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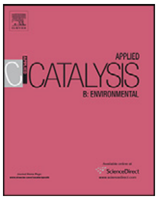

Selective catalytic reduction of NO_x on combined Fe- and Cu-zeolite monolithic catalysts: Sequential and dual layer configurations

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ABSTRACT

Iron and copper-based zeolites are effective catalysts for the lean selective catalytic reduction (SCR) of NO_x with NH_3. Cu-zeolites are more active at lower temperatures (≤350 °C) while Fe-zeolites are more active at higher temperatures (≥400 °C). The effectiveness of a catalytic system comprising Fe- and Cu-based zeolites was examined for the standard ($NO + O_2 + NH_3$) and fast ($NO + NO_2 + NH_3$) SCR reactions. Experiments carried out with in-house and commercial Fe- and Cu-zeolite monoliths of varying lengths quantified their relative SCR activities. The commercial Cu-zeolite achieved complete NO_x conversion for the standard SCR at 250 °C while the commercial Fe-zeolite achieved high NO_x conversion at higher temperatures (≥400 °C) where it out-performed the Cu-zeolite. Subsequently, three configurations of combined Fe and Cu-zeolite catalysts were compared:

- "Sequential brick" catalyst comprising Fe-zeolite and Cu-zeolite monolith.
- "Mixed washcoat" catalyst comprising a washcoat layer having equal mass fractions of Fe- and Cu-zeolites.
- "Dual layer" catalyst comprising monolith coated with individual layers of Fe- and Cu-zeolites of different thicknesses and mass fractions.

The sequential brick design with Fe-zeolite brick followed by a Cu-zeolite brick gave a higher conversion than the Cu/Fe sequence of equal loadings with the Fe(33%)/Cu(67%) achieving the highest NO_x conversion over a wide range of temperatures. The mixed washcoat catalyst achieved NO_x conversion that was nearly an average of the individual Fe-only and Cu-only catalysts. The dual layer catalyst with a thin Fe-zeolite (33% of the total washcoat loading) layer on top of a thicker Cu-zeolite layer (67%) resulted in very high NO_x removal efficiencies over a wide temperature range for both the standard and fast SCR reactions. The performance of this dual-layer system was comparable to the series arrangement of Fe and Cu-bricks. The Cu-zeolite on Fe-zeolite dual layer catalyst was not nearly as effective for the same loadings. The Fe/Cu dual layer catalyst also exhibited superior performance for the fast SCR reaction. The results are interpreted in terms of the activities of each catalyst for SCR and ammonia oxidation. An assessment of the extent of washcoat diffusion limitations shows that the dual layer configuration is superior to the sequential brick configuration. The existence of an optimal loading distribution of the Fe- and Cu-zeolite catalysts as well as other intangible benefits of the dual layer SCR catalyst are discussed.

1. Introduction

Diesel vehicles are highly efficient and economical in terms of fuel consumption compared to the gasoline vehicles. But as is the case of all lean combustion processes, the NO_x produced is difficult to eliminate due to the unreacted O_2 in the product stream. This fact, coupled with the increasingly stringent NO_x emissions from diesel vehicles, has prompted the development of various catalytic aftertreatment technologies. The two main ones that have emerged are NO_x storage and reduction (NSR) and selective catalytic reduction (SCR). SCR is now the preferred technology to achieve the large NO_x reductions mandated for medium and heavy-duty vehicles while NSR holds promise for light-duty vehicles.

SCR utilizes a variety of different reductants to convert NO_x to N_2. Amongst these, NH_3 (or urea) is the reductant of choice because of the high NO_x conversions that can be achieved at high space velocities encountered in vehicle applications. While NH_3-based SCR was first commercialized in the 1980s for stationary applications, it was only commercialized for diesel vehicles

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during the past decade. Various catalysts are being widely researched and used commercially for this purpose. Vanadia-based catalysts (e.g. $V_2O_5/WO_3/TiO_2$) are the most commonly used and widely investigated catalysts for SCR [1–5]. However, these catalysts have inadequate stability at the higher temperatures encountered in high load vehicle operation and are not suitable for systems including a particulate filter that actively regenerates at higher temperatures. Hence, the focus has shifted to Fe- and Cu-based zeolite catalysts, both of which have demonstrated very high NO_x reduction efficiencies at high space velocities. Cu-based catalysts are particularly effective at lower temperatures (≤350 °C) [6–9] which is desirable for vehicles that operate at low load for a large fraction of their use. Moreover, NO_x removal efficiencies on Cu-based catalysts are found to be rather insensitive to the amount of NO_2 in the feed at lower temperatures [6,10]. On the other hand, Fe-based catalysts are active at higher temperatures (>350 °C) and give very high NO_x reduction efficiencies even at very high temperatures (up to 600–700 °C) [11–15]. The presence of feed NO_2 accelerates the NO_x conversion on Fe-zeolite catalysts, particularly at lower temperatures [6,12,13].

The catalytic reactions occurring during SCR have been extensively studied in the literature on the aforementioned vanadia, Fe-zeolite, and Cu-zeolite catalysts. There are three SCR reactions defined according to the composition of the feed NO_x ($NO + NO_2$). Each is catalyzed by either Fe- or Cu-zeolite materials and is highlighted as follows:

- *Standard SCR*: This reaction involves NO and NH_3 reacting in presence of O_2

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \quad \Delta H = -4.07 \times 10^5\ \text{J/mol}\ NH_3 \tag{1}$$

- *Fast SCR:* This reaction is called the “fast SCR” reaction (2) because it has a much higher rate than the standard SCR reaction (1) due to the presence of NO_2 in the feed:

$$2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O \quad \Delta H = -3.78 \times 10^5\ \text{J/mol}\ NH_3 \tag{2}$$

- *NO_2 SCR:* This overall reaction occurs when the feed NO_x consists of only NO_2:

$$4NH_3 + 3NO_2 \rightarrow 3.5\,N_2 + 6H_2O \quad \Delta H = -3.41 \times 10^5\ \text{J/mol}\ NH_3 \tag{3}$$

In our recent study [11], we showed that NO oxidation is the rate determining step for the standard SCR reaction on Fe-zeolite catalyst. A recent study by Luo et al. [16] used a modified FTIR method to spatially resolve gas concentrations in Fe-zeolite monolithic catalyst for various SCR reactions. They determined the catalyst length required to achieve desired NO_x conversions for various SCR reactions at different temperatures. Under the investigated conditions (Fe-beta zeolite catalyst, 1.2% Fe content, silica-alumina ratio 35:1, gas hourly space velocity (GHSV) = 28,000 h^{-1}, cell density: 400 cpsi), they found that the catalyst lengths needed to achieve 80% NO_x conversion at 300 °C were 2.4, 1.2 and 0.5 cm for the standard SCR, NO_2-SCR and fast SCR reactions, respectively. These results confirm findings from other investigators [6,13] that an equimolar mixture of NO and NO_2 gives the highest NO_x conversion rates.

An important side reaction is the oxidation of NH_3 by O_2. This reaction is undesirable since NH_3 is the reductant of NO_x. Both Fe- and Cu-zeolites catalyze NH_3 oxidation to N_2:

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \quad \Delta H = -3.12 \times 10^5\ \text{J/mol}\ NH_3 \tag{4}$$

Ammonia oxidation has been well studied on various zeolite catalysts in the literature [17,18]; both Fe- and Cu-zeolite catalysts have been found to be highly selective in oxidizing NH_3 to N_2. For Fe-zeolite catalysts, NH_3 oxidation starts at higher temperature (300 °C) and is slower compared to that on Cu-zeolite (ca. 250 °C). The consumption of NH_3 on Cu-zeolites is significant and leads to a sharp decrease in NO_x conversion activity at high temperatures [6,7]. In contrast, NH_3 oxidation is less pronounced on Fe-based zeolites, becoming important only at very high temperatures. Other side reactions like NO oxidation, ammonium nitrate formation and its decomposition to N_2O also take place on these catalysts [19].

Given the differences in activities of the Cu- and Fe-based catalysts, it seems plausible that a combination of Fe-zeolite and Cu-zeolite catalysts might achieve high NO_x conversions over a broader temperature range than the individual catalysts. A few literature studies considered such combined Fe- and Cu-zeolite systems [20,21]. Krocher and Elsener [20] studied various combinations of Fe-zeolite, Cu-zeolite and V_2O_5/WO_3-TiO_2 and found that a Fe-zeolite section followed by a Cu-zeolite (in series) gives higher NO_x conversion efficiencies. Girard et al. [21] carried out similar studies on combinations of Fe- and Cu-zeolite monolith catalysts and came to the same conclusion. In their study, they found that the series combinations of (33%) Fe-zeolite followed by (67%) Cu-zeolite gives the highest NO_x reduction efficiency throughout the temperature range. Similar studies of a series arrangement of Fe- and Cu-zeolite catalysts with different individual catalyst lengths were carried out by Theis and McCabe [22]. In an actual diesel engine exhaust aftertreatment system, a SCR unit is preceded by a diesel oxidation catalyst (DOC) unit, which has the function of oxidizing hydrocarbons to CO_2 and H_2O and NO to NO_2. The NO oxidation generates the NO_2 needed to increase the effectiveness of the downstream SCR. However, the high cost of Pt is a major issue for the DOC unit. It is therefore of practical interest to develop alternative, more cost-effective SCR catalysts that can achieve high NO_x removal efficiencies with a reduced reliance on NO_2 generation using expensive precious metals (e.g. Pt).

The approach of combining two or more distinct catalysts to achieve improved performance has been considered in other reaction systems [23–25]. Xu et al. [24] used a physical mixture of zeolites with Na-rich, Fe-Cu Fischer–Tropsch catalysts to get improved activity for the hydrogenation of carbon dioxide. A few other studies [25–28] reported the use of so-called dual-layer monolithic catalysts for SCR of NO_x with hydrocarbons (e.g. propene) as reducing agents. The particular catalyst had a Pt/Al_2O_3 or Pt/SiO_2 in the bottom layer and, H- or Cu-zeolite (ferrierite or ZSM-5) in the top layer. The idea is to use the precious metal (e.g. Pt/Pd) in the bottom layer to oxidize NO to NO_2 which then diffuses back to be reduced by hydrocarbons (e.g. propene) in the upper layer containing a zeolite. The dual layer catalysts were found to be superior for NO_x reduction compared to the single layer catalyst (e.g. Pt/SiO_2). To our knowledge no literature study has focused on such dual layer catalyst configurations using NH_3 as a reductant.

The objective of the current study is to determine if a dual-layer Fe/Cu zeolite catalyst can exhibit improved performance for lean NO_x reduction. To this end, we examine in detail various combinations of sequential brick and dual-layer catalysts. Our approach is to systematically vary the lengths of the Fe- and Cu-zeolite monoliths in order to identify superior axial configurations, along the lines of the aforementioned pioneering studies at Ford. Various catalysts