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Cerium-exchanged zeolites grown on metal gauze: A new catalyst system applicable for NO_x reduction in mobile engine exhaust

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Abstract

ZSM-5 and mordenite (MOR), directly grown on a stainless-steel metal gauze support and subsequently exchanged with cerium ions, were applied as a NO reduction catalyst. These supported cerium-zeolite catalysts were found to show turnover frequencies comparable to that of an unsupported cerium-exchanged mordenite. Furthermore, the thermostability of these materials was examined by a calcination-activity test cycle and Ce-ZSM-5 was found to be more stable than Ce-MOR. The present approach to grow zeolite directly on a support offers a new possibility to apply zeolite efficiently on a metal monolith applicable for NO_x emission control of mobile sources.

Keywords: Zeolites; NO_x; Mobile engine exhaust; Mordenite; ZSM-5

1. Introduction

In the past few years, NO_x emission control of diesel or lean-burn engine vehicles has drawn much attention and many catalysts have been investigated for catalytic reduction of NO_x under oxygen-rich conditions [1]. Among others, a variety of zeolite catalysts have been reported for NO reduction with hydrocarbons [2]. For a mobile emission control, the usage of a hydrocarbon reductant is generally preferred to the conventionally employed reductant: NH_3, since hydrocarbons can be carried much safer in vehicles, and a part of the fuel can also potentially be utilized as a reductant.

By contrast, we are engaged in the development of a NO_x reduction system with an aqueous urea solution as a reductant. A urea solution is also applicable in a compact and safe form with much less corrosion problems, compared to NH_3. The system with a urea reductant is already in application for a marine diesel exhaust treatment [3]. We have recently found that cerium-exchanged zeolites, mordenite and ZSM-5 in particular, are highly active and selective catalysts for NO reduction with ammonia [4,5] and urea [6]. Several aspects of these catalysts, such as the influence of H_2O and SO_2 on the reaction [6], the reaction kinetics [6] and the reaction mechanism [7,8] have been already examined. In addition, we have found that cerium-exchanged zeolites can employ NH_3 at a certain excess to NO without an ammonia-slip problem under model reaction conditions [9]. This is a very promising property, since it may circumvent the NH_3-slip problem in a practical application of the NO reduction system with a urea solution as well.

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Besides the investigations on NO_x reduction catalysis, we should also consider the last necessary step in an automobile catalyst research with zeolite; the preparation of a zeolite monolith. Zeolite is currently applied on monolith by gel-coating [10,11], by gluing [12] or it may be directly extruded with binders. The gel-coating is the most used method among these, though it has a disadvantage to dilute zeolite catalyst with silica or other gel-materials. The amount of exposed zeolite catalyst would be therefore limited in this case and it would result in a lower utilization of catalytically active zeolite material.

We have recently developed a new method to grow zeolite directly on a support [13,14]. In particular, ZSM-5 was found to grow easily on a stainless-steel metal support and when applied with exchanged copper ions to a model NO reduction with NH_3 it turned out to give a comparable performance as a commercial NO_x reduction catalyst: V_2O_5-TiO_2/SiO_2 [15]. This new approach is supposed to utilize zeolite material more efficiently than a gel-coating method, since zeolite crystals are fully exposed on the support surface without dilution by any other material.

We report here the application of ZSM-5 and mordenite (MOR), directly crystallized on a stainless-steel support and subsequently exchanged with cerium ions, for NO reduction with NH_3, which is employed as a model reaction of NO reduction with a urea aqueous solution. The synthesis conditions, the characterization, the catalytic performance in NO reduction and stability against a high temperature treatment are reported here.

2. Experimental

Supported ZSM-5 was hydrothermally synthesized in a 40 ml teflon lined autoclave under rotational conditions. The gel was prepared with 6.16 g of tetraethyl orthosilicate (Janssen Chemica), 0.162 g of sodium aluminate (Riedel De Haen AG), 1.50 g of 40% tetrapropyl ammonium hydroxide (Chemische Fabriek Zaltbommel) and 32.1 g of demineralized water. The synthesis mixture was shaken overnight. A rolled piece (1.5–3.5 g) of fine stainless-steel metal gauze (AISI 316, 35μm thickness, 45 μm mesh size; Miko Metaalhandel) was treated in toluene under boiling conditions for 4–7 h and dried at 130°C for 20 h. The synthesis gel and the metal gauze were put together in an autoclave, and placed in a preheated oven of 180°C for 4.5 h. The mordenite synthesis was performed in a similar manner, using a gel composed of 3.92 g of silica-alumina (LA-SHPV, Akzo-Nobel), 0.785 g of NaOH and 35.3 g of water. The synthesis was carried out at 160°C for 140 h. After synthesis, the samples were well washed with demineralized water and calcined at 450°C for 20 h. Cerium was then exchanged in a 6 mM cerium(III)acetate solution at 100°C for 5 h. The metal gauze surface after the zeolite synthesis was characterized by scanning electron microscopy (SEM). Furthermore, X-ray diffraction (XRD) analysis was carried out with crystals grown in the liquid phase of the same zeolite syntheses, in order to examine the crystallinity of the synthesized materials. A small amount of zeolite (ca. 10 mg) was carved from an excessively grown part on the metal gauze piece and analyzed by inductively coupled plasma-atomic emission spectroscopy to establish its elemental composition. In addition, the micropore volume of the supported zeolite sample was measured with liquid nitrogen using Autosorb-6B (Quanta Chrome Co.).

The model reaction of NO reduction with NH_3 in the presence of oxygen was carried out in an automated fixed bed reactor (BTRS-900; Autoclave Engineers). A piece of zeolite-loaded gauze (1.86–2.25 g) was rolled around a quartz stick ($d = 5$ mm) and fit in a quartz reactor tube ($d = 10$ mm). In this way, a high linear gas velocity through the gauze piece was obtained. The reactant gas employed consisted of NO (470 ppm), NH_3 (485 ppm) and O_2 (1%) in Ar, and was applied at 400 ml/min.

3. Results and discussion

3.1. Sample characterization

The gauze surface after the hydrothermal treatment was examined by SEM (Fig. 1 and Fig. 2) and the metal surface was found to be reasonably covered by zeolitic materials. Most crystals observed in Fig. 1 are ZSM-5 of typical elongated prismatic shape and small crystals were present on top of them. The metal gauze after the mordenite synthesis (Fig. 2) exhibited agglomerates of very small crystals on the surface, which are sometimes found in mordenite synthesis [16]. Since the morphology of the crystals formed in the liquid phase was same as those found on the metal gauze, the XRD analysis was performed with the crystals grown in the liquid phase (Fig. 3). The peak positions and the intensity ratios of peaks were in good agreement with a XRD-pattern of mordenite, confirming the growth of mordenite on the metal gauze support.

Fig. 1. SEM photograph of ZSM-5 on metal gauze. The white bar is 10 μm.

Fig. 2. SEM photograph of MOR on metal gauge. The white bar is 5 μm.

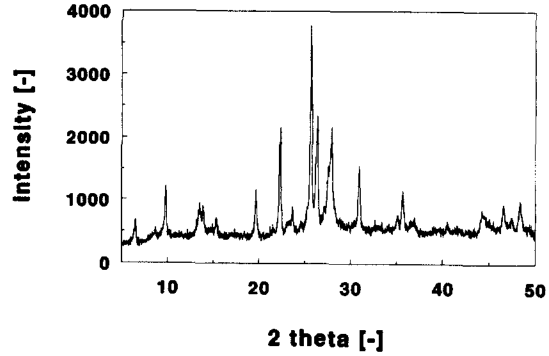

Fig. 3. X-ray diffraction pattern of crystals grown in the liquid-phase upon the MOR-on-metal gauze synthesis.

As shown in Table 1, the loading of zeolite was much higher with ZSM-5 than with MOR. The elemental analysis of the cerium-exchanged zeolite samples indicated the presence of small amounts of impurity metals, which are assumed to originate from the gauze. Iron and nickel were present, particularly much in ZSM-5, whereas no chromium was found above the analysis detection limit (0.0004 wt.-%). It should be noted that the cerium amounts found in these two samples were much higher than expected from their stoichiometric exchange of Ce^{3+} per three Al sites in the zeolite. This might be explained by cation exchange on silanol groups [17], or the possible

Table 1
The elemental composition of Ce-ZSM-5 and Ce-MOR grown on the metal gauze. Except for the loading of zeolite, the weight percentage (wt.-%) of each element was calculated against zeolite weight

Sample	Loading[a] wt.-%	Si/Al ratio	Ce[b] ex.-%	Ce wt.-%	Fe wt.-%	Ni wt.-%	Na wt.-%
Ce-ZSM-5	11.2	31	152	3.0	0.4	0.40	0.3
Ce-MOR	2.8	5	132	14.0	0.1	0.03	2.3

[a] The loading of zeolite on a metal gauze support; the weight percentage of zeolite against a total weight of metal gauze piece with zeolite.
[b] Ce ex.-% indicates the exchange level of cerium, which is defined as follows; Ce ex.-% = 100 × 3 × Ce(mol) / Al(mol).

exchange of cerium hydroxide species, e.g., Ce $(OH)^{2+}$, Ce $(OH)_2^+$, of which the effective charge is lower than three.

The pore-volume analyses of these samples showed micropore volumes of 0.15 and 0.11 ml/g for supported Ce-ZSM-5 and Ce-MOR samples, respectively. Compared to the micropore volume of ZSM-5 and MOR generally found (ca. 0.17 ml/g), our samples exhibited lower values. This may be due to a pore blockage by excessively exchanged cerium, which may have turned to cerium oxide-like clusters upon the heat treatment in the preparation stage for pore-volume measurements. This effect might be more severely reflected on mordenite with a one-dimensional pore structure, than on ZSM-5 with a three-dimensional channel system.

3.2. *NO reduction with ammonia under oxygen-rich conditions*

NO reduction with ammonia in the presence of oxygen (named as a model SCR-reaction, hereafter) was performed over Ce-ZSM-5 and Ce-MOR supported on gauze (Fig. 4). The Ce-MOR on gauze showed a high NO conversion in spite of its lower zeolite content. In the second series of experiments, the activity of both samples was found to be reduced by approximately 10% at 200–400°C, compared to the activity measured in the first run. This can be accounted for by the first high-temperature experience (560°C) of the catalyst in the first run, which might have led to reorganization of the excessively exchanged cerium ions. Compared with the present unsupported mordenite catalyst, the turnover frequencies of both supported zeolites were in the same order or even a little higher (Table 2), proving the supported zeolite material to be equally efficient as unsupported zeolite catalyst. The metal-gauze support itself turned out to produce NO at and above 400°C, which was indicated as the negative NO conversions in Table 2. This is probably due to the oxidation of NH_3 by oxygen, which is often observed with SCR-catalysts at high temperatures [18]. It should be noted that the supported zeolite catalysts showed a decrease in NO conversion at high temperatures, while the unsup-

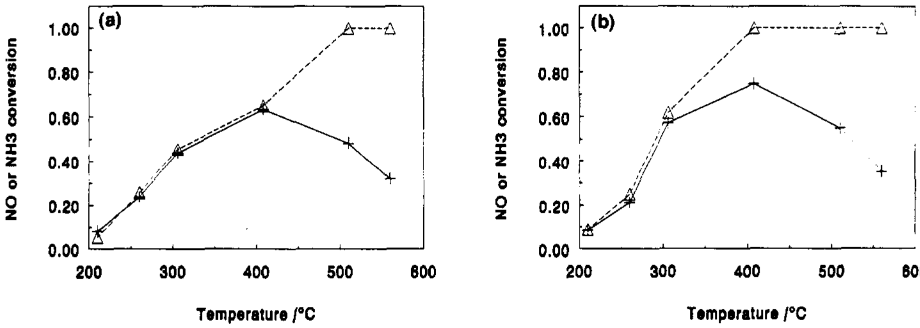

Fig. 4. A model SCR-reaction with (a) Ce-ZSM-5 on gauze and (b) Ce-MOR on gauze. NO (470 ppm), NH_3 (485 ppm) and O_2 (1%) in Ar. The results of the second run: (+) NO conversion and (■) NH_3 conversion. Catalyst weight include the gauze: 1.86 g (0.21 g zeolite) for Ce-ZSM-5 and 2.25 g (0.063 g zeolite) for Ce-MOR. Contact time: 0.032 and 0.0095 sg (zeolite) ml^{-1} for Ce-ZSM-5 and Ce-MOR, respectively.

Table 2
Comparison of the SCR-activities among the gauze-supported ZSM-5 (Ce-ZSM-5/G) and mordenite (Ce-MOR/G) and unsupported mordenite (Ce-Na-MOR)

Catalyst	NO conversion					TOF(mol NO/min/mol Ce)	
	210°C	260°C	306°C	408°C	510°C	210°C	260°C
Ce-ZSM-5/G	0.082	0.34	0.60	0.64	0.48	1.6×10^{-2}	6.7×10^{-2}
Ce-MOR/G	0.083	0.38	0.57	0.75	0.55	1.1×10^{-2}	5.1×10^{-2}
Gauze(2.25g)	0	0	0	−0.05	−0.29	–	
Ce-Na-MOR(1g)	0.69	0.82	0.85	0.87	0.86	1.8×10^{-2}	2.1×10^{-2}

NO (470 ppm), NH_3 (485 ppm), O_2 (1%) at 400 ml/min. Results of the second run.

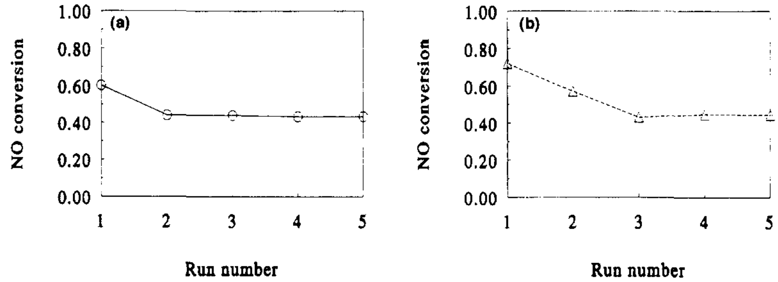

Fig. 5. Stability of the gauze supported Ce-ZSM-5 (a) and Ce-MOR (b) estimated by NO conversion at 300°C under the model SCR-conditions. See Fig. 4 for the details of the SCR conditions. The points Run 1 and 2 were the NO conversions observed in the two consecutive model SCR-reactions. After Run 2, the sample was calcined at 510°C under a flow of argon for 4–5 h each time before the NO conversion measurement (Run 3, 4 and 5).

ported mordenite catalyst maintained a high NO conversion up to 560°C. This may be accounted for by the negative influence of the gauze support or of the impurity metals (iron and nickel) in the zeolite, which may have additionally catalyzed the side reaction: NH_3 oxidation. The different state of cerium cations in the present supported catalysts (with over-exchanged cerium cations) and in the unsupported Ce-Na-MOR catalyst (with stoichiometric exchanged Ce^{III} with Na, 56% of total exchange sites occupied) might also be an important factor here. The former would tend to form oxide-like clusters, whereas the latter mainly provides isolated cerium cations, which may lead to a different catalytic performance.

Furthermore, the stability of the metal-gauze supported Ce-ZSM-5 and Ce-MOR catalysts was examined. The samples were subjected to repetitive calcination at 510°C in argon, and the model SCR-activity at 306°C was measured after each calcination, employed as an indicator for deactivation (Fig. 5). Though both catalysts showed some deactivation, Ce-ZSM-5 showed a higher stability than Ce-MOR. The lower stability of Ce-MOR on gauze might be ascribed to its easier dealumination due to its higher alumina content. For a practical application as an exhaust treatment catalyst, their thermostability in the presence of water will be also required to be examined in the future.

4. Conclusion

ZSM-5 and MOR were successively grown on a metal gauze support. These supported zeolites with exchanged cerium cations (Ce-ZSM-5 and Ce-MOR) were applied for a model reaction of NO reduction with NH_3 in the presence of oxygen. They exhibited turnover frequencies comparable to that of unsupported Ce-Na-MOR. The supported Ce-ZSM-5 was found to be more stable than the supported Ce-MOR upon high-temperature calcination.

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