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On the Cu species in Cu/beta catalysts related to DeNOx performance of coupled NSR-SCR technology using sequential monoliths and dual-layer monolithic catalysts

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ABSTRACT

Cu/beta catalysts are prepared starting from protonic or ammonic BEA zeolite following liquid ion exchange with copper. Alternatively, an intermediate ion exchange with Na ions is performed before copper ion exchange. Cu/beta catalysts are extensively characterized by XRF, N_2 adsorption–desorption, FT-IR of NO and CO adsorption, EPR, H_2-TPR, TEM and SEM in order to identify copper oxidation state (Cu^+ or Cu^{2+}) and copper species (agglomerated or Cu ions with different interaction with the support). Cu/beta catalyst prepared from ammonic BEA zeolite with intermediate Na ion exchange followed by copper ion exchange results in the most active catalyst in the NH_3-SCR reaction, which is related to the coexistence of Cu^+ and Cu^{2+} ions and to a more accessible location of such ions in the zeolite matrix. This catalyst is washcoated onto a monolithic substrate with an optimum loading of 0.32 g cm^{-3}, in order to be placed downstream a NO_x storage and reduction (NSR) monolithic catalyst, prepared by washcoating Pt-Ba/Al_2O_3 powder with an optimum loading of 0.25 g cm^{-3}. NSR-SCR catalyst in sequential beds results in a very active system with a NO_x removal of 97% and a N_2 selectivity of 96% at 275 °C. NSR/SCR catalyst prepared in a unique dual layer device shows that top SCR layer loading can be tuned in order to improve $DeNO_x$ performance. Optimum SCR layer loading is observed for 0.02 g cm^{-3}, enhancing the NO_x to N_2 efficiency of single NSR catalyst but far away from the catalytic performance observed for the sequential NSR-SCR configuration.

1. Introduction

The use of diesel engines and lean burn gasoline engines in vehicles application is increasing due to their higher fuel efficiency and lower CO_2 emissions compared to stoichiometric gasoline engines. However, the introduction of excess oxygen for fuel combustion produces an oxygen rich exhaust and makes NO_x reduction a challenging endeavor, because well-established three-way catalysts (TWC) are inefficient in such oxygen rich environment [1]. Two different approaches have been developed in order to mitigate NO_x emissions from diesel and lean burn engines, lean NO_x trap (LNT)—also denominated NO_x storage and reduction (NSR) catalysts—and selective catalytic reduction (SCR) catalysts [2].

Model NSR catalysts consist of a cordierite monolith washcoated with porous alumina on which an alkali or alkali-earth oxide (e.g. BaO) and a noble metal (Pt) are deposited. The NSR technology runs the engine under cyclic fuel lean and fuel rich conditions, producing net oxidizing and reducing environments, respectively. Usually, lean period duration is in the order of few minutes while rich period duration is few seconds. During the lean period NO_x are stored in barium sites in the form of nitrates and nitrites and during the rich period the stored NO_x are released and reduced to N_2, NH_3 and N_2O. One of the main drawbacks of the NSR technology is the emission of ammonia in the gas exhaust when using H_2 as reductant [3].

On the other hand, SCR technology runs the engine under continuous lean mode and needs an external source of reductant. Ammonia, obtained from the hydrolysis of urea, is used as reducing agent and is continuously added to the engine exhaust. Cu exchanged ZSM-5 was first reported to be an effective catalyst for NO_x reduction on lean exhaust [4]. Later, Cu^{2+} ion-exchanged BEA zeolite (Cu/beta) was shown to have excellent activity in the SCR of NO_x with NH_3 [5], and metal exchanged BEA zeolites are generally found to have greater hydrothermal stability than similar ZSM-5 catalysts [6]. Recently, it has been reported that Cu-exchanged zeolites with CHA structure show excellent activity for the SCR of

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NO_x [7], and more interestingly, improved hydrothermal stability when compared to Cu/ZSM-5 or Cu/beta [8,9]. Many efforts have been made in order to characterize copper species in zeolite structures, i.e. MFI, BEA or CHA [10–12]. Cu has been found to be present in zeolites in different nature, coordination or oxidation state, e.g. CuO aggregates, isolated $[Cu—O]^+$ or $[Cu—O—Cu]^{2+}$ oxocations. Furthermore, a number of different preferred crystallographic sites for isolated Cu^{2+} ions have been proposed depending on the zeolite structure. Thus, there is still an open debate in literature trying to identify specific copper active species for NO_x reduction.

Recently, a new approach has been proposed in order to mitigate NO_x emissions from diesel engines which combines NSR and SCR catalysts in consecutive reactors, firstly patented by researchers at Ford Motor Co. [13]. In the combined, sequential NSR-SCR technology, the limitation of NH_3 formation at the outlet of NSR catalyst is converted into an advantage. NH_3 is trapped or stored on acidic sites of the metal-exchanged zeolite and then is utilized to reduce NO_x that slips from the NSR during the subsequent lean period. The aim is to generate in the NSR as much NH_3 as needed to completely reduce NO_x, releasing to the atmosphere only innocuous compounds, such as nitrogen and water.

A dual-layer configuration is a potential alternative to the sequence of NSR-SCR monoliths. Nakatsuji et al. from Honda [14] proposed a catalyst system comprising a solid acid (Bronsted acid-based zeolite) on top of Pt/OSC (oxygen storage catalyst). While Honda's work provoked interest in this approach, it did not provide sufficient information about the catalyst or understanding of the fundamental workings of the NSR-SCR dual-layer catalyst. The first fundamental study to provide insight and understanding of the dynamic performance of a dual-layer LNT-SCR was reported by Liu et al. [15,16]. The dual-layer catalysts exhibited high N_2 selectivity and low NH_3 selectivity over the temperature range of 150–300 °C. In a dual-layer catalyst system the NSR and SCR catalysts are in intimate contact although the operating principle remains essentially the same as sequential NSR-SCR system. When the SCR layer is coated on top of the NSR layer, NO_x that diffuses into the SCR catalyst during the lean period may either react with NH_3 or diffuse to the underlying NSR layer where it is stored, and then may be reduced to N_2 or NH_3 during the next fuel-rich period [16]. These findings by Liu et al. [15,16] were interpreted in terms of the individual performance features of the LNT and SCR systems. With coupled systems, since only a fraction of the fed NO_x has to be reduced on the NSR, a fraction of the expensive NSR catalyst may be replaced by the less expensive SCR catalyst.

The objective of the current work is to gain insight and understanding on DeNOx performance features of NSR-SCR coupled systems in terms of the nature and distribution of Cu active species in the SCR catalyst, when two sequential monoliths and one dual-layer monolith are configured. We investigate the influence of Cu^{2+}, Cu^+ and CuO species in the based-zeolite SCR catalyst by using different preparation procedures. Different loadings of the resultant most active SCR catalyst were washcoated on monoliths and the influence of the washcoat layer thickness on the DeNOx performance was studied. Also the NSR catalyst washcoat layer thickness was varied, and the NOx removal and $N_2/NH_3/N_2O$ selectivities achieved with coupled NSR-SCR are compared for the sequential doubled monoliths and the single dual-layer monolith.

2. Experimental

2.1. Catalyst preparation

2.1.1. NH_3-SCR catalysts preparation

Four Cu/beta powder catalysts were synthesized by the following wet-ion exchange procedures. The first method consisted on ion exchanging an H/beta powder with $Cu(COOCH_3)_2$ aqueous solution. A protonated powder (H/beta) was obtained by calcining NH_4^+/beta at 500 °C for 4 h. Metal ion exchange was carried out by dissolving 1.51 g $Cu(COOCH_3)_2$ (Panreac, 98%) in 1.5 L miliQ water. Then, H/beta was added to this solution (8 g/L) and it was stirred for 24 h at 60 °C maintaining the pH value at 6 by ammonia addition (25% as NH_3, Panreac). The suspension was then filtered, washed with deionized water and dried overnight at 110 °C. Finally, the Cu/beta catalyst was obtained by calcining the powder at 500 °C for 4 h. This catalyst will be denoted as H/Cu. The second preparation method was carried out following the same procedure, but using the as received NH_4/beta powder instead of H/beta, which will be denoted as NH_4/Cu.

In the third method, NH_4/beta was ion exchanged with 0.1 M $NaNO_3$ in order to obtain Na/beta. The ion exchange was conducted for 24 h with continuous stirring at ambient temperature and neutral pH (≈7). The powder was obtained following filtration, washing and drying overnight at 110 °C. The Na exchange and drying were repeated twice to maximize the exchange ratio. The Cu/beta powder was obtained ion exchanging Na/beta with copper, as explained before. This catalyst will be denoted as NH_4/Na/Cu. The last preparation method was performed starting from H/beta zeolite and following an intermediate ion exchange with Na, as previously explained, leading to H/Na/Cu catalyst.

2.1.2. Monolithic NSR, SCR and dual layer NSR-SCR catalyst preparation

Several cordierite ($2Al_2O_3{\cdot}5SiO_2{\cdot}2MgO$) monoliths, 17 mm in diameter and 21 mm length, were cut from a commercial sample supplied by Corning, with a cell density of 400 cpsi, 1 mm^2 square channels and a wall thickness of 150 μm, to be used as substrates.

Pt(1.2%)-Ba(15%)/Al_2O_3 powder was prepared by wetness impregnation of γ-Al_2O_3 with $Pt(NH_3)_2(NO_2)_3$ solution and afterwards with $Ba(CH_3CO_2)_2$ solution, performing a drying step at 110 °C and a calcination at 500 °C for 4 h between impregnations. The monolithic Pt-Ba/Al_2O_3 catalysts were prepared by consecutive immersions of the monoliths into 10 wt.% Pt-Ba/Al_2O_3 aqueous slurry until desired catalyst loading was washcoated. After each immersion, the excess of liquid remaining in the monolith channels was blown out with compressed air and the monolith was dried at 110 °C for 1 h. The washcoated monoliths were calcined at 500 °C for 4 h. Several NSR monoliths were prepared with catalyst loadings ranging from 0.07 to 0.35 g cm^{-3}.

Monolithic SCR catalyst were prepared following the same procedure above reported but immersing the monoliths into 10 wt.% Cu/beta slurry. Similarly, dual-layer catalysts were prepared by first immersing the monoliths into Pt-Ba/Al_2O_3 aqueous slurry until 0.25 g cm^{-3} was washcoated and then several immersions were performed in Cu/beta slurry until the desired amount was deposited. Thus, Cu/beta layer was incorporated onto Pt-Ba/Al_2O_3.

2.2. Catalyst characterization

2.2.1. XRF

Wavelength dispersive X-ray fluorescence (XRF) analysis was carried out with AXIOS PANalytical spectrometer equipped with a Rh tube. Prior to analysis the samples were prepared by the fusion method using a Spectromelt A12 flux supplied by Merck.

2.2.2. Surface area

Textural properties were evaluated from nitrogen adsorption–desorption isotherms, determined at −196 °C with a Micromeritics TRISTAR II 3020 apparatus. The specific areas of the samples were determined in line with the standard BET procedure, using nitrogen adsorption taken in the relative equilibrium pres-