

BIFUNCTIONAL CATALYSTS FOR THE SELECTIVE CATALYTIC REDUCTION OF NO BY HYDROCARBONS

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ABSTRACT

Novel bifunctional catalysts combining two active phases, typically Cu-ZSM-5 and a modifier, were prepared and tested for the selective catalytic reduction of nitrogen oxides using propylene in order to overcome the hindering effects of water typically seen for single-phase catalysts such as Cu-ZSM-5. The catalysts were made by typical preparation techniques, but parameters could be varied to influence the catalyst. The physical characterization of the materials showed that the modification phase was added strictly to the external surface of the zeolite without hindering any internal surface area. Chemical characterization by temperature-programmed reactions, DRIFTS and x-ray absorption spectroscopy indicated strong interaction between the two phases, primarily producing materials that exhibited lower reduction temperatures. Two improvements in NO_x reduction activity (1000 ppm NO, 1000 ppm C₃H₆, 2% O₂, 30,000 hr⁻¹ GHSV) were seen for these catalysts compared with Cu-ZSM-5: a lower temperature of maximum NO_x conversion activity (as low as 250°C), and an enhancement of activity when water was present in the system. The use of a second phase provides a way to further tune the properties of the catalyst in order to achieve mechanistic conditions necessary to maximize NO_x remediation.

INTRODUCTION

Nitrogen oxide emissions from combustion sources, including chemical and power plants and gasoline and diesel-based engines, have become an increasingly important concern over the last several decades, as NO_x has been shown to be a major pollutant and a contributor to low-level smog and acid rain. Governments worldwide are issuing new restrictions on NO_x emissions over the next decade, which has driven several advances in NO_x abatement technology primarily under lean-burn conditions. The current industrial solution is the use

of ammonia in the selective catalytic reduction of NO_x (NH₃-SCR). While this method is effective at reducing NO_x emissions, there are two concerns with the use of ammonia. First, it must be available, either from a storage tank or generated in situ from urea. While stationary plants can add such capacities, neither solution is ideal from a transportation standpoint. The second concern with NH₃-SCR is the slippage of unreacted ammonia to the atmosphere. Ammonia is also a hazardous chemical, and while a single NH₃-SCR unit can keep the slippage to less than 5ppm, the large number of potential NH₃-SCR units expected to be installed may lead to a large increase in NH₃ pollution.

An alternate method has been proposed in the use of a light hydrocarbon, such as propene, propane, or methane, in place of the ammonia as the reductant during selective catalytic reduction (HC-SCR). Hydrocarbons can be provided from the fuel source, thus requiring no additional storage, and hydrocarbon slippage is not as drastic an issue as with ammonia slippage, though unconverted hydrocarbons can be oxidized easily to clean products if needed. A large body of catalysts has been found to work for HC-SCR, but primarily metal-exchanged zeolites appear to be the most promising, as first reported by Iwamoto [1]. While these catalysts are very active and selective for HC-SCR under lean conditions, they exhibit poor behavior in the presence of water, which is nearly always present from a combustion process. This hydrothermal deactivation is attributed to either dealumination of the zeolite, modification of the active metal sites inside the zeolite, or competitive absorption between water and other reactants on the active sites. Many groups in the literature have proposed ways to improve the water stability of these materials, typically by building some bifunctional activity into the zeolite using multiple metal sites [2, 3]. However, these bifunctional

materials tend to have drawbacks, either by having lower activity than the monometallic zeolite, or by being less selective towards N_2 formation.

In this paper, we describe a different approach to building bifunctional catalysts using a metal-zeolite and a metal oxide. In our process, the oxide is added from a nano-particle sol, such that the oxide cannot enter the zeolite pores, and thus ends up as a coating on the outside of the zeolite. In this manner, the oxide can interact with the water before it enters the zeolite, as well as any other species, and thus prevent the water from interfering with the metal sites. Additionally, the oxide can provide some additional functionality by aiding in the various reaction mechanism steps or by forming a new phase when combined with the metal.

EXPERIMENTAL

Synthesis

Zeolites were provided by Zeolyst in their ammonium forms. Two basic methods were used to prepare the bifunctional materials.

(1) Ion exchange – Metals were added to the zeolite using ion exchange methods. Typically a 0.01 M solution of the parent metal salt was prepared, though the concentration could be modified to split the ion exchange across several steps in order to achieve a desired loading or exchange level. The solution and zeolite were added at a ratio of 10mL/1g and stirred vigorously. In some cases, the pH was adjusted to 7.5-8 using a dilute ammonium hydroxide solution (Fisher). The stirring was allowed to continue for at least 12 hrs. After the exchange, the material was filtered, rinsed with water, dried, then calcined at 500°C.

(2) Impregnation – Metal oxide was added by incipient wetness impregnation of a nanoparticle sol (Nyacol, 20 wt% of oxide, 20-nm particles stabilized by acetate) on the zeolite, diluting the sol as necessary to achieve the desired loading level. After drying, the solid sample was calcined at 500°C. Additional impregnations were performed to achieve higher loadings.

The order of these steps could be varied, but typically two processes were examined: one in which the metal was exchanged on the zeolite, followed by metal oxide impregnation, and one in which the metal oxide was added first, followed by the metal. Materials made in these fashions were called “forward” and “reverse” materials,

respectively. In general, these materials are referred to as $(MIIO_x)/MI-Z$, where MI is the exchanged metal, MII the metal oxide, and Z the zeolite phase. Besides the bifunctional materials, samples of the metal-exchange only were made (M-Z) as well as samples where only the oxide impregnation was performed (MO_x/Z). These single-phase materials were generally taken as a portion of the intermediate samples prepared by the forward and reverse synthesis procedures, such that $CeO_2/ZSM-5$ could be considered as the parent material of the reverse $CeO_2/Cu-ZSM-5$ sample, for example.

Several metals were examined as provided by $Cu(NO_3)_2$, $Co(NO_3)_3$, $Ag(NO_3)$ and $Fe(NO_3)_3$ (...), while CeO_2 and ZrO_2 were considered as the main oxides. Numerous zeolite phases (ZSM-5, Beta, MOR, FER, and Y) were examined with various SiO_2/Al_2O_3 ratios (from 280 to 20). Primary focus was on the bifunctional catalyst system $CeO_2/Cu-ZSM-5$ with a SiO_2/Al_2O_3 ratio of 50. The metal was nominally added to achieve 100% exchange of the Al^+ sites, and the oxide loading of 20 wt%.

HC-SCR Reaction

A microscale plug flow reactor was used to test the catalyst activity. Gas flow rates [He (99.995%), 5% O_2 in He, 5% NO in He, and 3% C_3H_6 in He] were controlled using Brooks 5860e mass flow controllers to achieve a nominal gas concentration of 2% O_2 , 1000 ppm NO and 1000 ppm C_3H_6 , with the balance He at 100 cc/min. When used, water was introduced through a syringe pump as to achieve 10% by volume in the reactant feed; all lines after water introduction were heat traced to prevent condensation. The sample mass was typically 150 mg, diluted up to 2 g using SiC (Electrochem Abrasives) in order to thicken the bed to avoid channeling and other transport effects. Reactor temperatures between 150 and 600°C were examined.

The effluent from the reactor was monitored using two detectors. An MTI MicroGC 200 with a Molecular Sieve 5A and a PoroPak U column were used to identify the stationary gases (O_2 , N_2 , CO, CH_4 , CO_2 , N_2O , C_2H_2 , C_2H_4 , C_2H_6 , C_3H_6 and C_3H_8). The NO and NO_2 concentrations were monitored using a California Analytical Instruments NOx detector with a heated pump to prevent water condensation inside the instrument. Using both instruments allowed us to quantify the amount of side products (CO, N_2O and NO_2) that could potentially be produced by the HC-SCR reaction.

Prior to reaction, catalyst samples were flushed with He at 500°C. It was found that generating a carbon layer on these materials drastically improved the activity at low temperatures, thus the HC-SCR reaction was run for at least 2 hrs at 250°C prior to temperature changes in order to form the carbon layer, as observed by visual inspection of the catalyst and approach to pseudo-steady-state conditions.

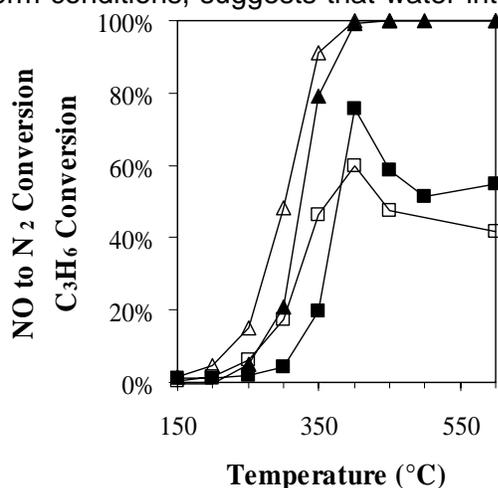
RESULTS AND DISCUSSION

The catalytic activities of four representative samples under wet and dry HC-SCR conditions are shown in Fig. 1. In general, these materials follow the trends normally seen for HC-SCR catalysts; NO conversion increases along with hydrocarbon conversion with increasing temperatures, but once the temperature where nearly 100% conversion of the hydrocarbon is reached, the NO conversion begins to drop. This step is usually accompanied by the formation of NO₂ in small amounts.

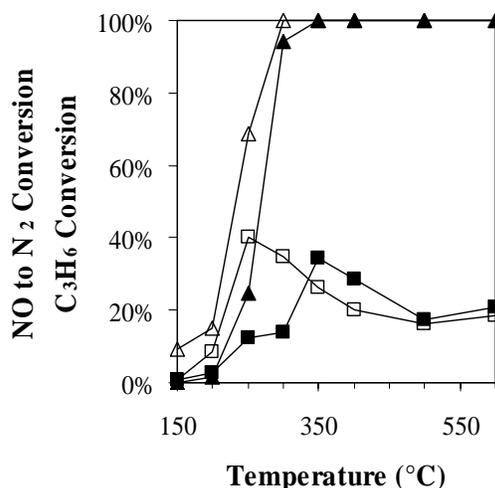
The Cu-ZSM-5 sample shows activity comparable to that reported in the literature. The maximum NO conversion was about 80% at 400°C under dry conditions, but dropped to 60% when water was present. The propylene conversion was near 100% at these conditions, but did produce a considerable amount of CO at lower temperatures. Very little N₂O or NO₂ was observed at 400°C, though NO₂ was more prevalent at higher temperatures. The loss of activity when Cu-ZSM-5 is exposed to a wet reactant feed, particularly under short-term conditions, suggests that water interferes

with the HC-SCR reaction either through competitive absorption with the reactants or by altering the active ionic sites into oxide species, rather than damaging the zeolite structure.

On the other hand, the bifunctional materials showed significant changes in their HC-SCR behavior. Under dry conditions, the materials were not as active as Cu-ZSM-5, with about 30% NO conversion, but their maximum activity was seen at a slightly lower temperature. No N₂O, NO₂, or CO was seen in the effluent. When water was present in the system, however, the maximum NO conversion shifted to even lower temperatures (as low as 250°C) and there was an increase in the conversion amount, up to 40-45%. There was no formation of the side products either under wet conditions, thus making these catalysts highly selective towards N₂ formation. At higher temperatures under both wet and dry conditions, the activity drop as previously noted, and there is a larger amount of NO₂ formed compared with the Cu-ZSM-5 catalyst. The forward sample had the most drastic temperature shift (about 100°C) under wet conditions compared with Cu-ZSM-5 but also the lowest activity, while the reverse sample showed activity comparable to Cu-ZSM-5 but with only a 50°C temperature shift. Thus, there are significant changes in the catalytic sites on the forward and the reverse sample that lead to competing effects (higher activity versus lower operating temperatures).



(A) Cu-ZSM-5



(B) metal oxide/Cu-ZSM-5

FIGURE 1 – NO to N₂ conversion (squares) and C₃H₆ conversion (triangles) during dry (closed) and wet (open) conditions over samples. SV ~35,000 hr⁻¹, 1000 ppm NO, 1000 ppm C₃H₆, 2% O₂, 10% H₂O when used.

To verify the usability of these materials for the HC-SCR at the industrial scale, space velocities tests were performed to determine where NO conversions between 80 and 90% would be met under wet operating conditions, as shown in Fig. 2. For the Cu-ZSM-5 sample, effective NO reduction would occur at a space velocity of about 10,000 hr⁻¹ at a temperature of 350°C. The forward bifunctional sample would require the same space velocity, but at 250°C, to meet the NO reduction requirements, while the reverse sample would be able to achieve the same at 8,000 hr⁻¹ at 300°C. Both bifunctional catalysts appear to be better than the Cu-ZSM-5 for the HC-SCR reaction at meeting the desired NO remediation needs.

Several other bifunctional systems were prepared and tested similarly to the CeO₂/Cu-ZSM-5 system. The maximum NO conversions and temperatures for these materials, as well as the metal-exchanged parent materials, are listed in Table 1. Materials with the late transition metals (Co, Cu, Ag) exchanged on the zeolite appeared to have benefits similar to those with the CeO₂/Cu-ZSM-5 system, while early transition metals did not show appreciable benefits. A 1:1 mixture of Cu and Co along with CeO₂ showed excellent performance under wet conditions. This follows the general literature trend that only the late transition metals have the appropriate absorption and chemical properties to be useful in the HC-SCR reaction. While ZrO₂ alone as the metal oxide phase did not provide as strong a change in catalytic behavior as CeO₂, a mixture of ZrO₂ and CeO₂ showed additional benefit. Given that mixtures of the rare earth and early transition metal oxides can be prepared to alter oxygen storage capacities, there may be additional multi-metallic oxides that could be used in this bifunctional material to further improve the catalyst. Of the zeolites, those with more open-pore networks such as ZSM-5, mordenite, and ferrierite were components of bifunctional materials with the observed water enhancement features, while the narrow pore zeolites of Beta and Y were not very effective for this reaction.

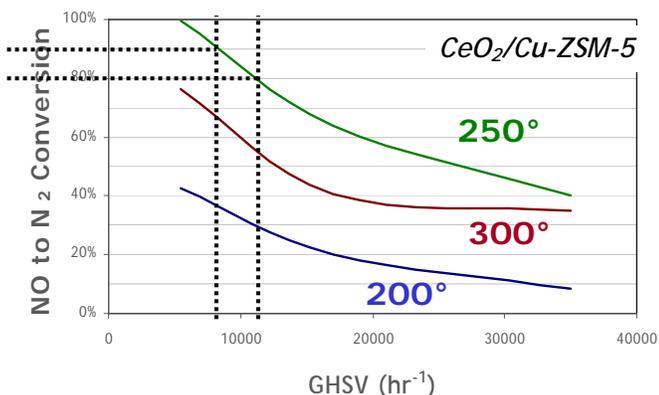


FIGURE 2 – Conversion versus space velocity at three temperatures.

Table 1. Activity for Various Exchanged Zeolites

Sample	Dry		Wet	
	Maximum NO to N ₂ Conv.	Temperature (°C)	Maximum NO to N ₂ Conv.	Temperature (°C)
Cu-ZSM-5				
CeO ₂ /Cu-ZSM-5				
Co-ZSM-5	30	550	25	500
CeO ₂ /Co-ZSM-5	32	450	47	400
Fe-ZSM-5	18	450	14	400
CeO ₂ /Fe-ZSM-5	18	400	16	350
Ag-ZSM-5	25	600	18	600
CeO ₂ /Ag-ZSM-5	35	500	27	400
Cr-ZSM-5	17	450	7	600
CeO ₂ /Cr-ZSM-5	10	400	8	400
Y-ZSM-5	10	350	0	N/A
CeO ₂ /Y-ZSM-5	20	600	18	550
CeO ₂ /(Cu,Co)-ZSM-5	25	450	47	400
ZrO ₂ /Cu-ZSM-5	42	500	45	450
(CeO ₂ ,ZrO ₂)/Cu-ZSM-5	35	450	42	400
Cu-MOR	62	350	27	350
CeO ₂ /Cu-MOR	55	350	30	300
Cu-FER	78	400	52	350
CeO ₂ /Cu-FER	72	400	52	350
Cu-BETA	56	500	32	450
CeO ₂ /Cu-BETA	50	500	30	450
Cu-Y	20	550	10	500
CeO ₂ /Cu-Y	17	450	15	400

CONCLUSION

A series of bifunctional catalysts composed of a metal-exchange zeolite with a metal oxide layer strictly on the outside of the zeolite have been prepared and shown to be excellent materials for the selective catalytic reduction of NO using propene as a reductant. The use of a nano-particle sol for the oxide source provides a method for preventing the insertion of the oxide inside the zeolite pore. Characterization of the materials by various means shows that these particles adhere to the external zeolite surface, and possibly form a mixed oxide phase with the exchanged metal on the external surface; this mixed oxide phase (???) can be easily reduced at low temperatures. The placing of the oxide and the formation of this mixed oxide phase leads to lower-temperature HC-SCR reduction compared with the metal-zeolite only, and more importantly, activity enhancement when water is present in the reactant feed. The bifunctional catalysts appear to be strong candidates for the HC-SCR reaction in order to meet the pending requirements for NO emissions reduction.

ACKNOWLEDGMENTS

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