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Extruded Zeolite Catalysts for Lean Exhaust Application

R. Wusirika, S. Ogunwumi and W. Lucas
Corning Incorporated

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ABSTRACT

In lean burn engines, the conventional automotive catalyst is ineffective in reducing harmful nitric oxide (NO_x) wastes. This study has investigated the use of different materials with metal additives as supports for effective NO_x -controlling lean burn catalysts. A series of zeolite (ZSM-5) honeycomb samples were prepared via extrusion with low concentrations of transition metals. Samples were also impregnated with Pt to determine the effect on the catalytic activity. NO_x and hydrocarbon conversion under simple lean conditions were measured in a temperature-controlled fixed bed reactor. Ethylene and Propylene, both highly selective NO_x reductants, were used separately as the hydrocarbon species. Results have revealed that single and double component zeolites containing Ni, Mn, Cu, and Ag are highly effective in reducing NO_x . When these same samples were impregnated with Pt, they achieved conversion rates up to 100% at temperatures less than 300°C at a space velocity of 7000 h^{-1} . At higher space velocities, up to 80% NO conversion is observed for some catalysts. The performance of the Ni-Co catalyst remains encouraging and is not impaired by moderate aging conditions and by the presence of water.

INTRODUCTION

As environmental regulations concerning automobile exhaust emissions become more stringent, there is an urgent need for the development of a catalyst which can curtail harmful pollutants.

Automotive catalysts work as three-way catalysts converting carbon monoxide (CO), hydrocarbons, and nitric oxide (NO_x), the three major pollutants into CO_2 , N_2 and H_2O . Presently, the most widely used three-way catalysts in gasoline engines are ceramic honeycomb supports containing noble metals such as platinum (Pt), rhodium, and palladium. The gasoline engine operates at a stoichiometric air/fuel ratio of 14.6:1, in which the

catalyst is effective in oxidizing CO and hydrocarbon wastes while reducing NO_x at the same time. On the other hand, the diesel engine, relying on the burning of fuel in an excess of oxygen, typically operates at air/fuel ratios greater than 17:1. Under these lean conditions, the conventional three-way catalyst acts as an oxidation catalyst, only controlling the levels of CO and hydrocarbons. Overall, it displays poor conversion of NO_x . Hence, new highly active catalysts which can effectively reduce NO_x as well as other hazardous emissions under lean conditions are desirable. Both HC-SCR and NH_3 -SCR have been proposed and are being explored [1].

Several factors affect the performance of a catalyst. A strong ceramic structure, high surface area, thermal and chemical stability, and high heat resistance are all important characteristics of an active catalyst. Essentially, all of these variables are determined by the materials used for support. Thus, the selection of the proper material is the most critical requirement in the development of a catalyst.

According to published literature, several base metal catalysts for effective NO_x reduction exist [2-3]. Studies have suggested that in the absence of de NO_x inhibitors, such as H_2O , CO_2 , and SO_2 , in diesel exhaust, the addition of first row-transition metals to zeolite-supported catalysts results in a significantly improved reduction rate of NO_x . Among these supports, Cu-ZSM-5, a copper-exchanged zeolite catalyst, is used as a benchmark for hydrocarbon selective catalytic NO_x reduction. Numerous studies have been conducted on the exchange of one metal ion with zeolites [4]. Studies dealing with zeolites impregnated with two or more different transition metals and wash-coated on a cordierite honeycomb have been reported [5] to offer a wider NO_x reduction window. These studies are few and limited. However, no literature seems to be available or is limited on the study of one or two transition metals supported on extruded zeolite catalysts.

In this paper, NO_x reduction activities of extruded zeolite catalysts are discussed. ZSM-5 was impregnated with either one ion or two different transition metals. Because Cu-ZSM-5 has been already determined to be highly active, most double component zeolite samples were impregnated with Cu, in addition to another transition metal. Also, catalysts were doped with Pt, to improve NO_x conversion rates. Emissions control tests of each catalyst were operated under simple lean conditions. The feed concentration was carefully chosen with reference to a study on the selectivity of hydrocarbons towards the conversion of NO_x [6-7]. These extruded zeolites were shown to exhibit high NO_x conversion over wide temperature ranges depending on the space velocity and the reductant used. Ethylene and propylene which are highly selective NO_x reductants, were chosen as the hydrocarbons for the study. Water was not included in the flow exhaust for the majority of the tests conducted. A low space velocity was used initially so minor changes in activity could be observed. The scope of this study is to evaluate the feasibility of developing extruded zeolite catalysts for hydrocarbon selective reduction of NO_x in lean burn application. The successful development of such a catalyst would provide the option of a catalyst ready material without the need for a washcoat step. Potential issues of washcoat erosion could thus be avoided. Emphasis is placed on both the physical properties of the extruded catalysts and the performance. We also hope to gain a better understanding of how the reducing activities of extruded zeolite supported catalysts in diesel exhaust engines are affected by the addition of transition metals.

EXPERIMENTAL

CATALYST PREPARATION AND PROCESSING

ZSM-5 (55/1: SiO₂/Al₂O₃) was chosen as the zeolite for this study. The zeolite powder was supported with the selected transition metal via impregnation. The impregnated materials were prepared with two different concentrations of the transition metal, 0.5% and 1.5%. In case of the double component systems, the ratio of zeolite to metals catalysts was always 97% of the main powder, 1.5% of the first metal, and 1.5% of the second metal. The resulting slurry after the impregnation is dried and fired. The resulting hardened powder agglomerate is crushed into a fine powder. Organic and inorganic binders are added to powder and wet-mixed. The resulting paste is extruded into honeycombs (200 cells/in²) and rods. For the platinum promoted samples, selected fired powder batches with the transition metals

were mixed with a platinum derivative prior to the wet-mixing and binder addition. The platinum (0.5%) is added to the powder and mixed in an aqueous medium. The procedure is the same as described before from that point onward, consisting of drying the powder, firing the powder, wet mixing of binders and extrusion of the resulting paste. The resulting honeycombs and rods are dried in an oven followed by firing in an electric furnace.

CATALYST TESTING

Ethylene as a reductant

Catalytic activity was measured as a function of inlet temperature in a fixed-bed reactor containing a 200 cpsi honeycomb sample (1.0 in. diameter x 1.0 in. length). Activity was monitored as the electronically-controlled reactor temperature was ramped from 120°C to 600°C at a rate of 8°C/min. A feed composition of 1200 ppm of C₂H₄, 230 ppm of NO_x, and 7% O₂ (balance of N₂) at a space velocity of approximately 7000 hr⁻¹, was used to represent a typical diesel exhaust. The rate of NO_x conversion was measured by a Rosemount Model 951A NO/ NO_x Analyzer chemiluminescence detector, while hydrocarbon data was collected by a Rosemount 3-4 Model 400A flame ionization detector.

Propylene as reductant

The activity tests were carried out in a conventional stainless steel tubular reactor flow system. The analysis of NO, N₂O, NO₂, CO, CO₂, and H₂O in the inlet and outlet gas stream was performed using a 560 Nicolet Gas FTIR, which is equipped with an MCT (Mercury-Cadmium Telluride) detector and integrated with an MKS Type 250E pressure/flow controller from MKS Instruments. The effluent gases were monitored at 4 cm⁻¹ resolution. The following simulated exhaust gas mixture is passed through the reactor: 7% O₂, 0-10% CO₂, 250 ppm NO_x, 0-0.16% CO, 2000 ppm C₃H₆, 560 ppm H₂, and 0-10% H₂O. The gas flow is nitrogen-balanced. By adjusting the feed flow rates of the gas mixture, the space velocity is varied between 7,000-30,000 h⁻¹ depending on the condition of the experiment. Typically, the experiments were conducted in the temperature range of 150 to 600 °C. The ramping rate is set for 8.5 °C/min. Prior to each run, the gases are quantified. A mass balance of the initial NO_x concentration with respect to the amount of N₂O and NO₂ formed is used to determine the amount of N₂ produced.

Temperature programmed desorption

The temperature programmed desorption (TPD) experiments were performed with crushed powder samples on a Altimira 200 analyzer. In a typical experiment, about 1.0 gram ground catalyst sample was loaded in an Altimira-200 sample holder. The sample is pre-conditioned by heating in a 10% O₂/He gas mixture at 300°C for 30 minutes. Following this treatment, the sample is flushed with Ar gas after cooling to room temperature. The catalyst sample is then exposed to a 10% nitric oxide in helium at 25 ml/minute with a thirty minutes hold. Argon is introduced as a sweep gas to flush any excess NO physically adsorbed on the sample until the thermal conductive detector (TCD) detector baseline stabilizes. The sample is then heated to 550°C with a ramp rate of 10°C/minute, while the effluent is monitored continuously by the TCD.

EXTRUDED CATALYSTS PERFORMANCE WITH ETHYLENE REDUCTANT

The key results are discussed in this section of the activities measured on various catalysts extruded. As mentioned earlier, a feed composition of 1200 ppm of C₂H₄, 230 ppm of NO_x, and 7% O₂ (balance of N₂) at a space velocity of approximately 7000 hr⁻¹, was used for this portion of the experiment. A low space velocity was chosen to facilitate the easier comparison and detection of small changes in activity.

SINGLE METAL CATALYSTS

All metals compared initially in this series are from the first row transition metals with the exception of Ag. In all cases, similar trends can be observed in the catalytic activity. Under the experimental lean conditions, the transition metal impregnated ZSM-5 catalysts exhibited selective reduction of NO_x by hydrocarbons. In every sample, the conversion of NO_x was dependent on the behavior of the hydrocarbons. Maximum conversion of NO_x coincides with complete conversion of hydrocarbons, illustrating ethylene's selectivity towards the reduction of NO_x. Beyond the maximum conversion temperature, NO_x activity typically decreases as the remaining hydrocarbon pollutants are oxidized.

Upon comparison of the NO_x reduction activities of the catalysts containing 0.5% transition metal, Cu-ZSM-5 was among the least active samples, converting about 25-35% of NO_x, at temperatures between 400 - 500°C. For hydrocarbon NO_x selective catalytic reduction study,

the activity of Cu-ZSM-5 is typically used as a benchmark for comparison [4].

Ni-ZSM-5 was the most active catalyst, exhibiting a NO_x conversion rate as high as 55% at an inlet temperature of 399°C. The temperature window representing greater than 50% activity was between 365-440°C. Fe-, Mn-, and Ag-impregnated catalysts also had fair conversions of NO_x. The activities of these most active samples are displayed in Figure 1. The highest NO_x conversion data is extracted and shown along with other metals used in the study in Figure 2.

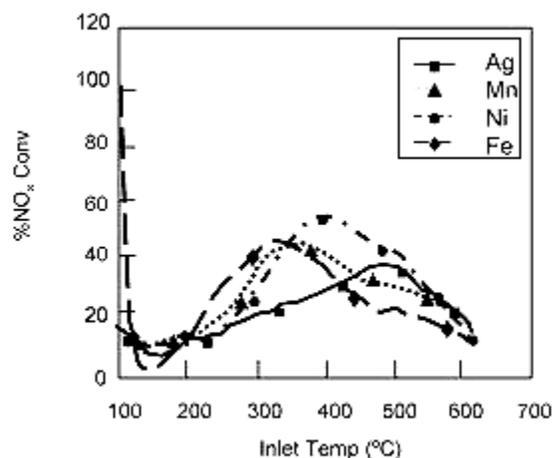


Figure 1. Most active single-ion impregnated extruded zeolite catalysts at 7000 hr⁻¹.

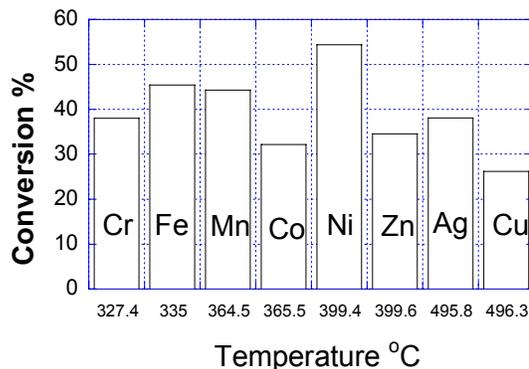


Figure 2. Highest NO_x conversion of single-ion impregnated extruded zeolite catalysts at 7000 hr⁻¹.

The effect of increasing the metal loading was also studied. The effect of increasing the concentration of transition metals to 1.5% varies from sample to sample, with NO_x conversion either increasing or decreasing.

Overall, an increase in the concentration of the metals did not account for much improvement in most catalysts. Ni-ZSM-5 showed the most significant improvement. The activity increased from 55% to 72%.

BIMETALLIC CATALYSTS

The addition of another transition metal to a metal-impregnated zeolite catalyst resulted in a significantly higher selectivity towards the reduction of NO_x by ethylene. The total loading for both metals was 3% per sample, where each metal was 1.5%. With the exception of a sample containing Cr and Cu, all of the catalysts displayed NO_x conversion rates greater than 60%. The Cu-ZSM-5 samples containing Ni, Ag, and Mn were the most active, achieving NO_x conversion rates of 80-90%. Figure 3 shows a comparison of the most active catalysts. The highest NO_x conversion for all the bimetallic catalysts used in the study is summarized in Table 1. Information about the temperature window representing greater than 50% conversion is also included in the table.

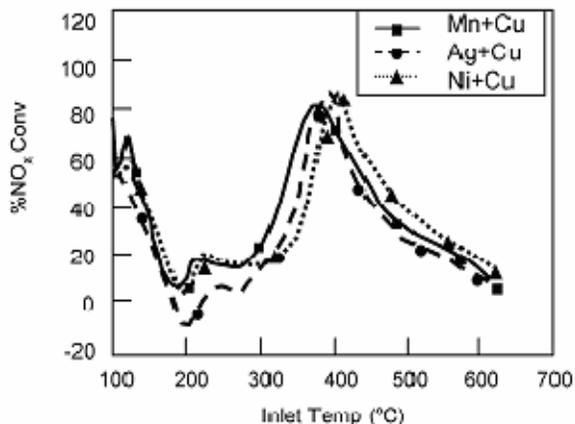


Figure 3. Most active bi-metallic impregnated extruded zeolite catalysts at 7000 hr⁻¹.

TABLE I Conversion data of bi-metallic zeolite catalysts

Catalyst	Max. NO _x Conv/Temp	Temp. Range (50% conversion)
Ni+Fe-ZSM-5	62% @ 474°C	390-525°C
Ni+Cu-ZSM-5	88% @ 401°C	350-430°C
Co+Cu-ZSM-5	69% @ 417°C	380-440°C
Ag+Cu-ZSM-5	86% @ 396°C	365-420°C
Mn+Cu-ZSM-5	82% @ 378°C	330-440°C
Fe+Cu-ZSM-5	70% @ 417°C	365-455°C

The double component zeolites exhibiting the highest conversions of NO_x corresponded with the most active single-metal impregnated zeolite catalysts also containing Ni, Mn, Ag, and Fe. This is an indication that the metals are able to retain their effectiveness, even when combined with a different ion. When overlaying the graphs of each single metal-impregnated ZSM-5 sample with its respective double component zeolite, a synergy between the two ions can be observed. An example is shown below in Figure 4.

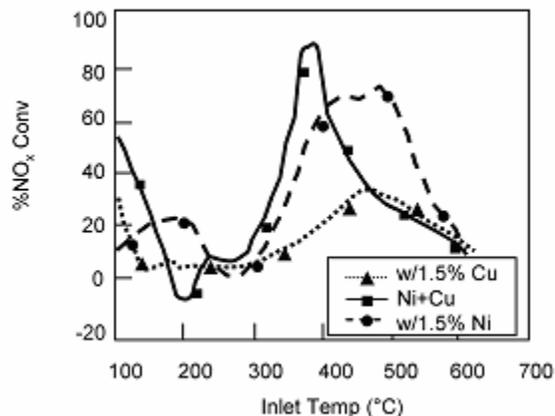


Figure 4. The synergy in a double component ZSM-5 catalyst

Additional characterization studies would be required to understand the synergetic effect observed. Such work is beyond the scope and objective of this paper.

Precious metal effects

Catalysts impregnated with Pt (0.5%) and transition metals not only showed greater reduction of NO_x but also displayed substantially lower light off temperatures

and broader temperature ranges for conversion than samples without Pt. Several catalysts containing combinations of Ni and Cu, Mn and Cu, and Fe and Cu, exhibited 100% NO_x conversion, while other samples achieved near-complete conversion. Overall, the Pt-coated samples had the highest conversion rates and the most activity at lower temperatures. The light off temperatures of both hydrocarbons and NO_x were completely shifted to lower temperatures between 160-320°C. Subsequently, there is a loss of the catalytic activity that transpires at higher ranges between 350-500°C in the absence of Pt.

Presented in Figure 5 is an example illustrating the change in activity with the addition of Pt to the Fe and Cu impregnated ZSM-5 zeolite.

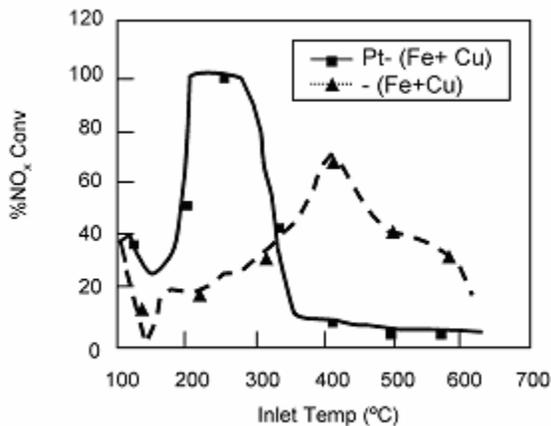


Figure 5. Difference between catalytic activities in samples impregnated with and without Pt.

The performance of other bimetallic impregnated zeolite catalysts in the presence of Pt is summarized in Figure 6. The plot represents the active NO_x temperature window corresponding to a minimum of 50% conversion. The highest NO_x conversion at temperature is also reported (see bar text insert in Figure 6).

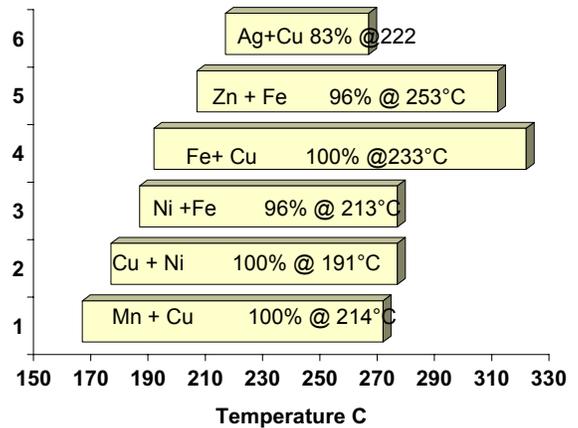


Figure 6. 50% NO_x conversion window activities for zeolite catalysts impregnated with two transition metals and Pt.

Upon comparison of the Pt-impregnated double component zeolites, the results suggest that the transition metals do not appear to contribute towards any NO_x conversion. Since the catalytic activities were similar in all cases, it is possible that there is not a synergy between the two transition metals and Pt. Instead, the high conversion rates of the catalysts are a result of Pt alone, while transition metals have no significant impact on activity in the presence of the noble metal.

EXTRUDED CATALYSTS PERFORMANCE WITH PROPYLENE REDUCTANT

For this series of catalysts activity tests, the bi-metallic series was chosen for the study. Based on the earlier results with ethylene above, the following series Ni-Cu, Cu-Ag, Fe-Cu were selected and their activities compared. Also included was a Ni-Co catalyst (prepared similarly) which was found to be active in a separate test. The NO_x reduction performance at 400°C, and tests conditions are shown in Figure 7.

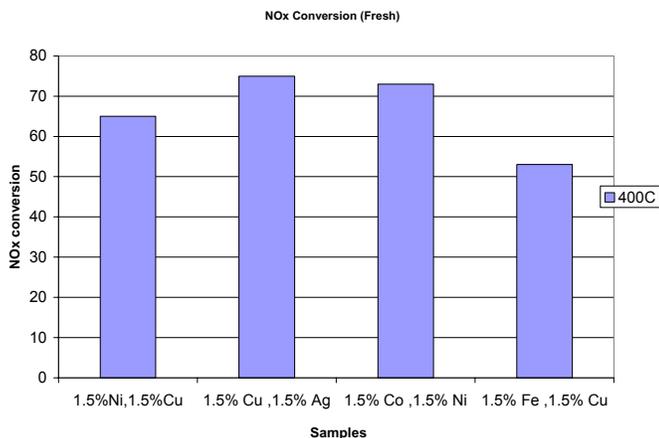


Figure 7. Comparison of NO_x activities at 400°C bimetallic zeolite catalysts. Test condition (230 ppm NO_x, 1200 ppm C₃H₆, and 7% O₂ at 7,000 h⁻¹ S.V).

Both the Cu-Ag and Co-Ni samples displayed NO_x conversion activity greater than 70% at 400°C. Upon comparison of the activity windows (Figure 8), the Ni-Co catalyst was found to display the broadest performance window in the series. The NO₂ and N₂O selectivity were also monitored during the test. Both NO₂ and N₂O levels for the Ni-Co and Fe-Cu catalysts were less than 10% for the activity range tested. The highest amount of NO₂ formation observed for the Ni-Cu and Cu-Ag catalysts were 22% and 13% respectively. Similarly, the highest N₂O observe for the Ni-Cu catalyst was 20%, and 23% for the Cu-Ag catalyst. Upon comparison of the hydrocarbon activity of Ni-Cu, Fe-Cu and Cu-Ag catalysts, the maximum NO_x conversion measured using propylene was slightly lower than with ethylene. With propylene, a slight shift to higher temperatures is observed with the lower temperature NO_x reduction peak. This causes the activity at lower temperatures with propylene to be slightly increased as well.

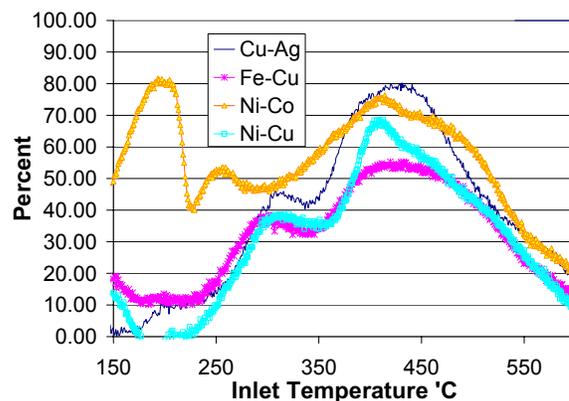


Figure 8. NO_x conversion for bimetallic zeolite catalysts, (test condition : 230 ppm NO_x, 1200 ppm C₃H₆, and, 7% O₂ at 7,000 h⁻¹ S.V).

NO desorption from the bimetallic catalysts in Figure 8 were analyzed by temperature programmed desorption (TPD). The results are presented in Figure 9. These catalysts displayed a wide range in temperatures for NO desorption. Above 200°C, the Ni-Co catalyst shows at least two broad maxima for NO desorptions within a wide temperature range (200 - 550°C). This result coincides with the high activity of the Ni-Co catalyst reported in Figure 8. Both the Ni-Cu and Cu-Ag catalysts display NO desorption peaks at 403 and 407°C, respectively. Both catalysts also demonstrate comparable NO_x reduction activities as shown in Figure 8. Above 300°C, the Cu-Ag shows a higher activity for NO_x reduction in Figure 8 compared to the Ni-Cu catalyst. This is possibly associated with the higher NO desorption of the Cu-Ag catalyst over the Ni-Cu catalyst above 300°C in Figure 9. The maximum NO desorption for the Fe-Cu catalyst appears at 338°C. This maximum appears to be slightly shifted relative to the Ni-Cu and Cu-Ag catalysts desorption maxima at 403 and 407°C respectively. Upon comparison of the Fe-Cu catalyst activity curve in Figure 8 with both the Ni-Cu and Cu-Ag catalysts activity curves, similar features are observed, but with a slightly decreased activity of the Fe-Cu catalyst. Based on micromoles of NO adsorbed per gram of sample (results not shown), the catalysts can be placed in the following order, Ni-Co > Fe-Cu > Cu-Ag > Ni-Cu. With the exception of the Fe-Cu catalyst, the order coincides with the NO_x conversion efficiency reported in Figure 7.

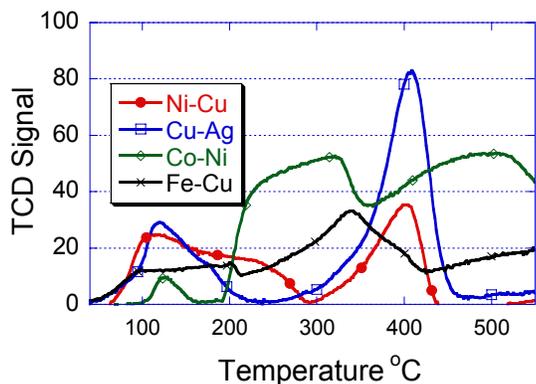


Figure 9. NO desorption TPD profiles
NO gas: 10% NO/He, Pretreatment O₂/He

To evaluate the durability of these extruded catalysts, one composition was selected in order to minimize the number of tests. Based on the broad and high activity window of the Ni-Co catalyst in Figure 8, it was chosen as the representative catalyst for study. The Ni-Co catalyst sample was aged at a moderate condition of 400°C for 8 hours with 3% water. After the aging, the catalytic tests were performed without water using the same conditions as the previous experiments conducted with propylene in Figure 7 at 7,000 h⁻¹. The post aging activity at 412°C (73%) was found to be comparable to the fresh sample reported in Figure 7 and 8. Thus, no drastic change is expected from these extruded catalysts after undergoing aging at 400°C for 8 hours with 3% water.

SPACE VELOCITY AND WATER EFFECTS

Additional tests were conducted based on the encouraging results presented thus far with these extruded zeolite catalysts. These tests provided information about the extruded zeolite catalyst performance at higher space velocities and in the presence of water.

The Ni-Co catalyst was again selected for this study based on reasons mentioned above. The performance of a fresh sample of the catalyst was evaluated at 20,000h⁻¹ using the same gas composition from the latter test: 230 ppm NO_x, 1200 ppm C₃H₆, and 7% O₂.

The performance is shown in Figure 10 below.

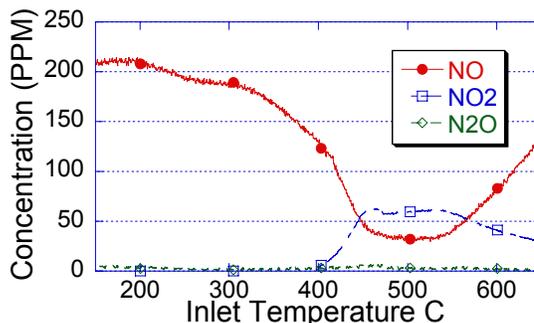


Figure 10. Ni-Co catalyst NO_x conversion efficiency at 20,000 h⁻¹. Gas Composition : 230 ppm NO_x, 1200 ppm C₃H₆, and, 7% O₂ at).

At 20,000 h⁻¹, the NO_x reduction activity of the catalyst was greater than 50% between 415 to 625°C. The highest conversion observed for the catalyst at this space velocity was calculated to be 85% at 503°C. Some NO₂ was generated within the active NO_x conversion range but less than 55 ppm. No significant amount of N₂O was observed.

The effect of water is compared in Figure 11 on the Ni-Co catalyst. The inclusion of 5% water vapor in the gas mixture did not suppress the conversion efficiency of NO_x. Instead, the maximum NO_x conversion increases; the range is broadened and shifted to higher temperatures.

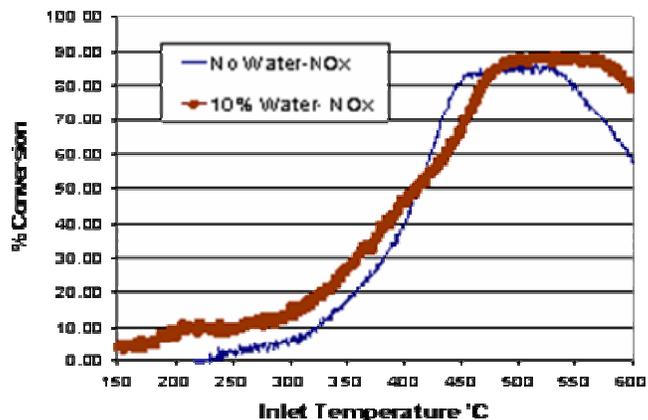


Figure 11. NO_x conversion for Ni-Co zeolite catalysts in the presence of 0 and 10% H₂O (other test condition : 230 ppm NO_x, 1200 ppm C₃H₆, and, 7% O₂ at 7,000 h⁻¹ S.V).

TABLE 2 Physical properties of selected metal supported zeolite catalysts

Sample	Porosity %	BET Surface Area, m ² /g	CTE at 800°C, cm/cm/°C x10 ⁻⁷	MOR, psi
ZSM-5+1.5% Ni	51	372	-16	1282
ZSM-5+1.5% Ni+1.5% Cu	51	368	-14	1167
ZSM-5+1.5% Ag+1.5% Cu	50	355	-19	1204
ZSM-5+1.5% Ni +1.5% Co	48	365	-14	777
ZSM-5+1.5% Fe+ 1.5% Cu	38	374	-13	760

This is probably linked with the suppression of the propene combustion activity observed (result not shown) in the presence of water. This is expected since NO_x reduction and propene oxidations are competing reactions. It is also possible that the addition of water helps to volatilize carbonaceous deposit in to CO, CO₂, and H₂. Both CO and H₂ are active for NO_x reduction. The maximum NO₂ observed increases from 55 ppm to 115 ppm in the presence of 10% water. The amount of N₂O generated was considered to be negligible. The activity of the Ni-Co was not suppressed by further testing at 30,000 h⁻¹. As expected due to the higher space velocity, the activity window was shifted to a higher temperature in comparison to the test at 20,000h⁻¹. However, the maximum NO_x conversion remained comparable.

The performance of the Ni-Co catalyst in the presence of water may not be the same as the other catalysts from the series. Additional experiments would be necessary in order to understand the performance of the remaining catalysts in the presence of water.

PHYSICAL PROPERTIES EVALUATION

In this work we impregnated ZSM-5 with various transition metals and extruded the zeolite honeycombs to study the catalytic activity as well as durability. Silicon resin was used as binder to provide strength to the honeycombs. Alternately γ-alumina can be used as a binder. In this work we refrained from using γ-alumina to avoid any ambiguity in interpreting the initial catalytic activity due to the additional presence of γ-alumina. The measured physical properties from the selected bimetallic series are provided in Table 2 below. An example result of a single metal extruded zeolite catalyst is included for comparison.

The surface area of ZSM-5 powder with SiO₂/Al₂O₃ ratio of 55:1 used in this investigation is 350m²/gm. After metal(s) impregnation, there is very little change in the surface area of ZSM-5 honeycombs fired to 600°C with silicon resin binder indicating no loss of catalytic activity or accessibility of gases to zeolite pores. The slight increase in surface area could be attributed to silica resulting from the inorganic binder. Further aging of these extruded catalyst at 600°C for ten hours in 3% steam resulted in less than 3% loss in surface area.

Rod modulus of rupture (MOR) of cordierite with 45% porosity is around 2000 psi. The rod strength of extruded ZSM-5 catalysts rods on the other hand range from 750 to 1280 psi. The strength of the extruded ZSM-5 honeycombs catalysts comes from silica which is added as the silicon resin binder. The single metal impregnated catalyst appears to be slightly stronger than the bimetal impregnated catalysts. The strength can be increased by increasing the amount of silicon resin binder. Strength however has to be balanced against keeping zeolite pores open for catalytic activity.

Generally, low coefficient of thermal expansion (CTE) is an attractive attribute for high temperature exhaust application. The thermal expansion coefficient of a material would govern how a material expands and contracts during heating and cooling. Low CTEs are typically desired because they correspond to higher thermal shock resistance. The negative thermal expansion behavior of zeolites has been attributed to the highly open framework and 2- or 3- dimensional channel systems [8]. Their open structures can accommodate any structural expansion on heating into the pores and channels. Increasing the silica content and addition of alumina are both methods of balancing and attaining a zero CTE extruded zeolite catalyst. The measured elastic modulus (emod) values for these extruded catalysts at room temperature are low. A low emod for

such ceramic typically means a lower stress for a given strain. Using a non-destructive ultrasonic method, a value of 5.6×10^5 psi was measured for the Ni-Co catalysts. Values for the other catalysts in the bimetallic series are expected to be comparable.

A representative scanning electron micrograph of a polished section of the extruded Ni-Co catalyst is shown in Figure 12. The bar given in the micrograph provides the scale factor. The usual particle features shown in the micrograph are probably due to silica and other additives incorporated in the mixture prior to extrusion. The hollow oval structures observed at high magnifications are generated as result of the processing of the sample (drying and firing).

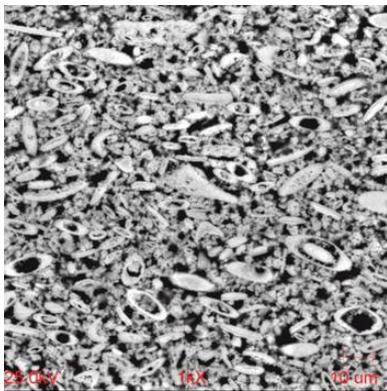


Figure 12. Scanning electron micrograph for the extruded Ni-Co zeolite catalysts (x5000).

Based on x-ray diffraction powder measurements, no significant differences were observed between the pattern of parent zeolite and metal supported extruded zeolite catalysts. This is probably because the metal(s) loading approaches the sensitivity limit of the instrument. On the other hand, this is also a possible indication that the metals are well dispersed on the zeolite. The EDX elemental map is shown below for the Ni-Co catalyst. Both Ni and Co particles appear to be uniformly dispersed on the zeolite matrix. The Co particles appear to be slightly more dispersed compared to the Ni particles. TEM indicates that the metal particles are fairly dispersed and about 200 nm in size .

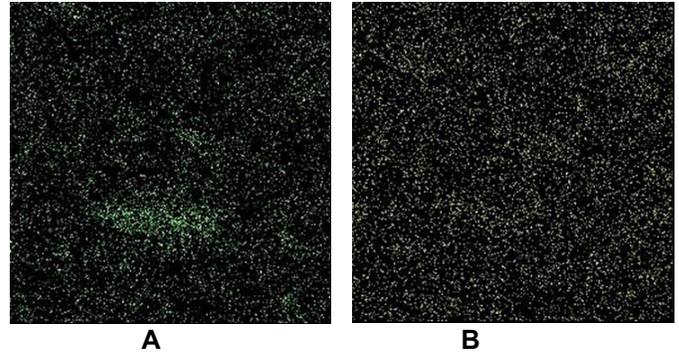


Figure 13. EDX-elemental map for Ni-Co extruded zeolite catalysts. (A. Co, B. Ni)

CONSIDERATION FOR A ZEOLITE BASED LEAN NO_x CATALYST

Zeolite based catalysts are probably the most investigated class of catalysts for lean NO_x reduction using hydrocarbon. Ion exchange and impregnation are two of the most common techniques associated with supporting metals on zeolite supports. The resulting catalyst is typically tested in a form of a powder, pellet or a wash coat on a cordierite or alumina honeycomb substrate.

In this work, we demonstrated that the extrusion of an active zeolite catalyst is possible. An advantage of the resulting extrudate is that it has the desired honeycomb configuration for exhaust application. This approach of using an extruded zeolite catalyst would offer most of the typical benefits of a low CTE ceramics such as low back pressure and high uniform porosity.

Prior to the extrusion, the reaction exhaust kinetics may be used to determine the metal(s) loadings. The choice of active metals would also depend on possible synergy existing between metals. Additional strength gain is possible by increasing the content of silicone binder, the silica source. Although alumina was not used in this study, further strength and CTE balance is also possible by alumina addition.

The thermal durability of zeolites is not so much a concern for this application as the durability in the presence of water (hydrothermal durability). The initial hydrothermal durability tests performed thus far appear to have no significant impact on the catalyst activity. A slight loss of zeolite surface area was observed (<3%). Additional hydrothermal durability tests using more

stringent conditions are necessary to evaluate the hydrothermal stability of these extruded zeolite catalysts.

Recent progress reports on improving the hydrothermal stability zeolites have been very encouraging. Co and In based ZSM-5 supported catalysts were reported in two separate cases to exhibit high stability in steam [9-10]. Such findings offer possibilities of developing a successful ZSM-5 catalyst that is stable in a hydrothermal environment. The recent discoveries of SUZ-4 and IM5 offer two additional zeolite supports for lean NO_x catalyst application [11-12]. Both materials have been reported to have excellent hydrothermal stability. Such materials are prime candidates for future extruded zeolite catalysts.

CONCLUSIONS

Developing an active catalyst is still an open challenge for lean NO_x catalysis. In view of this challenge, we demonstrated the possibilities and benefits of using an extruded zeolite catalyst for lean NO_x exhaust application. A summary of our findings is described below:

1. As a result of a synergistic effect, zeolite catalysts impregnated with two different transition metal ions have greater NO_x-reducing activity than samples impregnated with only one metal.
2. Ni-, Mn-, Ag-, and Fe- ZSM-5 catalysts are among the most active catalysts. In future study, the use of any of these metals as a base in double component ZSM-5 catalysts, in lieu of Cu, could possibly lead to better NO_x conversion.
3. Catalysts impregnated with Pt and two transition metals, have the highest conversion rates of NO_x at the lowest temperatures. However, with the addition of Pt, these double component samples lose their catalytic activity exhibited at higher temperatures.
4. Both ethylene and propylene were found to be effective for NO_x reduction with these extruded catalysts. The maximum NO_x activity measured using propylene was found to be slightly lower than with ethylene.
5. One of the initial catalysts found to be most promising is the Ni-Co catalyst. At 20,000 h⁻¹, the NO_x conversion was greater than 50% between 400-600°C. The presence of water did not appear to inhibit the NO_x conversion efficiency. The activity of the catalyst is maintained after aging in 3% water at 400°C for 8 hours.

Less than 3% loss in surface area was observed after additional aging at 600°C for 10 hours in 3% steam.

6. Future efforts need to be directed towards achieving similar conversions of NO_x under "true" lean conditions, which also includes the presence of SO₂ in addition to H₂O at higher space velocities of up to 50000 hr⁻¹. Additional durability tests would also be required with higher temperatures and at least 10% water content. For future studies, ion-exchange extruded honeycombs activities could be compared with impregnation activity reported here.

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