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Influence of the washcoat characteristics on NH_3-SCR behavior of Cu-zeolite monoliths

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ABSTRACT

The preparation procedure of a structured SCR catalyst is investigated by optimizing preparation method, varying active phase's incorporation order: on one hand, cordierite substrates were washcoated with bare zeolite and afterwards Cu ion exchange was carried out over the previously zeolite washcoated monoliths and, on the other hand, Cu ions were first exchanged over powder zeolite and then the Cu-zeolite was deposited on the cordierite monolith. BETA and ZSM-5 zeolites have been used. The copper content was also varied in prepared catalysts, i.e., 3% and 5%. A monolith of zeolite was also extruded and directly exchanged on the monolith with 2% of copper. Monoliths prepared by first exchanging the powder zeolite and using it for washcoating the monolith (IE–W) achieved better SCR behavior with respect to catalysts prepared in the opposite order (W–IE), for a feedstream with 750 ppm NO, 750 ppm NH_3 and 7.5% O_2 in Ar, and a space velocity of 30,000 h^{-1}, due to higher efficiency of the ion-exchange and to the better Cu distribution in the washcoat, as revealed from the XPS results. Besides, the extruded BETA catalyst achieved better SCR conversion than Beta zeolite washcoated monoliths.

1. Introduction

Diesel engines and lean burn engines operate under oxygen excess in the fuel combustion. This makes more complete the combustion and thereby lowers CO_2 emissions and the fuel cost. However, the presence of oxygen excess in the exhaust gases makes difficult to convert NO_x into N_2 becoming inefficient the conventional three-way catalysts. One of the major techniques being employed to reduce the emissions of NO_x is the urea/ammonia SCR [1–5].

TiO_2-supported V_2O_5 formulations used for NO_x removal in industrial applications have also been used for heavy duty diesel vehicles in Europe since 2005. However, due to the toxicity of vanadia, which begins to volatilized at 650 °C, recently copper [5–9] and iron [3,10–13] ions exchanged into different zeolites, mainly BETA and ZSM-5 [9,13–15] have received much attention by researchers in the field of light diesel emission control. The state of the art in selective catalytic reduction of NO_x by ammonia using metal-exchanged zeolite catalysts has been extensively reviewed by Brandenberger et al. [10]. This review attempts to correlate catalyst activity and stability with the preparation method, the exchange metal, the exchange degree, and the zeolite topology.

There is still debate in the literature about the copper chemistry on metal-exchanged zeolites. Iwamoto et al. [16] concluded that paired Cu^{2+} species are the active sites in Cu-ZSM-5 at 450 °C, which seems very likely in view of the strong increase in activity for NO decomposition with rising Cu content above a certain Cu/Al ratio. Komatsu et al. [17] observed similar relation between the specific SCR activity and the copper concentration and an increasing specific activity decreasing Si/Al ratio of the parent ZSM-5 zeolite. They also proposed paired Cu^{2+} to be the active copper species. More recently, Cu^{2+}-exchanged Beta zeolites (Cu-BETA) have been shown to have good activity in the NH_3-SCR of NO_x, and metal-exchanged BETA zeolites are generally found to have better hydrothermal stability than similar ZSM5 catalysts [5,10]. Also the specific zeolite preparation technique plays an important role in the nature and stability of active sites. In the very recent patent literature [18] Cu^{2+} ion-exchanged SSZ-13 (Cu-SSZ-13) has been discovered to exhibit NO_x conversions of 90–100% over a wide temperature range in the NH_3-SCR process, and its activity exceeded 80% even after extensive high-temperature hydrothermal aging [19]. In a recent paper [9], we prepared several Cu-exchanged powder zeolite catalyst, varying the preparation method (ion exchange and impregnation), the copper content (1–6%) and the type of zeolite (BETA and ZSM5). Cu^{2+} resulted the most active species in the catalysts, and copper

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loadings around 2 wt.% the optimal copper loading. Higher metal loadings decreased the maximum NO_x conversion although it was achieved at lower temperature, probably due to promotion of NO to NO_2 oxidation and subsequent activation of fast SCR reaction. Higher Cu loadings enhanced selectivity to N_2O, but it was always maintained below 6%, and NO_2 was not detected at the temperature of maximum NO_x conversion.

Most of the studies concerning the metal exchange degree and the nature of the active species have been made on metal-exchanged powder zeolites. However, the application of NO_x removal by SCR for the cleanup of diesel engine exhaust gases requires unequivocally some structured support, e.g., cordierite monoliths, due to the high volumetric flows, reduced space availability and the need of low pressure drop [20]. These cordierite monoliths have to be washcoated with a porous material as zeolite followed by the incorporation of the active phase. An alternative method for preparing monolithic SCR catalyst is based on direct extrusion of zeolite. This method has the advantage that the active phase can be uniformly distributed in the entire monolith and it is possible to withstand a small loss of zeolitic surface material without affecting the durability and effectiveness. Also, reduces significantly the number of steps necessary for the preparation [21].

In this paper, different Cu-supported zeolite/cordierite monoliths have been prepared with different order in the incorporation of the active phases: on one hand, cordierite substrates were washcoated with bare zeolite and afterwards Cu ion exchange was carried out over the previously zeolite washcoated monoliths and, on the other hand, Cu ions were first exchanged over powder zeolite and then the Cu-zeolite was deposited on the cordierite monolith. BETA and ZSM-5 zeolites have been used. Also a monolith of zeolite was extruded and the copper directly exchanged on the monolith. The objective of this study is to evaluate the impact of different preparation techniques, metal loadings and copper active species on the behavior of prepared monolith in the standard SCR reaction.

2. Experimental

2.1. Catalysts preparation

Several cordierite ($2Al_2O_3{\cdot}5SiO_2{\cdot}2MgO$) monoliths, 17 mm in length and diameter, were cut from a commercial sample supplied by Corning, with a cell density of 400 cells per square inch, 1 mm^2 square channels and a wall thickness of 150 μm, to be used as substrates. After calcination in air at 700 °C to remove possible impurities, the Cu-zeolite SCR monoliths were prepared following two different procedures: On one hand, the cordierite substrates were washcoated with the bare zeolite and afterwards Cu ion exchange was carried out over zeolite washcoated monoliths. On the other hand, Cu ion exchange was first performed over powder zeolite and then cordierite monoliths were washcoated with Cu-zeolite.

Two different zeolites, namely CP414E (BETA, Si/Al = 25) and CBV5524G (ZSM5, Si/Al = 50) supplied by Zeolyst International (BET surface of 680 and 425 $m^2\,g^{-1}$, respectively) and two different nominal loadings of copper, i.e., 3% and 5% (referred to zeolite weight) were used in the present study. Thus, 3 different variables with two different levels will be considered: (i) preparation procedure: washcoating/ion-exchange (W–IE) or ion-exchange/washcoating (IE–W); (ii) zeolite type: BETA or ZSM5; and (iii) nominal copper loading: 3% or 5%. Consequently, 8 SCR monoliths were prepared which are listed in Table 1. The preparation procedure can be identify by the nomenclature used for each catalysts, for example, Z-IE3–W means that ZSM5 powder zeolite (Z) was first ion exchanged with a nominal copper loading of 3% (IE3) and then washcoated (W) over the cordierite monolith. B-W–IE5 identifies the SCR catalysts prepared with BETA zeolite (B) which is first washcoated (W) and then ion exchanged with a nominal Cu loading of 5% (IE5).

Table 1
Prepared catalysts.

Monolith	Zeolite	Preparation procedure	Cu nominal loading (%)
B-IE3–W	BETA	IE–W	3.0
B-IE5–W	BETA	IE–W	5.0
B-W–IE3	BETA	W–IE	3.0
B-W–IE5	BETA	W–IE	5.0
B-E–IE2	BETA	E–IE	2.0
Z-IE3–W	ZSM5	IE–W	3.0
Z-IE5–W	ZSM5	IE–W	5.0
Z-W–IE3	ZSM5	W–IE	3.0
Z-W–IE5	ZSM5	W–IE	5.0

IE: ion exchange; W: washcoating; E: extruded.

Cu ion exchange over zeolite powder was carried out following the procedure detailed in our previous work [9]. Briefly, the required amount of $Cu(COOCH_3)_2$ (Panreac, 98%) was dissolved in water and then 12 g H-ZSM5 or H-BETA were added to 1.5 l of the Cu solution. The ion exchange was prolonged for 24 h at 65 °C under continuous stirring, while keeping the pH constant at 7.0 by the addition of NH_3. The ion exchanged samples were then filtered, washed twice in deionized water, dried during all night and calcined at 550 °C for 4 h.

The washcoating of cordierite monoliths was carried out by slurry dip-coating. In the case of ZSM5 or Cu-ZSM5 powders, the solid content of the slurry was adjusted to 40% by adding the required amount of water, while the solid content was 15% for BETA or Cu-BETA. Then, the slurries were milled with ceramic balls for 16 h until homogeneous slurry was obtained. After ball milling, 10 wt.% colloidal silica (Ludox-HS 40, Sigma–Aldrich) was added in order to enhance the mechanical stability and the adherence of the washcoat. The washcoating was made by immersion of the monoliths into the corresponding slurry for 3 min; afterwards the excess of liquid retained in the channels was blown out with compressed air and the monoliths were dried at 110 °C for 30 min. This procedure was repeated until $\simeq$1 g of zeolite or Cu-zeolite was washcoated. Finally, the monoliths were calcined at 550 °C for 4 h.

On the other hand, Cu ion exchange over zeolite washcoated monoliths was carried out by dipping the monolith in an aqueous solution containing the required amount of copper acetate. The ion exchange was prolonged for 24 h and the pH was adjusted at 7 by the addition of NH_3. Then the monoliths were removed from the solution and the excess of liquid was blown out. Finally, the catalysts were dried at room temperature in horizontal position and then calcined at 500 °C during 4 h.

Alternatively, a home-made zeolite type and honeycomb shape extruded monolith was prepared (B-E–IE2), i.e., no cordierite was used as substrate, and thus, the monolith was entirely composed of zeolite. A self-design die head permitted us to obtain circular geometry extrudates with a cell density of 123 cpsi. More details about the preparation procedure of zeolite type extrudates can be found elsewhere [21]. After extrusion, the monolith was dried in a humidity controlled chamber in order to minimize the formation of cracks and finally calcined at 550 °C. Cu ion exchange for a nominal loading of 2% was performed by dissolving the required amount of copper acetate in an aqueous solution and dipping the monolith for 24 h. Afterwards the liquid retained in the channels was blown out with compressed air, and the monolith was dried and calcined at 500 °C.

2.2. Characterization techniques

2.2.1. Particle size distribution

The particle size distribution of the prepared slurries was determined by laser scattering in a MasterSizer analyzer X v1.1. (Malvern).