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Hysteresis in activity of microporous lean NO_x catalysts in the presence of water vapor

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Abstract

Increasingly stringent ambient air quality standards coupled with the need to improve fuel economy has drawn significant attention to the search for emission control systems for lean burn engine vehicles. Much of the focus has been on zeolite-based catalysts for the conversion of NO_x to N_2 for automotive exhaust emission control. Under certain conditions, these catalysts are highly active catalysts for the reduction of NO_x using hydrocarbons as the reductant. However, many of these catalysts suffer from a variety of deactivation processes such as irreversible poisoning by SO_x or hydrothermal dealumination.

In addition to these deactivation processes, a recent focus of our research has been on the influence of water vapor on the activity of zeolite-based catalysts at *low* operating temperatures. We observe a hysteresis in catalytic activity of lean NO_x reduction (NO feed concentrations <100 ppm) upon increasing and decreasing temperature ramps at the low end of the operating window, that being from 100 to 300 °C using hydrocarbons as reductants. We describe these reversible influences of water vapor and the implications for this hysteresis in catalytic activity for the application of zeolite-based catalysts in lean NO_x catalysis, and compare these results to the instance of using ammonia as reductant.

Keywords: Lean No_x; Zeolite; Ammonia SCR; Water; Hysteresis

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1. Introduction

In the United States, Europe and Japan, increasingly stringent emissions requirements are being implemented or contemplated to maintain ambient air quality. In the US, the Clean Air Act Amendment of 1990 establishes tighter pollution standards for emissions of NO_x, CO, hydrocarbons and particulates from mobile sources including automobiles and trucks. New standards have been implemented on a phased-in basis beginning in model year 1994, and increasingly stringent reductions in emissions are contemplated beginning in model year 2004. The proposed US standards for light-duty vehicles are shown in Fig. 1. The future standards are independent of fuel type, meaning diesel engines that currently have no NO_x emissions control devices will be required to meet the same standards as gasoline engines with emissions control. Pressure for such a development also comes from the desire to reduce fleet fuel consumption, which is driving manufacturers to lean burn combustion engines, particularly for light-duty diesels for sport utility vehicles. Thus, in the US, the barrier to achieving increased fuel economy is the lack of an emissions control strategy for NO_x and particulates from lean burn engines [1]. Given these trends in the utilization of lean burn engines along with the increasingly stringent emissions standards, a solution must be found for emissions abatement systems for lean burn engines, and time is short. For NO_x abatement, given the current state of the art in lean engine design, it is necessary to achieve greater than 90% engine-out NO_x reduction to nitrogen to achieve the Tier 2 standard (right panel

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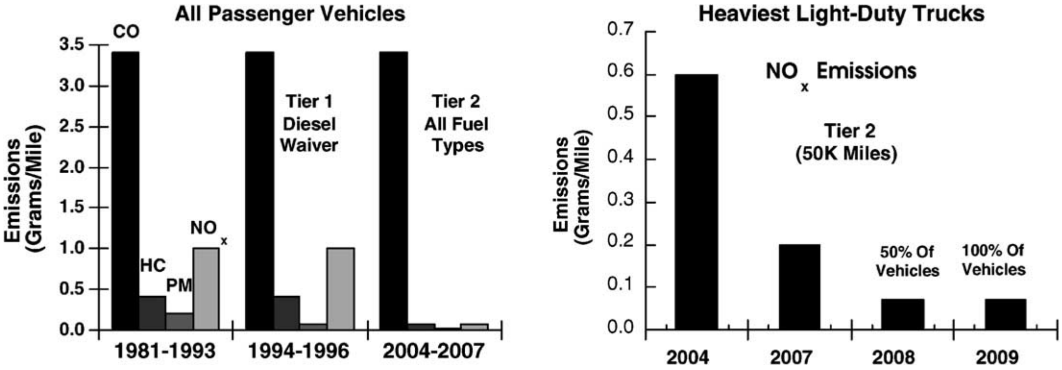

Fig. 1. Proposed emissions from passenger (left) and light-duty trucks (right) in US indicating the dramatic required reductions in tailpipe emissions of NO_x beginning in model year 2004.

in Fig. 1). This level of NO_x activity must be maintained over a broad temperature range, from less than 200 to 400 °C.

The search for lean NO_x catalysts that have the necessary activity and stability to reduce tailpipe emissions over the lifetime of the vehicle to the levels required by the future standards has included a vast number of materials types [2]. Among the promising candidates are zeolite-based catalysts that have shown promising activity for the reduction of NO_x with hydrocarbon reductants. Since the initial discovery by Iwamoto [3] and Held et al. [4] over a decade ago, a significant worldwide effort has been devoted to exploring and attempting to develop zeolite-based catalysts. Maintaining both the catalyst activity over a broad operating temperature range and the catalyst stability have been identified as the main barriers to the implementation of zeolite-based catalysts. Issues such as hydrothermal dealumination and subsequent deactivation of the catalyst, reversible loss of activity in the presence of the high concentration (ca. 10%) of steam in the exhaust gas, and irreversible poisoning of the catalyst by SO_x in the exhaust stream have all been identified by numerous studies. While partial solutions to these stability issues have been shown to exist in certain cases, to date a *simultaneous* solution while maintaining a level of NO_x conversion greater than 90% with hydrocarbons as reductant over the operating range of a lean burn engine (ca. 200–400 °C) has not been forthcoming for a zeolite-based or any other catalyst. Armor [5] concluded 5 years ago that with the myriad of problems zeolite-based catalysts face, catalyst researchers would do well to learn from the shortcomings of zeolite-based lean NO_x catalysts, but look elsewhere for solutions.

Our recent work has focused on broadening the temperature ‘window’ of activity for zeolite-based lean NO_x catalysts for light-duty diesel engines having engine-out $NO_x < 100$ ppm. Under these conditions, we have found a correlation of the breadth of the window with zeolite framework topology. These trends are depicted in Fig. 2. The topology of the zeolite framework influences the oxidative hydrocarbon conversion as a function of temperature (the so-called hydrocarbon light-off curve). We assume this is because of diffusional control over the rate of oxidation of the hydrocarbon, with small pore zeolites having a broader light-off curve than larger pore zeolites. Consistent with this idea, we postulate that the reduced rate of hydrocarbon oxidation in small pore zeolites allows for a persistent concentration of reductant at elevated temperatures allowing for a broad window of NO_x conversion.

We will discuss recent results that indicate that although these FER-based zeolite catalysts have interesting activities and can be made to be hydrothermally stable, the activity is significantly influenced by the recent thermal history of the catalyst in the presence of water. In particular, exposing the catalyst to water at low temperatures results in substantial hysteretic behavior. These effects have technological implications for the utility of zeolite-based catalysts for mobile lean NO_x applications using hydrocarbons as the reductant. Because of these effects and the generally low

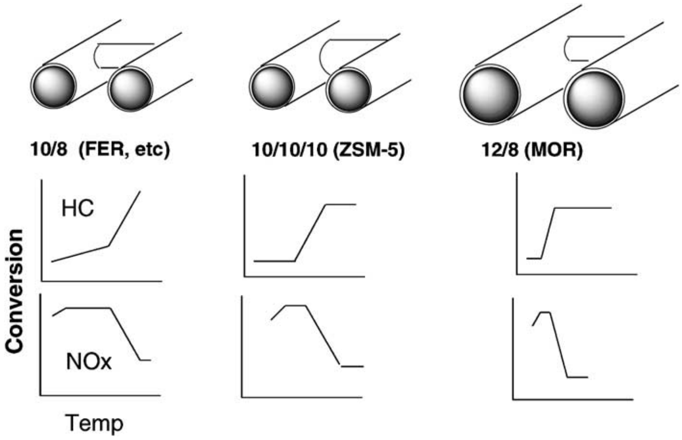

Fig. 2. Depiction of trends observed in hydrocarbon light-off and NO_x conversion as a function of temperature for different zeolite framework topologies.

catalytic activity found in lean NO_x systems, many researchers have shifted their focus to examining the use of ammonia derived from onboard hydrolysis of urea as a reductant for NO_x [6]. Zeolites, particularly iron-exchanged zeolites [7], have been shown to be highly active and stable catalysts in the presence of steam and SO_2 for the selective catalytic reduction (SCR) of NO_x with ammonia, although at rather high temperatures of greater than 375 °C. Will these zeolite catalysts systems that utilize ammonia as reductant also suffer from the effects of low-temperature water adsorption similar to that observed when using hydrocarbons as reductants? We will briefly describe preliminary results on the influence of water at lower operating temperatures on zeolite catalysts under ammonia SCR conditions to ascertain whether or not zeolite catalysts might be ruled out as being potentially practical for this application as well.

2. Experimental

2.1. Catalysts

Cobalt-exchanged zeolite catalysts were prepared using conventional aqueous ion exchange techniques. Starting zeolites were obtained from commercial sources. The FER (Zeolyst CP 914B-20), MOR (PQ CBV-10A #10A-1600-19-6) and MFI (Zeolyst CBV 3014G) zeolites were used as-received. The Tosoh FER (HSZ-720KOA) was first washed with ammonium fluoride solution (20 g zeolite:200 ml 0.1 M NH_4F; two exchanges, 24 h each), washed with deionized water, and dried at 110 °C for 24 h prior to ion exchange with cobalt (5 g zeolite:200 ml 0.01 M cobalt acetate solution, twice exchanged, 24 h per exchange). Co-exchanged zeolites were washed three times with deionized water and dried at 110 °C. Elemental analysis of the catalysts was performed by Galbraith (Knoxville, TN).

2.2. Lean NO_x catalysis

Catalytic reactions were carried out using an automated catalyst testing apparatus (TDA). Zeolite catalysts were pelletized, the pellets were crushed, and the 20/30 mesh fraction collected. A known weight and volume of catalyst was placed onto a quartz frit in a tubular quartz reactor (8 mm i.d.) held vertically in an electrically heated, temperature-controlled tube furnace. Simulated light-duty engine exhaust gases were delivered by calibrated mass flow controllers. The feed mixture of 75 ppm NO, 50 ppm propene, 150 ppm propane, 600 ppm CO, 200 ppm H_2, 5% CO_2 and 12% O_2, with the balance being dinitrogen, was fed to the reactor at a space velocity of 25 000 $cm^3/(cm^3$ cat h). Liquid water, when fed, was metered using a syringe pump into a heated pre-mixer and evaporator packed with quartz wool. All transfer lines of the reactor were heat traced, and held at 150 °C. Detection of NO_x was by chemiluminescence (California Analytical), and total hydrocarbon was determined by flame ionization detection (California Analytical).

2.3. Adsorption/desorption studies

Thermal gravimetric analysis (TGA) was used to study adsorption and competitive adsorption of water and ammonia as a function of temperature. TGA data were obtained using an automated catalyst characterization apparatus (RXM-100, Advanced Scientific Designs) equipped with a Cahn microbalance. Samples were suspended in an electrically heated tubular quartz reactor and held in quartz pans. Water was delivered using a constant humidity generator (DPG 300, General Eastern). Ammonia was delivered as a blend in helium (Scott Specialty Gases).

3. Results and discussion

Because of the broad temperature window of activity the Co ferrierite catalysts have for the reduction of NO_x (<100 ppm) that is apparently due to reduced diffusivity of the hydrocarbon reductant in the smaller pores of ferrierite, we investigated this class of catalyst further. Ion-exchange preparation of the Co-ferrierite catalysts results in low levels of cobalt ion exchange. Finished Co-FER catalysts derived from the two commercial sources are similar in Si/Al ratio (9–10). The Tosoh-derived FER catalysts typically have Al/Co ranges from 8 to 20. For the Zeolyst-derived FER catalysts, Al/Co ranges from 125 to 440. Ga and In can be exchanged in at higher levels. Even with these very low concentrations of Co ions (<0.1%, well below the ion exchange limit) exchanged into FER, high rates of NO_x conversion to nitrogen over broad temperature ranges are observed using Co, Mn, Ga or In (Fig. 3). The FER-based catalysts prepared in this way are adequately stable to hydrothermal deactivation. In the presence of water vapor, competitive adsorption of water limits the rate of NO_x reduction, and the catalytic activity is reversibly diminished somewhat, and the window in which the activity exceeds 90% conversion narrows. Some FER-derived catalysts can maintain usefully high conversions of NO_x even in the presence of water in the 300–400 °C range, particularly the Ga- and In-exchanged materials. This is in contrast to what has been observed previously under different conditions where Ga- and In-ZSM-5 catalysts lose nearly all activity in the presence of water [8]. This reversible diminution in activity in the presence of water, particularly in the critical low-temperature range, is very common in many zeolite systems using hydrocarbon reductants, and represents a significant technical challenge to the implementation of zeolite-based lean NO_x catalysts. It is important to note that these data described so far were obtained while ramping the temperature down from high temperature, and holding at a given temperature to obtain steady-state conversion data. This is a

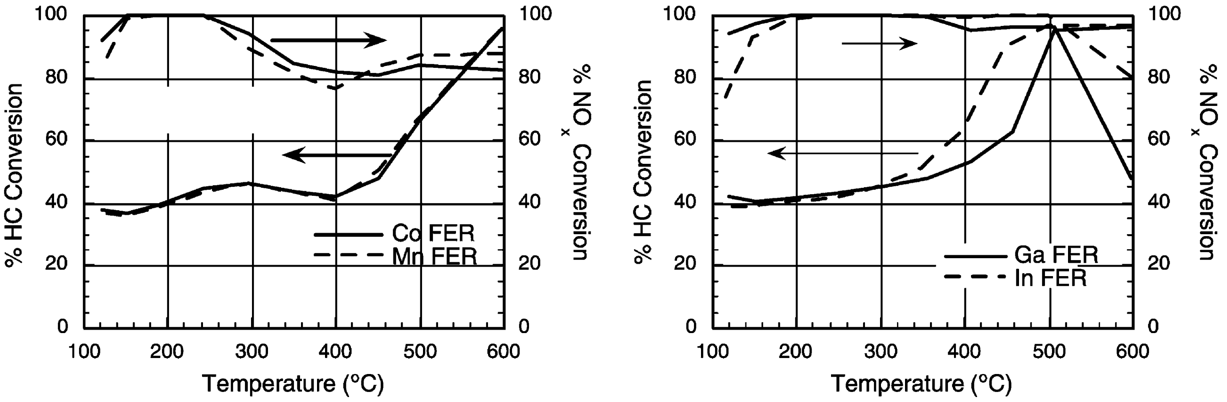

Fig. 3. NO_x conversion in the absence of added water.

common experimental detail employed to speed lean NO_x catalyst screening by minimizing the equilibration time for NO_x storage on the catalyst that must otherwise be deconvoluted from catalytic conversion.

We have found that screening zeolite-based lean NO_x catalysts using hydrocarbons as reductant using only ramp-down data acquisition does not give an accurate or practical assessment of catalytic activity. If we complete a down-ramp screening run in the presence of water, and then perform an up-ramp run, we observe a large hysteresis in catalytic activity, with the activity being dramatically lower on the up-ramp. To illustrate the hysteresis in catalytic activity in the presence of water vapor, plots of catalytic activity vs. time and temperature are shown in Fig. 4. For a sample of Co-FER heated to 600 °C prior to taking ramp-down data at 400 °C, the conversion data is 'well-behaved', i.e. a steady-state conversion is achieved quickly and is fairly stable at a fixed value for 2 h. Dropping the temperature to 300 °C and then 200 °C results in rapid attainment of a near steady-state conversion over periods of 2 h. If the catalyst is then allowed to sit for a longer time in the gas mixture, the activity decays to an even lower value. Upon reversing the ramp and heating the catalyst from 200 to 300 °C, a highly transient behavior is observed. The activity increases rapidly and dramatically to high levels, and then slowly decays to lower levels over 2 h. A similar transient is observed on going from 300 to 400 °C, with a more rapid return to a steady-state conversion.

Removing the added water vapor in the feed stream and taking the catalyst to temperatures greater than 400 °C completely restores the original activity. Also, as shown in Fig. 5, if no water is added to the feed, then the up-ramp and down-ramp conversions are typically very similar. There is some diminution in activity on the up-ramp that we ascribe to the water from hydrocarbon conversion being sorbed on the catalyst, and that amount of water depends on the time and temperature parameters of the experiment. This experiment suggests the catalytic hysteretic effect we observe is related to the adsorption of water at the lower operating temperatures, and is not caused solely by the adsorption of hydrocarbon at low temperature.

Microporous materials often exhibit adsorption–desorption hysteresis, with the rate of desorption being slower than the rate of adsorption because the sorbate diffusivity decreases with increasing loading [9,10]. Multicomponent adsorption/desorption is yet more complex, as the diffusivity of a strongly adsorbed component can dramatically influence the diffusivity of the other [11]. Fig. 6 indicates the water adsorption and desorption of Co-FER both as a function of temperature and as a function of time at 200 °C. Water desorbs very slowly relative to the rate of water adsorption from these catalysts at all

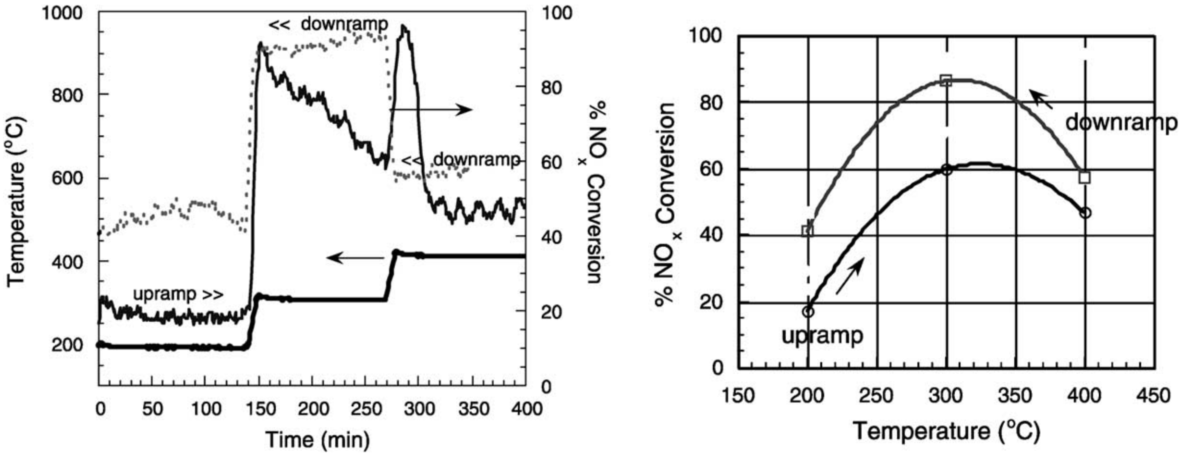

Fig. 4. Left panel: plots of NO_x conversion during ramp-down from 400 to 200 °C (dashed line) and up-ramp from 200 to 400 °C (solid line) in the presence of 5% water vapor. Right panel: plot of the value of up-ramp conversion and down-ramp NO_x conversion after 2 h at a given temperature.

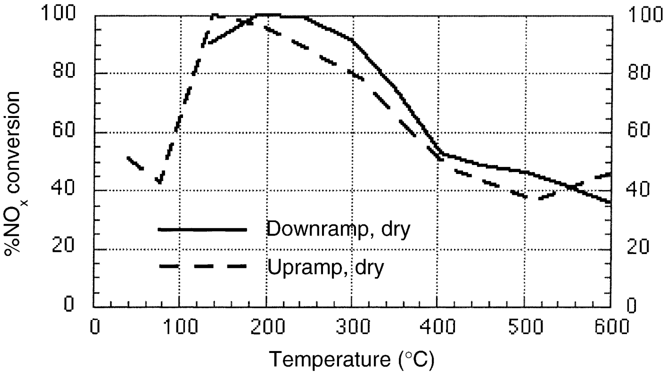

Fig. 5. NO_x conversion for Co-FER with no added water for a down-ramp followed by an up-ramp experiment.

temperatures as shown by the hysteretic behavior of the adsorption and desorption curves. During the up-ramp of catalytic activity tests, NO_x conversion is highly transient (Fig. 4, left). After quickly achieving a stable catalyst temperature, a very slow return to steady-state conversion occurs over a period of hours (at 300 °C) to minutes (at 400 °C) as is shown in Fig. 4. If the temperature is then taken to 500–600 °C, which removes nearly all of the water from the pores even in the presence of 5% steam (Fig. 6), the cycle can be repeated. This large hysteresis in activity is clearly related to the exposure of the catalyst to water vapor at low temperature, conditions where the loading of water in the pores is high. While decreased diffusivities at high sorbed water loadings strongly disfavor NO and NO_2 adsorption can help to explain decreased activity under conditions where water fills the pores; these arguments do not explain the long periods of time necessary to close the catalytic activity hysteresis loops we observe, especially for the ferrierite case. In addition, the hysteresis loop closes from the high activity down-ramp side to the low activity up-ramp side of the loop. One would expect high diffusivities on the down-ramp side to allow for rapid pore filling by water, and hence rapid closing of the hysteresis loop, but this is not observed. We speculate that the hysteretic behavior in activity may be related to Co moving off of its preferred, more catalytically active site(s) in the presence of high concentrations of water in the zeolite channels, but we have no data to support this supposition.

Because the up-ramp conditions more likely represent the majority of the catalyst duty cycle in an automotive application, and since the catalyst will be fully

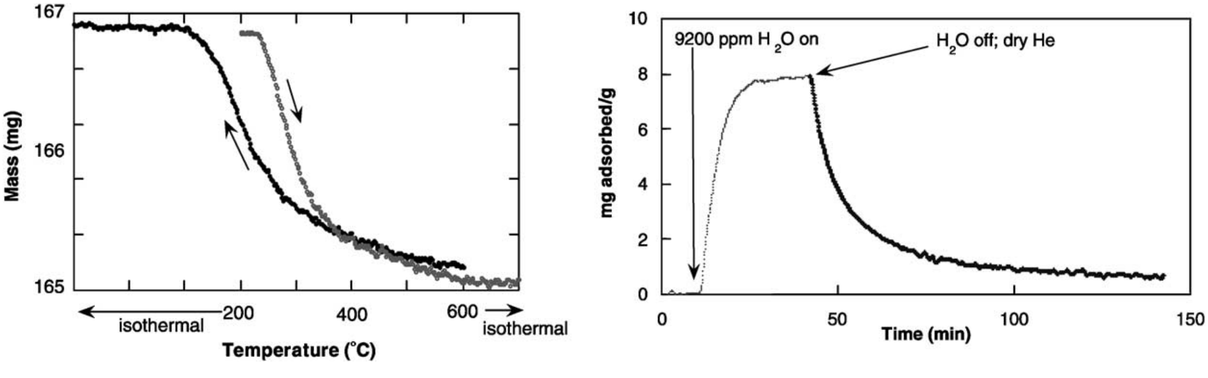

Fig. 6. The hysteretic sorption and desorption of water from Co-FER is shown under isothermal conditions (200 °C, right panel) and under temperature ramping conditions (10 °C/min, 35% relative humidity at 22 °C, left panel).

saturated with water under cold-start conditions, the dramatic decrease in the up-ramp conversions relative to the down-ramp conversions has significant technological implications. Conditions necessary to remove the water adsorbed in the pores (500–600 °C) are only anticipated to occur over a fraction of the duty cycle of a light-duty lean burn engine, and so the ability to operate on the upper activity leg of the hysteresis loop will only occur a small fraction of the time. Therefore, most of the duty cycle will operate on the lower leg of the hysteresis loop, this being at technologically uninteresting conversions. This hysteresis effect related to low-temperature adsorption of water is yet another problem that must be overcome with zeolite-based lean NO_x catalysts if they are to be technologically useful. Perhaps the only way around this issue is to run rich, hot excursions to desorb the water regularly. This will have an impact on fuel economy, and so may be impractical.

Are these effects seen in catalysts derived from other zeolite framework topologies, or is the hysteresis observed after adsorption of water at low temperatures unique to FER? To answer this question, we have compared other Co catalysts prepared from ZSM-5 ($Si/Al = 10$) and MOR ($Si/Al = 10$). Down- and up-ramp conversion plots are shown in Fig. 7. These plots were generated under conditions identical to that for the Co-FER catalyst. These plots indicate that the catalysts derived from the MFI and MOR frameworks also exhibit hysteretic behavior, but different than that of the Co-FER catalysts and have substantially lower activity in the higher temperature range relative to Co-FER. All these zeolite catalysts exhibit less than technologically interesting activity at 200 °C. While fairly stable steady-state conversion of NO_x with hydrocarbon reductants is seen for both Co-ZSM-5 and Co-MOR during the down-ramp portion of the experiments, significant transients are seen upon performing an up-ramp beginning at 200 °C. The peaks of these transients are what is plotted as the $t = 0$ up-ramp data in Fig. 7. The hysteresis loop for Co-ZSM-5 closes after 2 h at 300 °C, significantly faster than the Co-FER catalyst. Co-MOR also shows substantial transient behavior but the conversion returns to a steady state more quickly than FER- or MFI-based catalysts.

Our attempts to reduce or eliminate the hysteresis in the FER systems by increasing the hydrophobicity by increasing the Si/Al ratio, increasing the degree of ion exchange using solid-state exchange techniques, or changing the metal (from Co to Mn, Ga or In) has had little or no beneficial effect. The transient and hysteretic behavior exhibited by zeolite-based catalysts using hydrocarbon as reductants may substantially limit their implementation in an emissions control system. Using the decreased diffusivity of small hydrocarbon molecules in the FER framework is beneficial for broadening the temperature window of lean NO_x activity, but is deleterious in that the low-temperature diffusivity of water significantly inhibits NO_x reactivity.

As stated above, there is a pressing need to solve the lean NO_x problem. The lack of catalyst systems

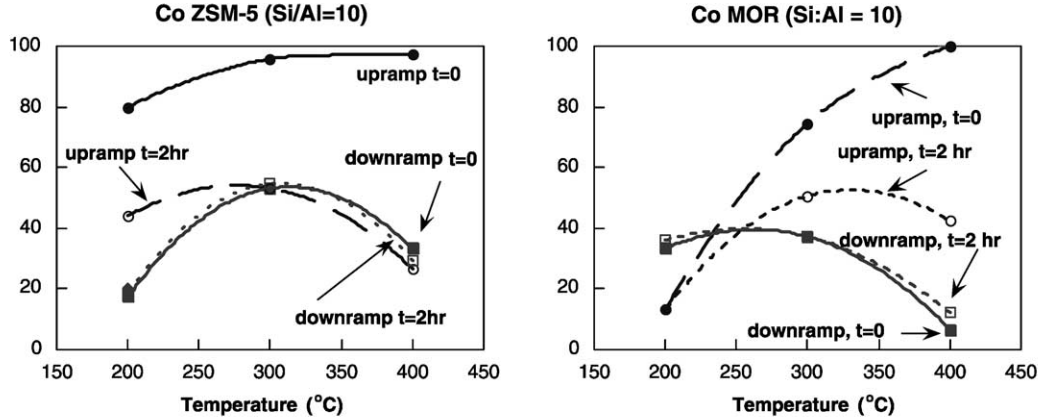

Fig. 7. Comparison of Co-ZSM-5 (left) and Co-MOR (right) catalysts having Si/Al ratios of around 10. Experimental conditions are as in Fig. 4. Time = 0 data represents instantaneous conversion taken as soon as the catalyst bed was at temperature following the ramp.

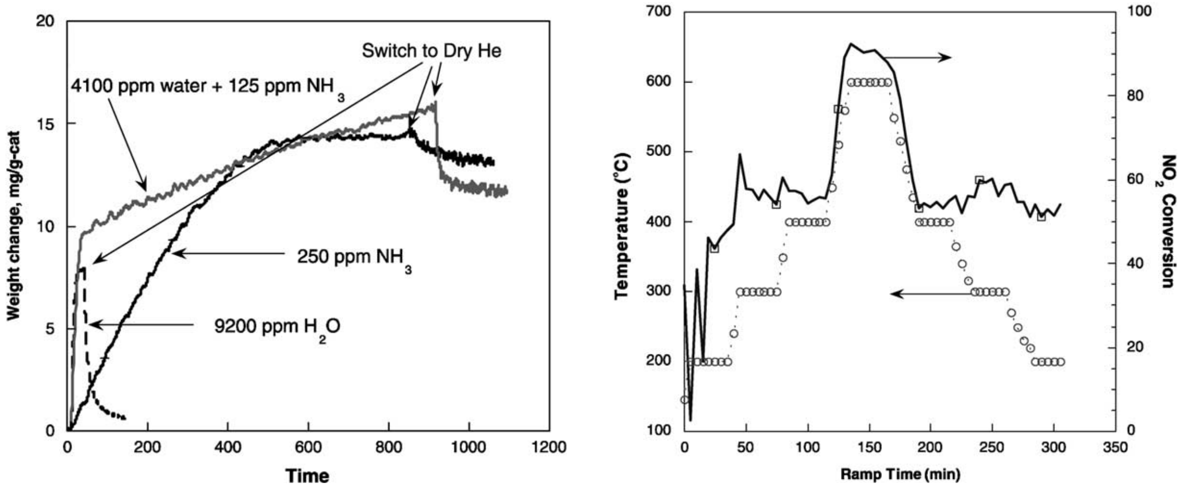

Fig. 8. Left panel: adsorption of water, ammonia and a water–ammonia mixture on Co-FER at 200 °C. Right panel: conversion of NO_2 with ammonia in the presence of water vapor during up-ramp and down-ramp conditions.

using hydrocarbon reductants having high, stable activity over a broad temperature range has driven some of the research in this area toward an examination of using ammonia as the reductant for NO_x. As there must be significant mechanistic differences in the reaction pathways for hydrocarbons vs. ammonia as reductant, it is reasonable to expect that these mechanistic differences may override the problems that are encountered when using hydrocarbons. It is reasonable to expect that water will not thermodynamically outcompete the more strongly basic ammonia for acid adsorption sites on the catalyst, and that as long as the rate of NO–NO_2 oxidation is fast enough, that the adsorption of water may not influence the catalytic performance. Thus, the hysteresis in NO_x conversion might be minimized or non-existent. Therefore, we examined the competitive adsorption of ammonia and water, and a comparison of up-ramp vs. down-ramp conversion of NO_x with ammonia to confirm these expectations.

Preliminary results from thermogravimetry of the adsorption of water vs. ammonia indicates that the adsorption of ammonia is not influenced by the presence of water vapor to any great extent over Co-FER samples, as expected. Although the kinetics of water adsorption are more favorable when water is in great excess relative to ammonia, thermodynamics prevail, and ammonia displaces water from the catalyst as shown in the left panel of Fig. 8. TGA results using Co-FER indicate that the presence of water does not impede the rate of reaction of NO_2 with preadsorbed NH_3 (data not shown). Comparison of up-ramp vs. down-ramp data for ammonia SCR in the presence of water (Fig. 8, right panel) indicates that there may be a slight hysteresis in activity at temperatures at or below 200 °C, but that any hysteresis in activity above 200 °C is absent. It is rather difficult to tell precisely about the presence of hysteresis at the lower temperatures, because as the temperature is ramped up from 200 °C, ammonia begins to desorb from the catalyst, and transients in NO_x conversion are observed. We have also observed evolution of N_2O during an up-ramp after periods of time at or below 200 °C. This is consistent with the formation and decomposition of ammonium nitrate at lower operating temperatures [12].

4. Conclusions

Using a simulated light-duty exhaust stream where $NO < 100$ ppm, zeolite-based catalysts suffer from hysteresis in activity in the presence of water vapor that depends on the recent thermal history of the catalyst. The up-ramp activity for Co-FER is significantly less than the down-ramp activity. While we cannot suggest the specific mechanisms of this hysteresis, it appears that the hysteresis is related to the adsorption and desorption of water in the micropores at low temperatures, a phenomenon that also shows significant hysteresis, and a strong competitive adsorption in favor of water over NO_x. These data suggest that zeolite-based catalysts suffer from transient effects during increasing temperature, and this may represent yet another significant problem for the utilization of zeolite-based catalysts for lean NO_x reduction with hydrocarbons. The situation for ammonia SCR with zeolite catalysts appears to be less of a problem, apparently because of significant differences in reaction mechanism that involves NO_x reaction with adsorbed NH_3, processes that are not as significantly impacted by the presence of water vapor. While more work is needed to understand the influence of water on ammonia SCR over zeolite catalysts, preliminary results suggest that the adsorption of water at the lower operating temperatures is not as deleterious as it is for hydrocarbon SCR, and zeolite-based catalysts are viable candidates for further research for ammonia SCR for mobile applications.

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