4 mm diameter by 1 mm high cylinders) or powders were introduced into each well. Impregnation was allowed until all of the solution evaporated at room temperature. Co-impregnation was practiced whenever possible. However, when conflicting solubility requirements were present, different active metals were
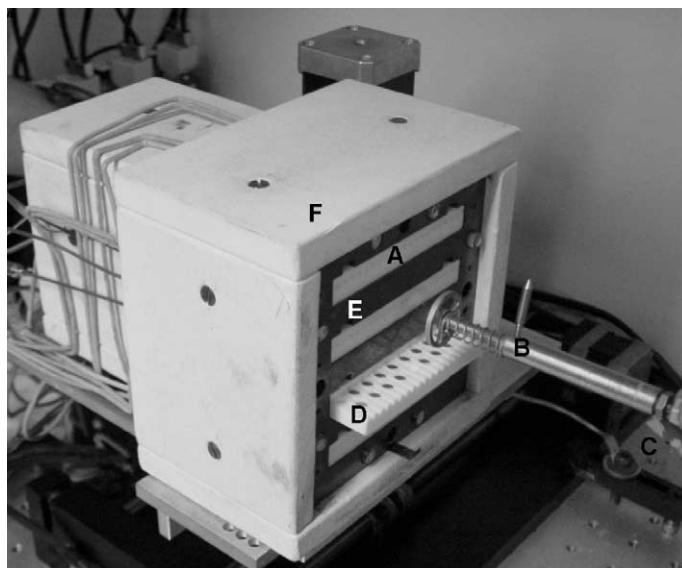
Fig. 1. Array channel microreactor system coupled to mass spectrometer: (A) reactor arrays; (B) heated sampling micro-probe; (C) mass spectrometer; (D) catalyst pellet or powder in the well; (E) heating block; (F) thermal insulation.

incorporated into the support by sequential impregnation. After impregnation, the entire library was dried for 2 h at 90 °C, and for another 2 h at 120 °C. The library subsequently was calcined for 4 h at 550 °C under air atmosphere.

For zeolitic materials, multimetallic formulations were also either co-ion-exchanged or sequentially incorporated into the structure. In this case, substantially larger volumes of precursor solutions, also containing predetermined concentrations of active elements, were prepared and contacted with pellets or powders of support materials. After the completion of the exchange process, the solution was removed and if necessary another metal solution was introduced for sequential ion-exchange. Finally, the supernatant was removed and the library was washed with de-ionized water, dried and calcined as before. The pellets and powders of catalytic materials prepared were then transferred into the array channel microreactors for testing.

2.2. Catalyst testing

Details of the catalyst testing system have been described before [23,24], thus only a brief description will be provided. Catalyst testing was accomplished using four microreactor arrays that were placed inside a temperature controlled heating block as shown in Fig. 1. Each array contains 20 parallel channel microreactors, with cylindrical wells to accommodate the catalytic materials. Thus, it was possible to simultaneously test 80 different catalysts. In the present experiments, duplicates of selected combinations of catalysts as well as blanks were used to explore reproducibility and the effects of supports. Pellets as well powders of were used, with insignificant differences in observed catalytic properties. Reproducibility of the results were +10% in all the experiments. The reactor block was placed on a computer controlled precision x–y–z movement mechanism, thus it was possible to automatically and sequentially analyze the exhaust streams of each reactor channel. The complete analysis of the entire 80 array channel reactors took less than an hour.

Libraries of catalytic materials were screened under the exhaust gas simulant conditions of 3000 ppm NO, 3000 ppm C_3H_6, 10% O_2, 6–12% H_2O and the balance helium, at a gas space hourly velocity (GSHV) of 60,000 h^{-1}. Calcined pellets or compacted powders were placed into the wells of the array channel microreactors [24] and tested for NO reduction activities over a temperature range of 200–600 °C. Gas

analysis was accomplished by withdrawing samples from the exhausts of channel microreactors using a heated capillary sampling probe, followed by electron impact ionization quadrupole mass spectrometry [26]. Catalyst screening was accomplished by monitoring the NO (mass 30) signal at the reactor exit. Although the formation of other species, such as NO_2 and N_2O, may also contribute to mass 30 signal, monitoring the mass 30 still represents a good primary screening diagnostics to assess NO elimination [26].

Among the numerous multimetallic combinations searched so far, we were able to generate several leads for high-performance catalytic materials, in terms of NO_x reduction activity and durability, that were superior to the most successful catalysts reported earlier in the literature [6,9,18,30]. Specifically, we discovered that a combination of Cu and Os ion exchanged 13X zeolitic materials provide excellent NO reduction activities with C_3H_6 over a broad temperature range and maintained their activities over a 36 h test period in the presence of steam and excess oxygen. Other materials prepared and tested to date in reference to Table 1 were inferior to the CuOs/13X system.

Specific preparation of the reported catalytic materials: CuOs/13X catalysts were prepared by a two stage ion-exchange process. In first stage an aqueous solution of $Cu(NO_3)_2 \cdot 6H_2O$ (Alfa Easar), with a concentration that would lead to the desired Cu loading of the final product was allowed to ion exchange with 13X (Aldrich, $SiO_2/Al_2O_3 = 2.8$) for 2 days. After the incorporation of the Cu, the supernatant was removed and the solids were washed and further contacted with a solution of $(NH4)_2OsCl_6$ (Alfa Easar) for 2 days. After the completion of the second stage, the solids were washed and dried in air at 120 °C for 2 h and then calcined for 4 h at 550 °C. We also prepared Cu/ZSM-5 and used in activity tests as a reference material following the procedure described in the literature [5]. Activity trends observed with this reference material were found to be in complete harmony with literature reports [27–29].

3. Results

Among the various Cu and Os loadings explored, 10 (wt.%) Cu and 1 (wt.%) Os as initial levels were found to give the best results. In Fig. 2 the fractional NO conversions of a *fresh* CuOs/13X catalyst are compared to those observed on Cu/ZSM-5 both in the absence and presence of 10% steam in the feed mixture. As can be seen from Fig. 2, CuOs/13X provided significantly higher conversions of NO when compared to Cu/ZSM-5 over a broader temperature range. In addition, CuOs/13X also exhibited a lower light-off temperature of about 250 °C, compared to 350 °C for Cu/ZSM-5. In fact at 300 °C, the NO reduction activity of CuOs/13X was about a factor of 10 higher than Cu/ZSM-5. In the absence of steam, NO conversions in excess of 0.70 were readily attainable over a
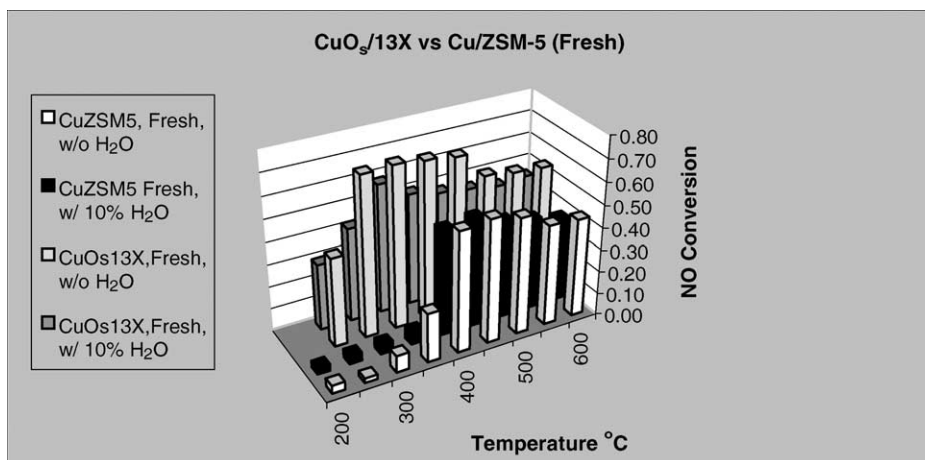

Fig. 2. NO Conversions of fresh catalysts both in the absence and presence of water vapor.

temperature range of 300–450 °C for the CuOs/13X catalyst, yet the peak NO conversions were at best 0.5 for Cu/ZSM-5 at 450 °C. The superiority of the CuOs/13X was even more pronounced in the presence of steam, as evidenced by its substantial activity over the entire temperature range, with NO conversions reaching almost 0.6 at 400 °C. In comparison, the onset of NO reduction activity of Cu/ZSM-5 was at 400 °C exhibiting a peak conversion of about 0.48. CuOs/13X also maintained a higher activity over the entire temperature range of 250–600 °C investigated. In contrast, the activity of Cu/ZSM-5 steadily decreased with increasing temperature after its peak at about 400 °C. It should also be noted that the extent of NO reductions observed in single component Cu/13X [15] or Os/13X were significantly inferior to the bimetallic CuOs/13X combination reported in Fig. 2.

However, the most significant aspect of the CuOs/13X catalyst was its superior *durability* in steam when *compared* to Cu/ZSM-5. As shown in Fig. 3, CuOs/13X catalyst exhibited significant NO conversions over the entire 250–600 °C temperature range even after 36 h of aging in 12% steam at 450 °C. It is particularly important to note that CuOs/13X also maintained significant low temperature activity as well. For example, at 350 °C the NO conversion of 0.48 for the CuOs/13X was an order of magnitude higher than the Cu/ZSM-5. The significant deactivation of Cu/ZSM-5 over the same 36 h testing period is consistent with the results reported in the literature

[27–29]. As seen in Fig. 3, this deactivation was particularly severe at lower temperatures. These results are somewhat surprising because 13X with its SiO_2/Al_2O_3 ratio of 2.8 would have been expected to deactivate via steam dealumination more rapidly than ZSM-5 which has a significantly higher ratio.

Clearly safety, durability and cost issues will ultimately determine the commercial viability of any catalytic material. For example, the incorporation of osmium into the zeolite crystal structure, as well as the potential toxicity of osmium tetroxide that may form under certain conditions, must be considered as part of the commercial catalyst development process. Since our 36 h aging tests were successful, the structure and composition of the CuOs/13X must have remained the same during the testing period. This suggests that the loss of the incorporated cations must have been small during the aging period, giving us hope that CuOs/13X or its variants may be viable catalytic materials. It should also be pointed out that, even the 36 h aging period is inadequate to fully assess the commercial potential of a catalytic material. However, further durability tests were not practical under the combinatorial test strategy. Nevertheless, our ability to discover a catalytic material that is superior to the Cu/ZSM-5 in a short period of time is encouraging.

In summary, through the implementation of combinatorial heterogeneous catalysis tools, the 10% Cu and 1% Os ion-exchanged 13X has been determined to be an effective catalyst lead for the HC-SCR of
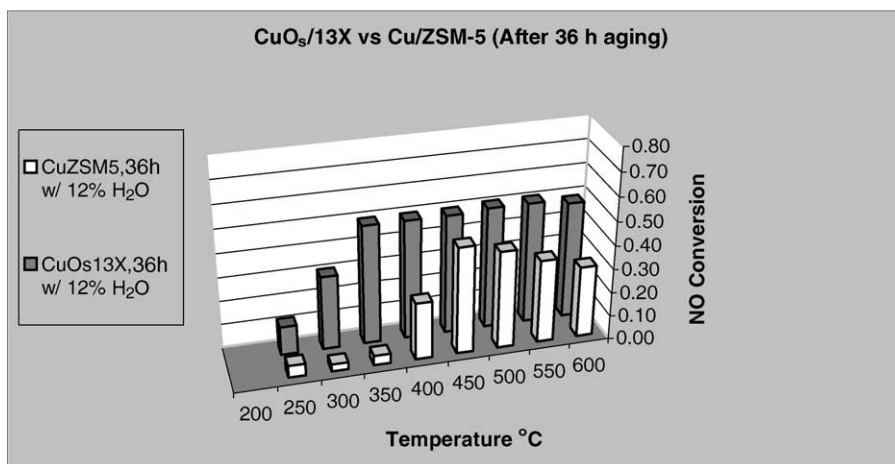

Fig. 3. NO conversions of catalysts after 36 h of aging process in 12% steam at 450 °C.

NO_x with C_3H_6 under simulated automotive lean burn exhaust conditions. These results immediately call for the further investigation of this material and its analogs both with regard to their chemical and physical structures and the precise nature of the reaction products and by-products. Our findings are particularly significant in demonstrating how combinatorial approaches can produce new leads in a short period time and can generate renewed optimism in a challenging old research area.

Acknowledgements

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