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Steam deactivation of CoZSM-5 NO_x reduction catalysts

Prastawa Budi, Russell F. Howe*

Department of Physical Chemistry, The University of New South Wales, Sydney 2052, Australia

Abstract

The effects of high-temperature steam treatment on the activity and selectivity of CoZSM-5 catalysts for the selective catalytic reduction of NO with methane have been examined. Loss of activity and selectivity on steam treatment is due to framework dealumination of the zeolite, causing an irreversible change in the coordination state of the Co^{2+} ions. Pre-exchange of the zeolite with La^{3+} cations inhibits the dealumination while stabilizing the catalysts.

Keywords: NO_x reduction; CoZSM-5; Steam; Catalyst stability; Dealumination

1. Introduction

The selective catalytic reduction (SCR) of NO with hydrocarbons in the presence of excess oxygen has recently attracted wide interest in light of growing environmental concerns over NO_x emissions from diesel and lean-burning gasoline engines [1]. The use of hydrocarbons in the SCR of NO as an alternative to ammonia over CuZSM-5 zeolite catalysts was first proposed by Iwamoto et al. [2–4]. More recently, the SCR of NO_x using methane as the reducing reagent over CoZSM-5 was demonstrated by Li and Armor [5].

A key issue in the practical implementation of metal zeolite catalysts for NO_x reduction is catalyst durability. In particular, steam which is unavoidably present in combustion gases will irreversibly deactivate CuZSM-5 catalysts above a certain temperature [6–8]. We have recently shown that this deactivation is due to dealumination of the zeolite rather than to structural collapse; the resulting loss of ion-exchange capacity causes an irreversible change in the coordination state of the Cu^{2+} and some migration of Cu to the external surface of the zeolite [9]. Steam deactivation of CuZSM-5 catalysts can be inhibited by co-exchange of lanthanum ions into the zeolite, which prevents or at least reduces the extent of dealumination [10]. The effect of H_2O on the activity of SCR of NO by methane over CoZSM-5 was investigated by Armor et al. [11]. They suggested that the water effect is a kinetic phenomenon rather than due to structural damage of the catalyst, and concluded that CoZSM-5 was more stable in wet NO streams at high temperatures than CuZSM-5. We have reported briefly [9] that CoZSM-5 catalysts are not durable under long steam aging. In this paper, we examine the stability of CoZSM-5 catalysts to steam treatment in more detail, and show that co-exchange of lanthanum can also stabilize these catalysts.

2. Experimental

All catalysts were prepared from HZSM-5 provided by PQ Corporation ($SiO_2/Al_2O_3 = 35$). The zeolite was converted to either the ammonium or sodium

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*Corresponding author. e-mail: r.howe@unsw.edu.au

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forms by conventional ion exchange. CoZSM-5 zeolites were prepared by ion exchange of NH_4ZSM-5 with aqueous $Co(NO_3)_2$ solution. CoLaZSM-5 and CoCeZSM-5 were prepared by successive ion exchange of NaZSM-5, first with rare earth then with Co. Chemical analysis (ICP atomic emission spectroscopy) indicated the following compositions: CoZSM-5, Co/Al = 0.46; LaZSM-5, La/Al = 0.28; CeZSM-5, Ce/Al = 0.30; CoLaZSM-5, Co/Al = 0.39 and La/Al = 0.12; CoCeZSM-5, Co/Al = 0.40 and Ce/Al = 0.14.

Hydrothermal treatment of catalysts was undertaken in a quartz fixed-bed microreactor. Two standard treatment protocols were used: medium steam treatment comprising 72 h exposure to 114 torr of water vapour at 500°C, and severe steam treatment comprising 24 h exposure to the same vapour pressure at 800°C.

Catalytic measurements were carried out in a quartz microreactor under steady-state plugged-flow conditions. The reaction mixture comprising NO (1000 ppm), CH_4 (1000 ppm), O_2 (20 000 ppm), balance He, was flowed over the catalyst at a GHSV of 40 000. Effluent gas was monitored by on-line gas chromatography and NO_x chemiluminescence.

Zeolite catalysts were characterized before and after steam treatment by X-ray powder diffraction, magic angle spinning (MAS) ^{29}Si and ^{27}Al nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy (FTIR), electron spin resonance (ESR), extended X-ray absorption fine-structure spectroscopy (EXAFS) and X-ray photoelectron spectroscopy (XPS). ^{27}Al and ^{29}Si MAS NMR spectra were recorded on a Bruker MSL 300 spectrometer at 78.2 and 59.6 MHz, respectively, under the conditions described previously [9]. ESR spectra were recorded at 4 K. X-ray absorption measurements were performed at Beam Line 20B at the Photon Factory, Japan. EXAFS analysis used the UWXAFS 3.0 and FEFF 5.0 codes distributed by the University of Washington [12]. XPS measurements were performed on pressed wafers of catalysts using a Kratos XSAM 800 instrument (AlK_α as an excitation source).

3. Results and discussion

After an initial break-in of 30 min, all zeolite catalysts gave stable NO conversions and product selectivities over a period of 180 min. For the purpose of comparing catalysts, conversions and product distributions after 90 min on stream were chosen. Fig. 1 shows percentage of NO conversion after 90 min on stream as a function of reaction temperature for CoZSM-5 and CoLaZSM-5 catalysts; the fresh catalyst, and the same catalyst after severe hydrothermal treatment (24 h at 800°C). The fresh CoZSM-5 catalyst gave a maximum NO conversion of approx. 70% at a reaction temperature of 450°C. At this temperature, total methane conversion was 80%, and the selectivity of methane reaction with NO approx. 45%. These data are consistent with literature reports of the performance of CoZSM-5 catalysts under similar conditions [5,11,13]. At higher temperatures, the NO conversion falls, as does the methane selectivity (although above 550°C, the methane conversion reaches 100% as the methane combustion increases). In comparison, the severely steamed CoZSM-5 catalyst showed a dramatically lower conversion of NO at all temperatures, and the temperature at which maximum activity was observed shifted to 500°C. These changes were mirrored by a corresponding decline in the selectivity for methane reaction with NO (although the total methane conversion decreased at lower temperatures, methane conversion remained complete at 550°C over the steamed catalyst). The fresh CoLaZSM-5 catalyst shows slightly lower NO con-

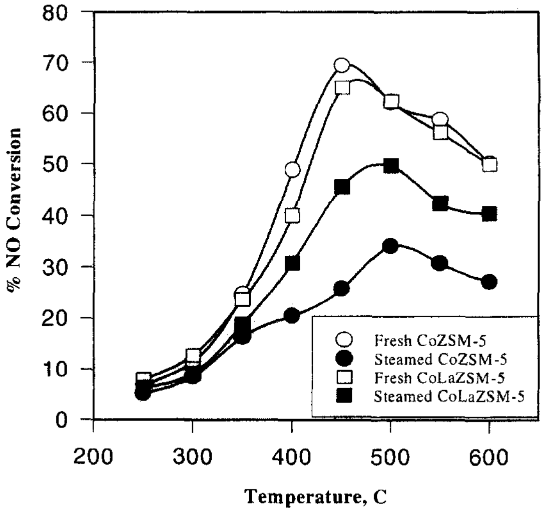

Fig. 1. NO conversion as a function of temperature over different catalysts.

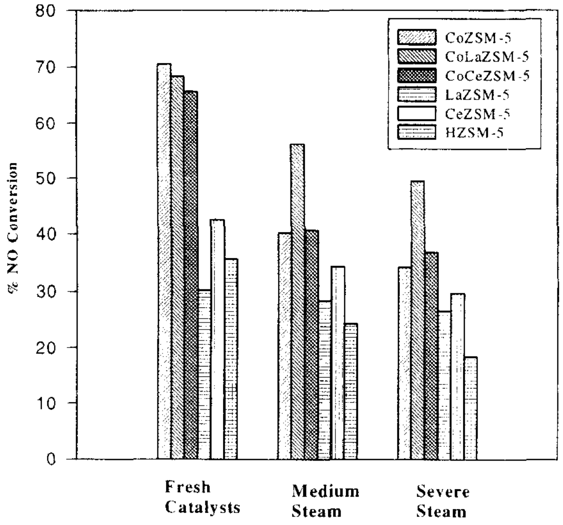

Fig. 2. Maximum NO conversions over different catalysts.

versions than the La-free catalyst, consistent with the reduced cobalt content; the methane selectivity is quite similar. The severely steamed CoLaZSM-5, however, gave NO conversions only slightly lower than the fresh catalysts (e.g., 50% conversion at 450°C compared with 65% at the same temperature for fresh catalyst). The methane conversions as a function of temperature were identical within experimental error for fresh and steamed CoLaZSM-5 catalysts; the lower NO conversions of the steamed catalysts are reflected in the methane selectivity. Catalysts, steamed less severely, showed correspondingly less dramatic changes in NO conversion. The stabilizing influence of La cations was still evident, however, in the data obtained with CoLaZSM-5 catalysts.

Fig. 2 shows the maximum NO conversions achieved for fresh, medium and severely steamed, HZSM-5, CoZSM-5, CoLaZSM-5, LaZSM-5, CoCeZSM-5 and CeZSM-5 catalysts, using the two standard steaming treatments. HZSM-5 shows some activity for NO reduction with methane [14], but this is reduced on steaming. The activity of fresh LaZSM-5 in the absence of Co is much lower than that for HZSM-5, while the activity of fresh CeZSM-5 without Co is slightly higher than that for HZSM-5. The maximum NO conversions achieved with CoLaZSM-5 exceeded those of CoZSM-5 after medium and severe steam treatment. Also shown in Fig. 2 are corresponding data for a CoCeZSM-5 catalyst; it can be seen that the presence of Ce has a slight influence only on the catalyst stability.

X-ray powder diffraction measurements showed that all of the catalysts studied in this work remained crystalline ZSM-5; i.e., the losses of activity on steaming are not caused by collapse of the zeolite lattice. The ^{29}Si NMR spectra of fresh CoZSM-5 catalyst exhibited a major signal at approx. 112 ppm with a higher field shoulder at 117 ppm which is due to Si(0Al) sites, and a lower field shoulder at 106 ppm due to Si(1Al) sites. As reported previously, steam treatment causes extreme lattice dealumination of HZSM-5, and the Si(1Al) signal is completely lost [15]. A similar loss of the Si(1Al) signal occurs for CoZSM-5 after severe steam aging, whereas for CoLaZSM-5 the Si(1Al) signal is still observed after steaming, although less intense than in the fresh catalyst. ^{27}Al NMR spectra confirmed that severe steam treatment caused dealumination; the CoZSM5 catalysts after steaming exhibit two signals at approx. 60 ppm due to tetrahedral aluminium and at approx. 0 ppm attributed to the extra lattice octahedral aluminium in the zeolite lattice. The extralattice aluminium signals were, however, absent in the steam-treated CoLaZSM-5 catalyst, suggesting that dealumination of the zeolite lattice occurs to a much lesser extent in the catalyst containing lanthanum. Extensive dealumination of the ZSM-5 lattice during steam treatment will destroy the ion-exchange capacity of the zeolite and should therefore alter the nature and location of Co species in the catalyst.

Fig. 3 shows EPR spectra of two catalysts; the fresh CoZSM-5 and CoLaZSM-5 catalysts and the same catalysts after severe hydrothermal treatment. All spectra show similar broad anisotropic signals characteristic of high spin Co^{2+} [16]. There is, however, a significant change in the shape of line of the signal obtained from the severely steamed CoZSM-5 catalyst, suggesting either a change in the coordination environment of the Co^{2+} or that some aggregation of Co has occurred, causing broadening of the signal. To investigate this situation further, Co*K*-edge EXAFS measurements were carried out on the fresh and severely steamed samples (Fig. 4). The fresh catalyst showed a single Co–O coordination shell at a distance of 0.205 nm and a coordination number of 5.6. On steaming, the coordination number was unchanged (5.8), but the Co–O distance shortened to 0.201 nm.

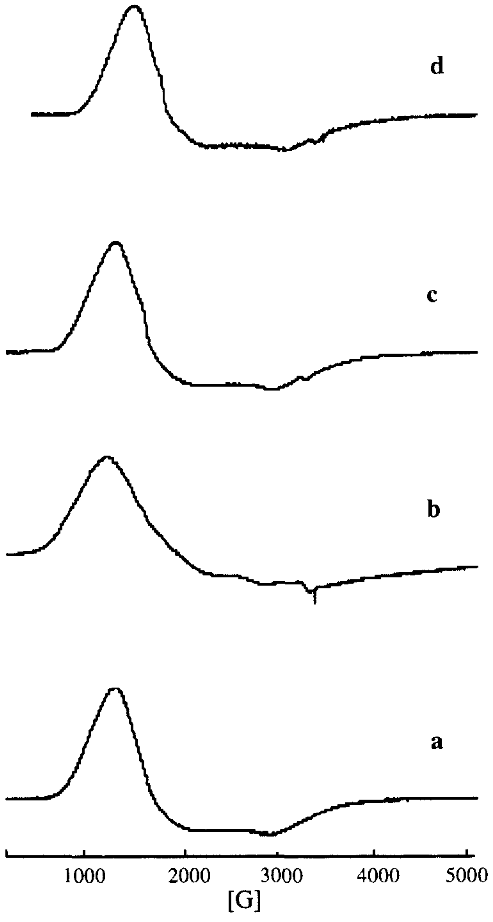

Fig. 3. ESR spectra of (a) fresh and (b) severely steamed CoZSM-5; and (c) fresh and (d) severely steamed CoLaZSM-5 catalysts, measured at 4 K.

Furthermore, no second shell Co–Co interactions were detected in the severely steamed catalyst, suggesting that there is no significant aggregation of Co species occurring (unlike the situation in severely steamed CuZSM-5 [9]). This conclusion is supported by XPS measurements which showed that there was no migration of Co towards the external surface of the zeolite on steaming. We suggest that Co in the severely steamed catalysts may be associated with extraframework aluminium species remaining in the zeolite pores, although we have no direct evidence for such association.

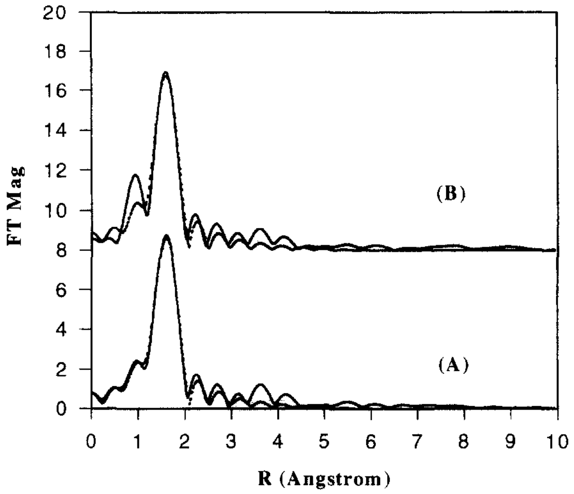

Fig. 4. FT-EXAFS of (A) fresh and (B) severely steamed CoZSM-5 catalysts: solid line – experimental and dotted line – fitted curves.

In contrast to the La-free catalysts, the Co^{2+} EPR signal obtained from the fresh CoLaZSM-5 catalyst was unchanged on severe steam treatment (Fig. 3), consistent with the observation that dealumination of the zeolite lattice is inhibited by the presence of La. The line shape of the signal obtained from both fresh and steamed CoLaZSM-5 does differ from that of the La-free catalysts, but it is unclear at this point whether that is due to a specific La–Co interaction.

FTIR spectra of adsorbed pyridine showed that there is a small concentration of residual Bronsted acid sites giving a band at 1545 cm^{-1} for the fresh metal exchange zeolite catalysts despite the high metal-exchange levels. It has been reported that in the case of HZSM-5, the Bronsted acid sites decreased dramatically upon steaming [15]. Steam treatment caused some small decrease in the residual Bronsted acid site density in CoZSM-5, but no significant differences were observed between the acidity measured by pyridine adsorption of CoZSM-5 and CoLaZSM-5 catalysts. Rare-earth exchanged large pore zeolites find wide application as hydrocarbon cracking catalysts. The role of the rare-earth cation in such cracking catalysts is twofold: to stabilize the zeolite by forming stable complexes with oxide ions in the sodalite cages, and to produce additional acid sites through hydrolysis of La^{3+} cations [17]. O'Connor et al. [18] have examined lanthanum exchanged HZSM-5 zeolites and concluded that lanthanum exchange reduces the number of strong acid sites in the zeolite as measured by ammonia TPD, without altering the available pore volume. Pre-exchange with La did not, however, reduce the concentration of Bronsted sites in CoZSM-5, suggesting that the stabilizing effect of La is not due to removal of acid sites where hydrolysis of the framework may be initiated. The failure of Ce to stabilize the catalysts suggests that a specific interaction of La with the zeolite is in some way responsible for the enhanced stability of CoLaZSM-5.

4. Conclusions

Steam induced lattice dealumination of CoZSM-5 zeolites is the primary cause of irreversible deactivation of these catalysts during NO_x reduction by methane in the presence of water. The resulting loss of ion-exchange capacity alters the coordination state of cobalt, rendering it inactive, although it remains dispersed through the zeolite pores.The presence of La inhibits the dealumination process and reduces the deactivation effects of steam. The mechanism of this stabilization requires further investigation.

Acknowledgements

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