

Effect of Transition Metal Ion Properties on the Catalytic Functions and Sulfation Behavior of Zeolite-Based SCR Catalysts

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ABSTRACT

Copper- and Iron- based metal-zeolite SCR catalysts are widely used in US and European diesel aftertreatment systems to achieve drastic reduction in NO_x emission. These catalysts are highly selective to N₂ under wide range of operating conditions. Nevertheless, the type of transition metal has a significant impact on the key performance and durability parameters such as NO_x conversion, selectivity towards N₂O, hydrothermal stability, and sensitivity to fuel sulfur content. In this study, we explained the differences in the performance characteristics of these catalysts based on their relative acidic-basic nature of transition metal present in these catalysts using practically relevant gas species present in diesel exhaust such as NO₂, SO_x, and NH₃. These experiments show that Fe-zeolite has relatively acidic nature as compared to Cu-zeolite that causes NH₃ inhibition and hence explains low NO_x conversion on Fe-zeolite at low temperature under standard SCR conditions. Similarly, relatively basic nature of Cu-zeolite results in more prominent SO_x storage and performance deactivation in the presence of acidic contaminant like SO_x and required higher temperatures for desulfation as compared to Fe-zeolite.

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1. INTRODUCTION

Selective Catalytic Reduction (SCR) of NO_x with NH₃ is a proven technology and widely practiced to reduce the NO_x emissions from lean-burn diesel engines. NH₃-SCR technology uses urea solution which gets decomposed into gaseous NH₃ reductant to continuously convert NO_x to N₂. Zeolites exchanged with transition metal ion, typically Fe and/or Cu, and V/W/TiO₂ are commonly used as NH₃-SCR catalysts for NO_x reduction. Cu- and Fe-zeolite catalysts exhibit a number of qualitative and quantitative differences with regards to their catalytic performance, sensitivity towards hydrothermal aging and sulfur poisoning. It has been shown that at low temperatures, under standard SCR conditions, Cu-zeolites show higher steady-state NO_x conversion than Fe-zeolites and that the opposite is true at the upper end of the typical exhaust temperature range. In addition, under NH₃ partial pressures of practical relevance, NH₃ can inhibit NO_x conversion over Fe-zeolites and not on Cu-zeolites. These differences have been reported explained in earlier publications [1, 2, 3, 4].

Notwithstanding their outstanding performance and durability characteristics, these catalysts are not immune to various deactivation mechanisms. Sulfur oxides (SO₂ and SO₃, commonly referred to as SO_x) are ubiquitous in exhaust gases and are detrimental to SCR catalyst performance. Despite their presence in trace amounts in the exhaust gas, over a period of time SO_x species get accumulated on the SCR catalyst, leading to a decline in NO_x conversion.

In this study the impact of the type of transition metal ion and SO_x adsorption and desorption on acid-base and redox functions of transition metal exchanged zeolite catalysts were investigated. Several probe reactions were employed for the above characterization to explain the observed differences in the performance of Cu-zeolite and Fe-zeolite NH₃-SCR catalysts.

2. EXPERIMENTAL

2.1 Experimental Setup

A bench-flow reactor system with transient measurement capability, the details of which can be found elsewhere [5], was used to probe the overall performance and specific functions of the studied catalysts. Synthetic exhaust gas was supplied to the catalyst sample with the gas hourly space velocity (GHSV, or more frequency referred as SV) of approximately 40 kh⁻¹. All the stainless-steel lines used in this setup were temperature-controlled at 190°C in order to minimize the adsorption of H₂O, NH₃, and sulfur-containing compounds. Additionally, the lines which came in contact with sulfur were coated with SilcoNert or Dursan (SilcoTek) to reduce the corrosion from the sulfur containing compounds that may potentially cause some NH₃ storage in the lines. Water was injected into the heated synthetic exhaust gas through capillaries connected to Teledyne ISCO pumps. The gas mixture thus prepared was fed to the quartz reactor tube placed in a three-zone furnace (Thermo

Scientific). The reactor tubes contained multiple thin, quartz pre-heater tubes for mixing the gases and preheating the feed mixture. The pre-heated gas was then passed to the catalytic monolith wrapped with quartz mat. For every experiment, temperature was measured at the gas inlet, catalyst inlet, and catalyst outlet locations using K-type thermocouples. In this work, catalyst inlet temperature is reported as catalyst temperature. Prior to each experiment, a catalyst core was de-greened in a base feed mixture containing 10% O₂, 7% H₂O, and 8% CO₂ in N₂, at 550°C for 4 h. Composition of reactants and products were analyzed using Multigas 2030 FTIR (MKS).

A separate dedicated reactor, described in detail elsewhere [5], was used for loading catalyst with sulfur, in order to minimize contamination of the primary bench-flow reactor which was used for catalytic performance characterization. Catalytic oxidation of propane over Pt/Al₂O₃-based DOC was used in this sulfur loading rig as a source of heat and of basic combustion gas constituents such as CO₂ and H₂O. Filtered dry air (using 2 micron filter) was passed through a Naphion™-based humidifier (Permapure™), maintained at 60°C to generate ~ 5% H₂O concentration in air. The concentration of propane was varied to attain the required SCR temperature. Once the required temperature was attained, SO₂ was fed to the inlet of the DOC, which oxidized part of the SO₂ to SO₃ and H₂SO₄. The gas mixture thus produced was then used to sulfur-poison the downstream SCR catalysts. The SCR catalyst was exposed to a mixture of SO₂ and SO₃ along with H₂O and CO₂, at 400°C for 12 h. The cumulative amount of sulfur stored on the catalyst and the rate of SOx release from sulfated SCR catalysts were estimated using temperature-programmed desorption (TPD) of sulfated catalyst up to 950°C. The impact of sulfur on metal zeolite catalysts were evaluated by analyzing NOx reduction, NO oxidation, NH₃ oxidation, and NH₃ storage before and after sulfation.

2.2 Catalysts

In order to isolate the impact of transition metal ions on catalytic functions and SOx/deSOx behavior and to avoid other potential interferences, a single source of BEA zeolite was used in the preparation of H-BEA, Fe-BEA, and Cu-BEA SCR catalysts. These catalyst samples were provided by Johnson Matthey Inc. Similar weight percentage of Cu and Fe were maintained in Cu-zeolite and Fezeolite respectively. Since molecular weight of Cu (63.5) is 14% higher than Fe (55.8), the number of metal sites present in the Cu-BEA is expected to be 14% lower than in Fe-BEA. All three catalysts were washcoated on 4.6" diameter and 3" long cordierite substrates of 400 cpsi cell density. Cylindrical samples of 1" diameter and 3" long were cored from the above element, for the laboratory studies.

BET surface area of the three catalysts was measured using Micrometric BET instrument and their values were 107, 119, and 99 m²/g for H-BEA, Fe-BEA, and Cu-BEA, respectively. There were some differences in the BET surface area of studied formulations, i.e., as compared to H-BEA, Cu-BEA has 7% lower while Fe-BEA has 11% higher BET surface area.

2.3 Experimental Protocol

The SCR catalysts were de-greened at 550°C for 4 h in a base feed mixture containing 10% O₂, 7% H₂O, and 8% CO₂ in N₂, prior to testing their catalytic activity. Various aspects of catalyst performance were quantified using a comprehensive four-step protocol, conducted in the presence of base gas mixture while varying the amounts of NOx and NH₃ [6]. In a nutshell, the first step pre-conditions the catalyst. The second step is focused on various static and dynamic measures of the SCR reaction using equimolar mixture of NOx and NH₃. In particular, it yields information about NOx and NH₃ conversion, N₂O formation, as well as the equilibrium NH₃ storage under SCR conditions, or dynamic NH₃ storage. Step 3 and step 4 utilize NH₃-only and NO-only feeds, respectively, to calculate NH₃ oxidation and NO oxidation activities. Finally, the total NH₃ storage is measured during step 4 by means of reacting the stored ammonia with NO.

Table 1. Experimental conditions used in this study

Catalyst Cores	1" diameter x 3" length a. H-BEA, b. Cu-BEA, c. Fe-BEA
Catalyst State	De-greened: 550°C 4 h in base feed
Base Feed	10% O ₂ , 8% H ₂ O, 7% CO ₂ , Rest N ₂ , SV=40 kh ⁻¹
Performance Evaluation: Standard SCR NO₂/NOx=0.0 and Fast SCR NO₂/NOx=0.5 in base feed	
Step 1. NOx	200 ppm NOx
Step 2. NOx and NH ₃	200 ppm NOx, 200 ppm NH ₃
Step 3. NH ₃	200 ppm NH ₃
Step 4. NOx	200 ppm NOx
Impact of NH ₃ /NOx Ratio	NH ₃ /NOx = 0.4 – 2.0 with 0.2 interval at 250°C with NO=200ppm
NH₃ TPD (Temperature Programmed Desorption)	
NH ₃ Storage	200 ppm NH ₃ at 150°C for 3 h in base feed at SV = 40 kh ⁻¹
TPD	150 to 500°C with 10°C/min ramp in base feed without O ₂
NO₂ TPD (Temperature Programmed Desorption)	
NO ₂ Storage	200 ppm NO ₂ at 150°C for 1h in base feed
TPO	150 to 500°C with 10°C/min ramp in base feed
SOx TPD (Temperature Programmed Desorption)	
SOx Storage	33 ppm SOx (SO ₃ /SOx = 0.7) at 400°C for 12 h
TPO	150 to 950°C with 10°C/min ramp in base feed

Note: Concentrations are reported on the volumetric/molar basis.

3. RESULTS AND DISCUSSION

Various probe reactions were used to characterize acid-based properties of H-BEA, Fe-BEA, and Cu-BEA SCR catalysts. The findings of those probe reactions were utilized to explain the catalytic performance of these catalysts in the de-greened and sulfated states.

3.1 Probing Acidic and Basic Nature of Metal-Zeolites

The type of probe molecules for characterizing the acidic-basic nature of the SCR catalyst were chosen from the typical SCR feed gases.

For example, a typical SCR feed gas contain ppm level of NO_2 , NH_3 , and SO_x in the abundance of O_2 , H_2O , CO_2 , and N_2 . Therefore, these three formulations were probed using acidic (NO_2 or SO_x) and basic (NH_3) molecules in the presence of feed gas environment containing 10% O_2 , 8% H_2O , 7% CO_2 in N_2 . NO_2 and SO_x were considered acidic species as NO_2 react with neutral species like H_2O to form HNO_3 which is a known acid and SO_2 and SO_3 combines with H_2O to form H_2SO_3 and H_2SO_4 , respectively. Similarly, NH_3 reacts with H_2O to form NH_4OH which is a known base. The storage of these molecules and their release profiles with temperatures were compared for relative acidity and basicity of the SCR catalysts.

3.1.1 Probing Basic Nature using NO_2 Storage

As mentioned, NO_2 is an acidic species and it is used to probe relative basicity of the SCR catalysts. 200 ppm of NO_2 in the base feed mixture was introduced to each catalyst formulation at 150°C for 1 h to attain saturation. It was followed by temperature-programmed desorption (TPD). Figure 1 shows that peak temperature of NO_2 release from Cu-BEA was $\sim 50^\circ\text{C}$ higher than Fe-BEA. Furthermore, the cumulative amount of NO_2 released during TPD suggests that the total amount of stored NO_2 was largest for Cu-BEA followed by Fe-BEA, and negligible amount of NO_2 release was found for H-BEA. The cumulative NO_2 storage was separately estimated both from the NO_2 storage step at 150°C as well, and compared to the NO_2 release during TPD - the two were in agreement. NO was not detected among gaseous products during either NO_2 storage or subsequent TPD, suggesting that these catalyst were not active for NO_2 decomposition or disproportionation reactions under humid feed environment in the presence of O_2 .

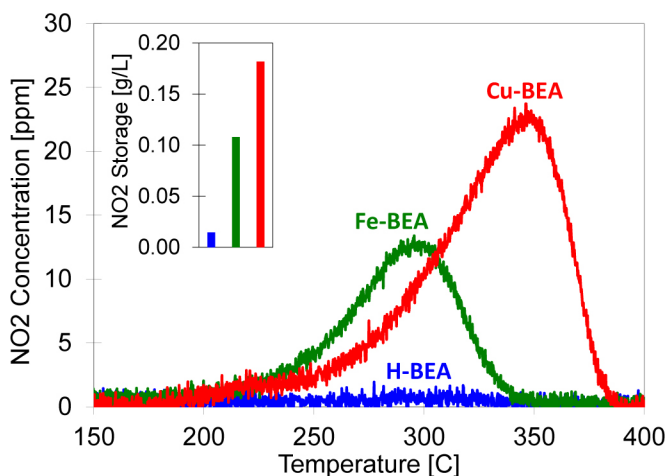


Figure 1. NO_2 release profiles during TPD after NO_2 storage at 150°C for 1 h with 200 ppm NO_2 in base feed mixture with temperature ramp of $10^\circ\text{C}/\text{min}$. Figure in inset shows cumulative NO_2 storage estimated during TPD.

This experiment highlights the Cu-BEA has larger cumulative amount of NO_2 storage as compared to Fe-BEA, despite of a 14% lower density of metal sites. Additionally, this probing experiment further

emphasizes that in the absence of metal-exchanged sites, H-form zeolite does not participate in the storage of such acidic molecule as NO_2 , because of very low affinity of the Brønsted acid to acidic molecules. Overall, this probing technique implies the trends of relative acidity of the exchange ions $\text{H-BEA} > \text{Fe-BEA} > \text{Cu-BEA}$.

3.1.2 Probing Basic Nature using SO_x Storage

Similar to the above experiment, all three catalysts were probed by SO_x storage, followed by TPD. In particular, these samples were exposed to 33 ppm of SO_x ($\text{SO}_3/\text{SO}_2 = 0.7$) at 400°C for 12 h. This exposure was previously demonstrated to be sufficient achieve complete catalyst saturation with sulfur [5]. As we also showed previously, under such conditions, SO_3 substantially converts to gaseous H_2SO_4 , due to the presence of 5% H_2O in the gas feed.

Figure 2 shows SO_x removal profiles, combining SO_2 and H_2SO_4 , as function of temperature. Only insignificant quantities of SO_3 were detected in the gas feed, due to its complete conversion to H_2SO_4 . In contrast to NO_2 TPO where all of the stored NO_2 was released by 450°C , SO_x removal requires much higher temperatures. SO_x TPD was performed with $20^\circ\text{C}/\text{min}$ temperature ramp up to 950°C where BEA zeolite structure collapses and hence these are destructive experiments. Complete sulfur removal was achieved by $\sim 800^\circ\text{C}$ in this experiment.

It may be worth pointing out that high temperatures required for complete removal of sulfur in these temperature-programmed experiments may be a reflection not only of the strength of adsorption, but also of the time required for the desorbing SO_x molecules to diffuse through and out of the zeolite pores. In fact, as shown in our previously published work, complete sulfur removal from a Cu-CHA catalysts with much narrower pore openings than Cu-BEA ($5.95 \text{ \AA}$ vs. $3.72 \text{ \AA}$, respectively), required substantially higher temperatures, on the order of 950°C [5, 7].

Cumulative sulfur removal shows that despite of 14% lower density of metallic sites in Cu-BEA sample, it exhibited substantially higher sulfur storage than the Fe-BEA. Both Cu-BEA and Fe-BEA TPO patterns showed multiple desorption peaks, suggesting that multiple types of sites were present in each catalyst. Furthermore, peaks of SO_x removal for Cu-BEA ($\sim 650^\circ\text{C}$, $\sim 700^\circ\text{C}$) occurred at higher temperatures as compared to Fe-BEA ($\sim 490^\circ\text{C}$, $\sim 660^\circ\text{C}$). Thus, Cu-BEA clearly has higher affinity to SO_x than Fe-BEA, based on both the SO_x removal temperature and the cumulative sulfur storage. HBEA catalyst sample featured insignificant sulfur storage. Since the same parent zeolite, substrate, and binder material were used in preparation of these samples, their SO_x storage can be unambiguously attributed to the respective exchanged ions. This shows that Brønsted sites or zeolite sites do not store sulfur, but metallic exchange sites like Cu and Fe do. The trends of binding energy (based on SO_x removal temperatures) of stored sulfur with metal-zeolite and amount of sulfur stored on these catalyst are consistent with the relative acidity trend of the exchange ions $\text{H-BEA} > \text{Fe-BEA} > \text{Cu-BEA}$, derived from previously discussed NO_2 probing experiment.