Journal of Catalysis 315 (2014) 1–5

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Priority Communication

Stabilization of bare divalent Fe(II) cations in Al-rich beta zeolites for superior NO adsorption

Masaru Ogura[a,b,*], Keiji Itabashi[c], Jiri Dedecek[d], Tatsuki Onkawa[c], Yumiko Shimada[a], Koutarou Kawakami[a], Kenzo Onodera[a], Shinnosuke Nakamura[a], Tatsuya Okubo[c]

[a] *Institute of Industrial Science, The University of Tokyo, Komaba, Meguro, Tokyo 153-8505, Japan*
[b] *Unit of Elements Strategy Initiative for Catalysts & Batteries, Kyoto University, Katsura, Nishikyo, Kyoto 615-8510, Japan*
[c] *Department of Chemical System Engineering, The University of Tokyo, Hongo, Bunkyo, Tokyo 113-8656, Japan*
[d] *J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejskova 3, Prague 8 CZ-182 23, Czech Republic*

ARTICLE INFO

Article history:
Received 2 March 2014
Revised 29 March 2014
Accepted 1 April 2014
Available online 8 May 2014

Keywords:
Nitric oxide
Adsorption
Fe(II) ion
Beta zeolite
OSDA-free synthesis

ABSTRACT

Fe(II)-beta zeolites with a Si/Al molar ratio of 5, synthesized in the absence of an organic structure-directing agent, showed remarkably efficient NO chemisorption, as compared to conventional Si-rich beta zeolites (Si/Al = 12–20) and common zeolites such as A-type zeolite, ZSM-5, and faujasite.

1. Introduction

Zeolites are aluminosilicate minerals in which micropores multidimensionally penetrate the crystalline structure. The negative charge derived from trivalent aluminum in the silicate framework is compensated for by a positively charged cation on the zeolite extraframework. In aqueous solutions, this cation is exchangeable with specific metal ions to be loaded onto the solid surface; this is known as the ion-exchange ability of aluminosilicate zeolites [1,2]. Monovalent cations such as Na^+, K^+, and H^+ are easily inserted into the exchangeable sites of zeolites in accordance with the rules of the Hofmeister series and the size of the bare or hydrated ions. Moreover, it is well known that Ag^+ can be ion-exchanged in zeolites to impart antibacterial activity. As for divalent and trivalent cations, a metal-siting model has been widely accepted for which M^2(II) and M^3(III) cations coordinate with one and two hydroxyl ions (OH^-), resulting in monovalent $[M^2(OH)]^+$ and $[M^3(OH)_2]^+$ ions, respectively [3–5]. The existence of the OH group on those cations can be observed through infrared (IR) spectroscopy. Furthermore, treatment with high temperatures affords a coordinatively unsaturated $[MO]^+$ ion such as GaO^+, InO^+, or LaO^+ [2,6].

However, the location of multivalent cations within zeolites, with the exception of cobalt, has not been investigated in detail [7–9]. Co(II) ions located on zeolites have been reported to show a high catalytic performance for stationary deNO$_x$ [10,11], a technique of removal of nitrogen oxides (NO$_x$) from stationary sources such as boilers and turbines. Many researchers have investigated the location of Co(II) in zeolite microporous cavities. A group of researchers used ultraviolet–visible absorption (UV–vis) spectroscopy and magic-angle-spinning nuclear magnetic resonance (MAS NMR) analysis to show that there are three distinct ion-exchangeable sites—α, β, and γ—in various zeolites, which accommodate bare divalent cations [12,13]. Co(II) is always and Cu(II) is often exchanged as a M(II) hexa-aqua complex to zeolites. They also suggested that the siting strongly depends on the distribution of aluminum in the zeolite framework. The concentration of bare divalent cations in Si-rich zeolites is controlled by the distribution of framework Al atoms between Al pairs (Al–O–(Si–O)$_2$–Al sequences in one ring) that accommodate bare divalent cations and single Al atoms, which are balanced by monovalent species. On the other hand, the distribution of bare divalent cations between α, β, and γ sites depends on the concentration of Al pairs in the rings of these sites. Information about the nature and siting

---

* Corresponding author at: Institute of Industrial Science, The University of Tokyo, Komaba, Meguro, Tokyo 153-8505, Japan. Fax: +81 3 5452 6322.
E-mail address: oguram@iis.u-tokyo.ac.jp (M. Ogura).

http://dx.doi.org/10.1016/j.jcat.2014.04.001
0021-9517/© 2014 Elsevier Inc. All rights reserved.

of monovalent metal-oxo species is strictly limited in comparison with information about the bare divalent cations.

A rise in environmental concerns has led to stringent legislation all over the world regarding emission control of noxious gases, such as NO_x from the exhausts of automobiles equipped with gasoline and diesel engines [14]. Selective catalytic reduction (SCR) using urea is currently the most promising method of removing NO_x. Storage and reduction of NO (NSR), developed by Toyota [15], also requires oxidation of NO to store as NO_2 on barium or other alkaline compounds installed along with a platinum catalyst. Therefore, a highly active catalyst for NO oxidation is needed in all cases. Platinum (Pt) is widely utilized as an oxidation catalyst for unburned hydrocarbons, carbon monoxide, and nitric oxide. However, a large quantity of Pt must be installed on three-way catalysts and diesel-oxidation catalysts. From a thermodynamic standpoint, the formation of NO_2 is favored at low temperatures, such as that in a diesel engine exhaust. However, this reaction is quite slow at low temperatures, primarily due to the low concentration of NO. Adsorption techniques for the removal of low-concentration adsorbates [16], such as NO formed in tunnels, have been investigated. Furthermore, this problem has been examined using various approaches, including zeolites as a host for active NO adsorbents [17]. Among the tested zeolites, copper-loaded zeolites effectively adsorbed NO, but inhibition of NO adsorption by oxygen coexisted in the stream. Therefore, we propose a new approach for the development of a selective adsorbent of NO and its storage by cage-type zeolite micropores. The Fe(II) ion was selected as the adsorption center for NO, because Fe(II) is known to be active in the selective adsorption of NO in nitric oxide reductase (NOR), an Fe(II)-containing enzyme [18], and in the biological and pharmacological delivery of NO in digestive systems [19]. If successful, our proposed approach could be a viable tool for increasing the local concentration of NO to facilitate the oxidation to NO_2, ultimately without Pt or direct decomposition of NO.

2. Experimental

A variety of zeolites having different topologies, such as Linde type A (LTA; Si/Al = 1.0, commercially available), ZSM-5 (MFI; Si/Al = 12, Tosoh Corp.), beta (Si/Al = 5.0 [30], 13 (Zeolyst), 20 (Tosoh Corp.), and faujasite-Y (FAU; Si/Al = 2.8, Tosoh Corp.), were tested as hosts of Fe cations for NO adsorption. The zeolites were ion-exchanged with ferrous or ferric sulfate to obtain Fe(II) or Fe(III) zeolites, respectively. To avoid oxidation of Fe(II) to Fe(III) during the preparation of Fe(II) zeolites, we added an amount of ascorbic acid twice that of Fe(II) ions to the aqueous ferrous sulfate solution. The amount of Fe species was measured by the use of inductively coupled plasma-atomic emission spectrometry (ICP-AES), X-ray fluorescence (XRF) analysis, and temperature-programed reduction by hydrogen (TPR-H_2). NO adsorption capacity was evaluated using a pulse reactor with gas chromatography-thermal conductivity detection (GC-TCD) and an online chemiluminescence NO_x detector. Heat pretreatment at 300–400 °C was conducted prior to the adsorption test. One pulse (5.0 cm^3) including 1000 ppm NO was carried by a helium or air stream of 50 cm^3/min to 10–50 mg of the Fe-containing sample, typically at room temperature.

3. Results and discussion

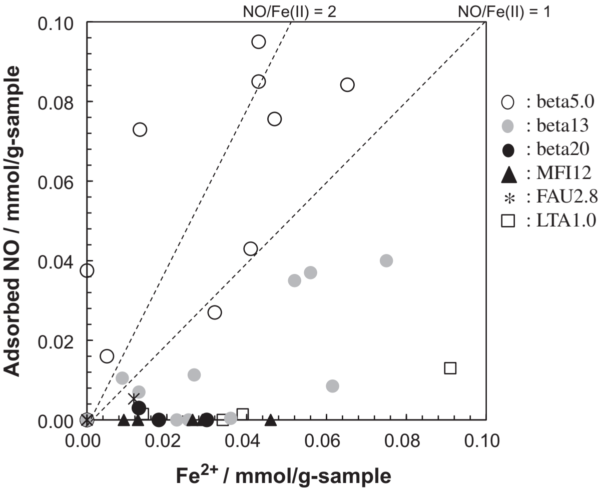

Fig. 1. NO adsorption capacity and efficiency for Fe(II)-exchanged beta5.0, beta13, beta20, MFI, FAU, and LTA zeolites.

Fig. 1 illustrates the NO adsorption capacity versus the amount of Fe(II), which was calculated by subtracting the amount of Fe-oxo species, as defined by TPR-H_2 [20], from the total amount of Fe on the zeolites determined by ICP or XRF. IR spectroscopic studies reveal that Fe(III) zeolites barely adsorbed NO, while a band assignable to a mononitrosil species could be clearly detected in the IR spectrum of Fe(II) zeolites, an observation that is supported by the literature [21–29]. These results suggest that only Fe(II) ions act as the main adsorption centers for NO in Fe zeolites. A variety of NO adsorption capacities were observed on Fe(II)-zeolites. Zeolites might have had a promotive effect on NO adsorption as the host for Fe(II), due not only to their microporous nature, but also to their high Al content, resulting in a better stabilization of multivalent cations.

We further studied the effect of the Si/Al molar ratio of the zeolite host on NO adsorption. Generally, it is difficult to synthesize LTA zeolites with a Si/Al molar ratio greater than 1.0 and MFI with a Si/Al molar ratio less than 10. FAU with a variety of Si/Al molar ratios can be prepared by dealumination, but NO adsorption on FAU with Si/Al ratios greater than 5 can never be observed. Recently, we developed a technique for synthesizing beta zeolites without utilizing organic structure-directing agents (OSDA) [30] and found that the resulting beta zeolites have a much lower Si/Al molar ratio (ca. 5.0) than beta zeolites conventionally synthesized with OSDA (ca. Si/Al = 10–500) [31]. A NO adsorption test was performed on Fe(II) beta zeolites with Si/Al molar ratios of 5.0, 13, and 20, and the results are plotted in the same figure. A beta zeolite with a Si/Al molar ratio of 5.0 (beta5.0) was synthesized without using an OSDA [30], while beta zeolites with Si/Al molar ratios of 13 (beta13) and 20 (beta20) were supplied by Zeolyst and Tosoh Corp., respectively. Notably, when a small amount of Fe(II) was loaded onto the highly aluminated beta zeolite (i.e., beta5.0), the NO adsorption ability exceeded that of any other zeolite tested thus far. The other beta zeolite samples, despite having Fe(II) content similar to that of beta5.0, showed very little NO adsorption capacity. The adsorption efficiency (the molar ratio of NO/Fe(II)) was more than 2 when a small amount of Fe(II), specifically 0.020 mmol Fe(II) per gram of Fe(II)-beta sample, was loaded. The efficiency decreased to 1 when 0.15 mmol Fe(II) per gram of the Fe(II)-beta sample was loaded. This corresponds to a 10% ion-exchange level for beta5.0. The NO adsorption capacity increased linearly up to 200% Fe(II) ion-exchange level, which is equal to 0.3 mmol Fe(II) per gram of beta5.0. Compared to other zeolites, a greater amount of Fe(II) was required to reach the maximum NO adsorption capacity in beta5.0. After the maximum value was reached, the capacity declined, mainly because of pore-mouth clogging by Fe_2O_3 deposited on the surfaces of zeolites during preparation.

In order to understand the unique high efficiency of NO adsorption capacity per Fe(II) ion of Fe(II)-beta5.0, we obtained the IR