Stabilization of CuZSM-5 NO_x reduction catalysts with lanthanum

P. Budi, E. Curry-Hyde [a] and R.F. Howe [1]

Department of Physical Chemistry and [a]*Department of Chemical Engineering, The University of New South Wales,*
Sydney 2052, Australia

Received 8 March 1996; accepted 17 June 1996

The effects of high temperature steam treatment on the activity and selectivity of CuZSM-5 catalysts for the selective catalytic reduction of NO with propene have been examined. Loss of activity and selectivity on steam treatment is due to framework dealumination of the zeolite, which causes migration of Cu out of the zeolite pores to the external surface. Pre-exchange of the zeolite with La^{3+} cations inhibits the dealumination, preventing migration of Cu to the surface and allowing the catalyst to retain high activity and N_2 selectivity after steam treatment. The deactivation of the catalysts was monitored using X-ray powder diffraction, magic angle spinning ^{27}Al and ^{29}Si nuclear magnetic resonance, X-ray photoelectron spectroscopy and ion scattering spectroscopy.

Keywords: CuZSM-5; lanthanum; DeNOx; XRD; NMR; XPS; ISS

1. Introduction

The selective catalytic reduction 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]. Iwamoto et al. first described the use of CuZSM-5 zeolite catalysts for the reduction of NO with propene [2,3] and showed that such catalysts could achieve high NO conversions and selectivities to N_2 at moderate reaction temperatures. Since that time the CuZSM-5 system has been widely studied; the 1995 review by Shelef summarizes the extensive literature [1].

A key issue in the practical implementation of CuZSM-5 catalysts for NO_x reduction in lean burning gasoline or diesel engine exhausts is catalyst durability. In particular, steam which is unavoidably present in combustion gases will irreversibly deactivate CuZSM-5 catalysts above a certain temperature [4–7]. At least two different modes of steam deactivation can be envisaged; structural collapse of the zeolite accompanied by agglomeration of the active component, or at lower temperatures hydrolysis of aluminium from the zeolite lattice, the resulting loss of cation exchange capacity also causing agglomeration or at least a modification of the active component. Infrared data of Bell et al. [6] suggest that steam deactivation may also be associated with enhanced coke formation in dealuminated catalysts. Matsumoto et al. [7] examined the durability of CuZSM-5 for NO_x reduction in a lean burn engine exhaust and concluded that steam deactivation is associated largely with a change in the nature of the Cu species, while Kharas et al. [4,5] attributed catalyst deactivation to the formation of an inactive CuO phase and disruption of zeolite crystallinity and porosity. All authors agree that the instability of CuZSM-5 in the presence of water vapour at high temperature greatly restricts the usefulness of this catalyst.

We have recently undertaken a detailed study of the dealumination of HZSM-5 zeolite catalysts under conditions of methanol conversion to hydrocarbons [8]. It was shown in that study that prolonged exposure to water vapour at temperatures as low as 370°C will cause extensive hydrolysis of lattice aluminium and loss of Brønsted acid sites. The extent of dealumination was more severe in higher aluminium content zeolites. In this case however, catalyst lifetime for methanol conversion is enhanced by steam pretreatment, since coke formation is inhibited by a reduction in the Brønsted acid site concentrations.

In the present study we have extended this approach to examine the steam deactivation of CuZSM-5 and other zeolite catalysts in the selective reduction of NO by hydrocarbons under oxygen-rich conditions. The approach taken has been to examine catalyst performance in a standard test protocol before and after various degrees of steam treatment, and to examine the catalysts with a battery of characterization techniques to determine how the nature of the catalysts is affected by high temperature steam. Full details of the characterization and steaming studies will be described elsewhere [9]; the purpose of this communication is to report that hydrolysis of aluminium from the zeolite lattice and resultant deactivation of CuZSM-5 catalysts by steam can be largely inhibited by pre-exchange of lanthanum ions into the zeolite.

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[1] To whom correspondence should be addressed.

2. Experimental

2.1. Catalyst preparation

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 forms by conventional ion exchange. HZSM-5 was then prepared by calcining NH_4ZSM-5 at 500°C for 6 h in flowing air. CuZSM-5 zeolites were prepared by ion exchange of NaZSM-5 with aqueous $Cu(NO_3)_2$ solution (0.01 mol ℓ^{-1}, no pH adjustment). The Cu loading was controlled by the number of ion exchange repetitions, and the zeolites then calcined in flowing air at 500°C. CuLaZSM-5 was prepared by successive ion exchange. NaZSM-5 was first ion exchanged with aqueous $La(NO_3)_3$ solution (0.01 mol ℓ^{-1}, no pH adjustment), calcined in flowing air at 500°C, then exchanged with aqueous $Cu(NO_3)_2$ solution and calcined again at 500°C. Similar procedures were followed for CuCeZSM-5. Chemical analysis of the zeolites was undertaken by ICP atomic emission spectroscopy; catalyst compositions are summarized in table 1.

2.2. Hydrothermal treatments

Hydrothermal treatment of catalysts was undertaken in a quartz fixed-bed microreactor. Typically 2 g of catalyst was placed in the reactor and heated to the desired temperature in flowing nitrogen. The nitrogen flow was diverted through a bubbler containing deionized water. The water vapour pressure was varied by altering the temperature of the bubbler; all gas lines were heated to prevent water condensation. Three different standard hydrothermal procedures were utilized, as summarized below:

mild: $T = 500°\mathrm{C}$, $p = 114$ Torr, $t = 10$ h
medium: $T = 500°\mathrm{C}$, $p = 114$ Torr, $t = 72$ h
severe: $T = 800°\mathrm{C}$, $p = 114$ Torr, $t = 24$ h

Table 1
Bulk and surface composition of catalysts

Catalysts	Si/Al bulk	RE/Al bulk	Cu/Si bulk	Cu/Si XPS
CuZSM-5				
fresh	17	–	0.036	0.025
severely steamed	17	–	0.036	0.087
LaZSM-5				
fresh	17	0.28	–	–
CuLaZSM-5				
fresh	17	0.12	0.025	0.018
severely steamed	17	0.12	0.025	0.031
CuCeZSM-5				
fresh	17	0.18	0.026	0.020
severely steamed	17	0.18	0.026	0.036

2.3. Catalytic measurements

Catalytic measurements were carried out in a quartz microreactor under steady state plugged-flow conditions. 200 mg of zeolite were pelletized, crushed and sieved to 60–80 mesh prior to loading in the reactor. Standard catalyst pretreatment consisted of heating the calcined zeolite under flowing He to 500°C, maintaining at this temperature for 1 h, then cooling to the desired temperature. The reaction mixture comprising NO (1000 ppm), C_3H_6 (1000 ppm), O_2 (2%), balance He, was flowed over the catalyst at 200 ml min^{-1} ($SV = 30000\ \mathrm{h}^{-1}$). Effluent gas was monitored by on-line gas chromatography (Shimadzu 14A, Porapak Q and Molecular sieves 5A columns, TCD detector) and NO_x chemiluminescence analyzer (model 9841).

2.4. Characterization

Zeolite catalysts were characterized before and after steam treatment by X-ray powder diffraction, X-ray photoelectron spectroscopy (XPS), magic angle spinning (MAS) ^{29}Si and ^{27}Al nuclear magnetic resonance (NMR), and ion scattering spectroscopy (ISS). X-ray diffraction measurements used a Siemens D500 powder diffractometer (Cu Kα radiation). ^{27}Al and ^{29}Si MAS NMR spectra were recorded on a Bruker MSL 300 spectrometer at 78.2 and 59.6 MHz respectively. ^{27}Al NMR spectra measurements used a 4 mm zirconia rotor with a spinning rate of 10 kHz, spectral width of 50 kHz, acquisition time of 0.02 s, pulse length of 1.0 μs (−15° pulse) and a pulse interval of 0.1 s. ^{29}Si NMR spectra measurements used a 7 mm zirconia rotor with a spinning rate of 2.5 kHz; single pulse Bloch decays were acquired with a spectral width of 10 kHz, acquisition time of 0.02 s, pulse length of 6 μs (90° pulse) and a pulse interval of 12 s. The ^{27}Al and ^{29}Si chemical shifts were referenced to kaolin as an external standard. XPS measurements were performed on pressed wafers of catalysts using a Kratos XSAM 800 instrument (Mg K αexcitation). Ion scattering spectroscopy was performed with a Perkin Elmer PHI 5500 instrument using 1 keV $^4He^+$ ions.

3. Results and discussion

3.1. Catalytic activity

After an initial break in period of 15 min, all zeolite catalysts gave stable NO conversions and product selectivities over a period of 90 min. For the purpose of comparing catalysts, conversions and product distributions after 90 min on stream were chosen. Fig. 1a shows NO conversion after 90 min on stream as a function of reaction temperature for two catalysts; the fresh CuZSM-5 catalyst, and the same catalyst after severe hydrothermal treatment (24 h at 800°C). The fresh catalyst gave a maximum NO conversion of ca. 80% at a reaction temperature of 400°C. At this temperature, total propene conversion was also 80%, and the selectivity of propene reaction with NO (plotted in fig. 1b) was 50%. These data are consistent with literature reports of the performance of CuZSM-5 catalysts under similar conditions [1,3,6]. At higher temperature, the NO conversion falls, as does the propene selectivity (although above 450°C the propene conversion reaches 100% as propene combustion increases).

In comparison, the severely steamed CuZSM-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 propene reaction with NO (although the total propene conversion decreased at lower temperatures, propene conversion remained complete at 500°C over the steamed catalyst). Very similar effects of steam treatment on NO conversion have been reported by Bell et al. [6] and Matsumoto et al [7]. Fig. 2 shows results of identical experiments carried out with CuLaZSM-5 zeolites. The fresh catalyst in this case shows slightly lower NO conversions than the La-free catalyst, consistent with the reduced copper content; the propene selectivity is closely similar. The severely steamed CuLaZSM-5, however, gave NO conversions only slightly lower than the fresh catalysts (e.g. 60% conversion at 450°C compared with 70% at the same temperature for fresh catalyst). The propene conversions as a function of

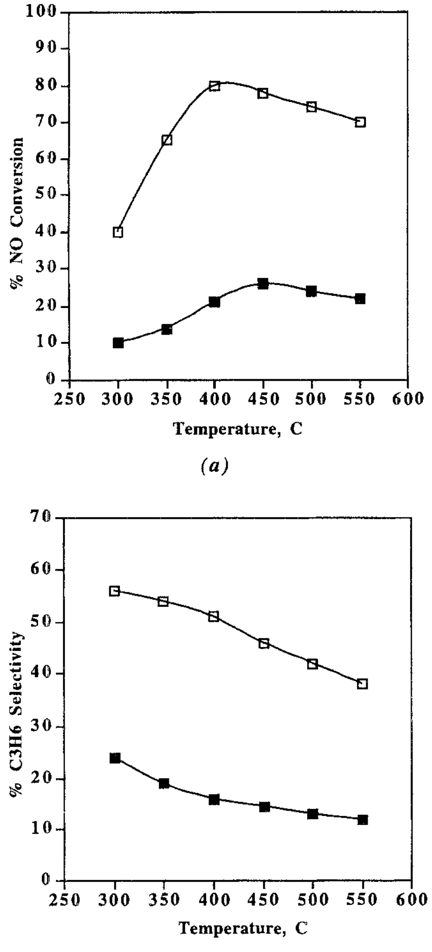

Fig. 1. (a) Steady state NO conversion data at different reaction temperatures for fresh (□) and severely steamed (■) Cu-ZSM-5. (b) Steady state propene selectivity data at different reaction temperatures for fresh (□) and severely steamed (■) Cu-ZSM-5. Propene selectivity was defined as propene consumed for NO reduction divided by total propene conversion (both reduction and combustion).

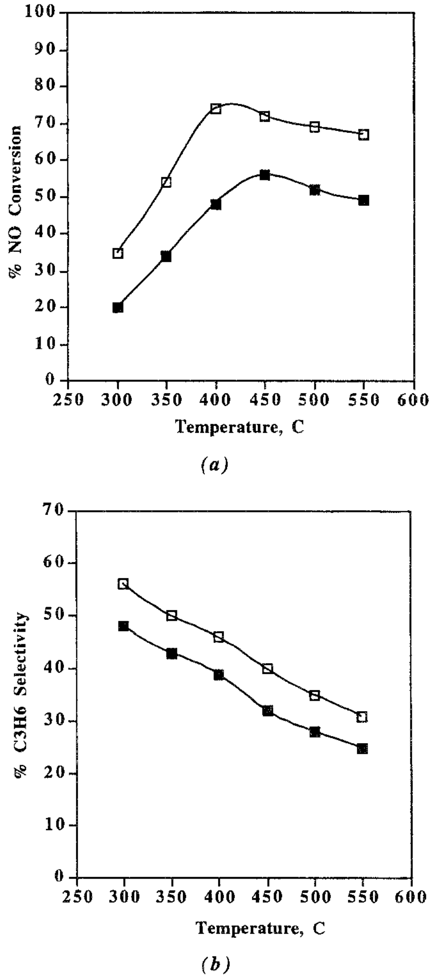

Fig. 2. (a) Steady state NO conversion data at different reaction temperatures for fresh (□) and severely steamed (■) CuLa-ZSM-5. (b) Steady state propene selectivity data at different reaction temperatures for fresh (□) and severely steamed (■) CuLa-ZSM-5. Propene selectivity was defined as propene consumed for NO reduction divided by total propene conversion (both reduction and combustion).

temperature were identical within experimental error for fresh and steamed CuLaZSM-5 catalysts; the lower NO conversions of the steamed catalysts are reflected in the propene selectivity curves plotted in fig. 2b.

Catalysts steamed less severely showed corresponding less dramatic changes in NO conversion. The stabilizing influence of La cations was still evident, however, in the data obtained with CuLaZSM-5 catalysts. Fig. 3 shows the maximum NO conversions achieved for fresh and steamed HZSM-5, LaZSM-5, CuZSM-5 and CuLaZSM-5 catalysts, using three different steaming treatments described in the experimental section. As reported previously by Hamada et al. [10], HZSM-5 shows some activity for NO reduction with propene, but this is reduced on steaming. The activity of fresh LaZSM-5 in the absence of Cu is lower than that for HZSM-5. The maximum NO conversions achieved with CuLaZSM-5 exceeded those of CuZSM-5 after moderate and severe steam treatment; the mild treatment had little effect on the activity of Cu-, La-, and CuLaZSM-5 catalysts. Also shown in fig. 3 are corresponding data for a CuCeZSM-5 catalyst; it can be seen that the presence of Ce has a slight influence only on the catalyst stability.

3.2. Catalyst characterization

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. Fig. 4 compares ^{29}Si NMR spectra of the HZSM-5, CuZSM-5 and CuLaZSM-5 catalysts before and after severe steam treatment. The major signal at −112 ppm with a higher field shoulder at −117 ppm is due to Si(0Al) sites, and the lower field shoulder at −106 ppm to Si(1Al) sites. As reported previously [8,11], steam treatment causes extreme lattice dealumination of HZSM-5, and the Si(1Al) signal is completely lost. A similar loss of the Si(1Al) signal occurs for CuZSM-5, whereas for CuLaZSM-5 the ^{29}Si spectrum is hardly changed by steam treatment. One difficulty with the use of ^{29}Si NMR spectra to determine the lattice aluminium content of zeolites is the possible contribution of Q_3 SiOH species to the −106 ppm signal [12]. Formation of such species during steam treatment may obscure the loss of lattice aluminium.

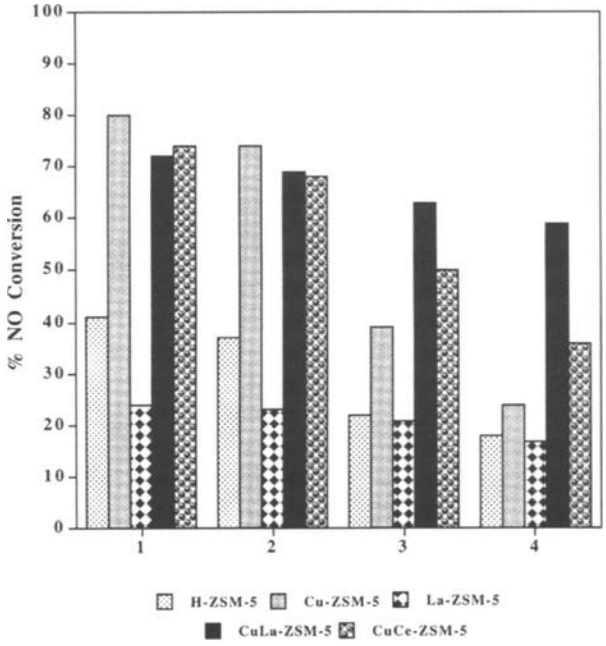

Fig. 3. Maximum NO conversion over: fresh (1), mildy steamed (2), moderately steamed (3) and severely steamed (4) $DeNO_x$ catalysts.

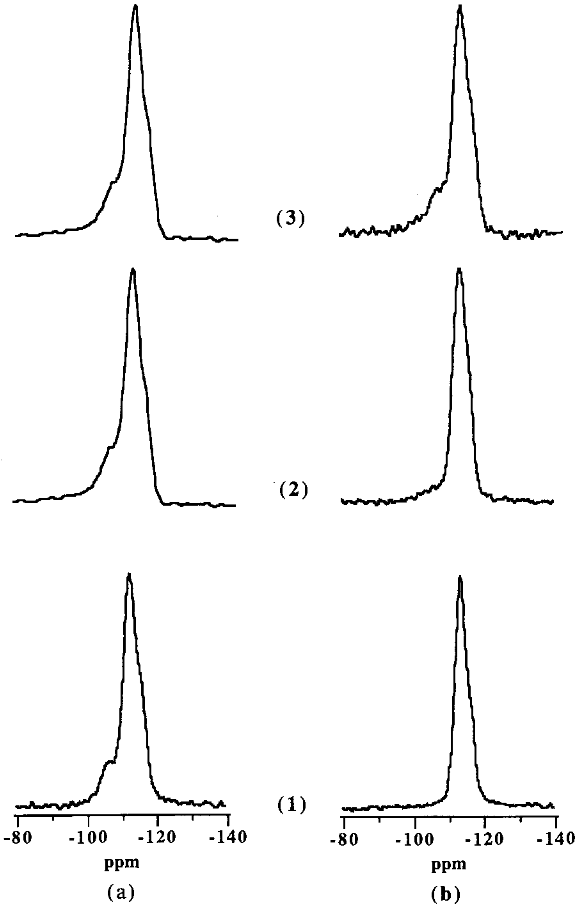

Fig. 4. ^{29}Si MAS-NMR spectra of fresh (a) and severely steamed (b) catalysts. (1) HZSM-5, (2) CuZSM-5, (3) CuLaZSM-5.

The corresponding ^{27}Al NMR spectra in fig. 5 show clearly that the extent of lattice dealumination is influenced by the presence of lanthanum. The fresh HZSM-5, CuZSM-5 and CuLaZSM-5 catalysts give a single ^{27}Al signal at 60 ppm due to tetrahedral aluminium in the zeolite lattice. Steam treatment of HZSM-5 at 800°C caused the appearance of two new ^{27}Al NMR signals at 0 ppm and ca. 30 ppm assigned respectively to 6 and 5 coordinate extralattice aluminium species [12]. The 30 ppm signal could not be resolved in the corresponding spectrum

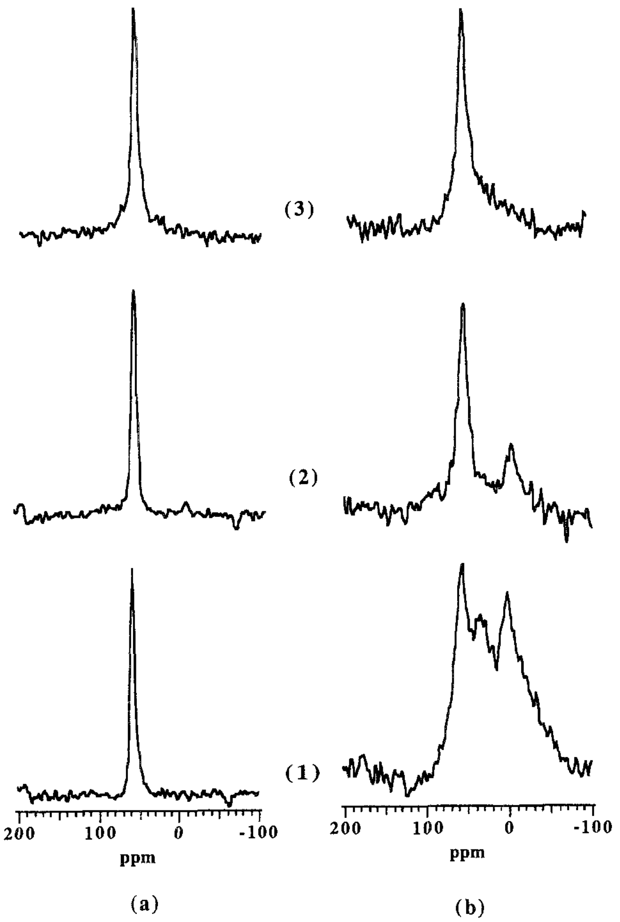

Fig. 5. ^{27}Al MAS-NMR spectra of fresh (a) and severely steamed (b) catalysts. (1) HZSM-5, (2) CuZSM-5, (3) CuLaZSM-5.

of steam treated CuZSM-5, and the relative intensity of the octahedral Al signal at 0 ppm in CuZSM-5 is only about half that of HZSM-5 after the same treatment. The most striking feature of the ^{27}Al spectra, however, is the almost complete absence of the extralattice aluminium signals in the steam treated CuLaZSM-5 catalyst, suggesting that dealumination of the zeolite lattice occurs to a much lesser extent in the catalyst containing lanthanum.

The CuZSM-5 result is contrary to that reported by Matsumoto et al. [7], who found no extralattice aluminium signals in ^{27}Al NMR spectra of steam treated CuZSM-5, and suggested that no serious dealumination occurred during steam treatment. They did, however, report a decrease in the intensity of the Si(1Al) ^{29}Si NMR signal on steaming, as also found here. The NMR visibility of extralattice aluminium does depend on the measurement conditions used and the extent of hydration of the sample. Extralattice aluminium is clearly produced in our experiments with CuZSM-5 steamed at 800°C.

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 Cu species in the catalyst. XPS measurements of the Cu : Si ratios for fresh and steam treated catalysts are given in table 1. For the fresh CuZSM-5 and CuLaZSM-5 zeolites the Cu : Si ratios measured by XPS are less than those corresponding to the bulk composition of the zeolites, indicating that the Cu concentrations in the outer 3 nm of the zeolite crystals sampled by XPS are lower than those in the interior. After steaming at 800°C the Cu : Si ratio measured by XPS for CuZSM-5 increases by a factor of 4, suggesting strongly that Cu has migrated towards the external surface of the zeolite crystals. There is a much smaller increase in the XPS Cu : Si ratio on steaming of the CuLaZSM-5 catalyst; in this case the ratio after steaming is still less than the value corresponding to the bulk composition.

Direct evidence for migration of Cu to the external surface the zeolite following steam treatment comes from ion scattering spectroscopy (ISS). The ISS technique identifies elements on solid surfaces by measuring the kinetic energy distribution of inert gas ions scattered inelastically from surface atoms; the energy loss by an inert gas ion on scattering depends on the mass of the surface atom encountered [13]. For zeolite samples, the technique will detect only those elements present at the external surface of the zeolite crystal. The 1 keV He^+ ion beam used to obtain these spectra causes negligible sputtering of the surface over time needed to record the data (5 min). The major elements presents on the surface are oxygen and silicon (the mass difference between Si and Al cannot be resolved by ISS); the fresh catalysts do show an additional small peak at the energy corresponding to Cu ($E/E_0 = 0.85$ at the scattering angle employed).

For the fresh CuZSM-5 catalyst, argon ion sputtering removes the very small Cu signal initially present (figs. 6a and 6b), suggesting it is due to excess Cu remaining on the external surface from the ion exchange. The steamed catalyst shows a dramatic increase in the Cu signal (fig. 6c). Absolute determination of the surface composition by ISS is not possible, since the scattering cross-sections of the elements present are not known. The relative intensity ratio $I_{Cu} : I_{Si}$ increased from 0.167 for fresh CuZSM-5 to 1.115 for the steamed sample. Argon ion sputtering reduced but did not remove (even after 30 min) the Cu signal from the steamed CuZSM-5, showing that excess Cu is present not only on the external surface but also in the outer regions of the zeolite crystals.

The corresponding experiments with CuLaZSM-5 are shown in fig. 7. The ISS spectra of fresh CuLaZSM-5 before and after argon sputtering are identical to those of fresh CuZSM-5 (figs. 7a and 7b). The steamed CuLaZSM-5 showed, however, almost no change in the Cu signal intensity, and argon ion sputtering removed the small Cu signal just as for the fresh catalyst (figs. 7c and 7d). The ISS results thus confirm the conclusion reached from XPS measurements that the presence of La inhibits migration of Cu to the external surface during severe steam treatment.

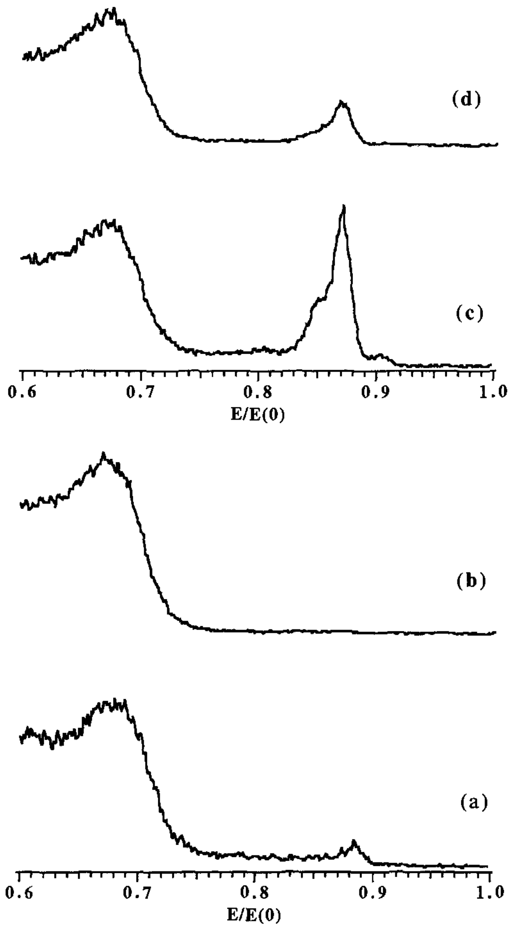

Fig. 6. $^4He^+$ ISS spectra of fresh and severely steamed Cu-ZSM-5 catalysts. (a) Fresh catalyst as measured, (b) fresh catalyst after 5 min argon sputtering, (c) steamed catalyst as measured, (d) steamed catalyst after 5 min argon sputtering.

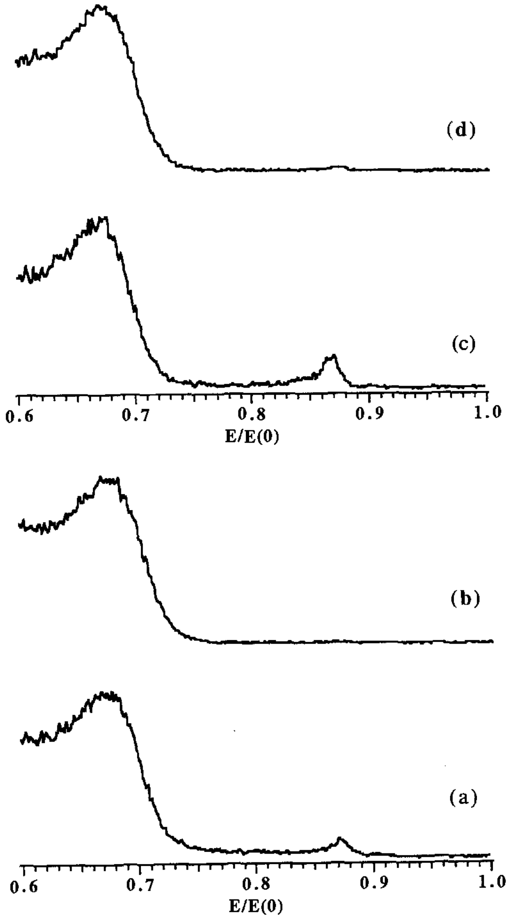

Fig. 7. $^4He^+$ ISS spectra of fresh and severely steamed CuLa-ZSM-5 catalysts. (a) Fresh catalyst as measured, (b) fresh catalyst after 5 min argon sputtering, (c) steamed catalyst as measured, (d) steamed catalyst after 5 min argon sputtering.

3.3. Role of lanthanum

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 [14]. O'Connor et al. [15] 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. The reduction in strong acid sites was accompanied by an increase in the number of weak acid sites similar to that found on sodium exchange.

The CuZSM-5 zeolites used in this work contain a small concentration of residual Brønsted acid sites, despite the high Cu exchange level [9]. If these sites provide the point of attack of water molecules in the steam induced dealumination of the zeolite (and the concentration of Brønsted acid sites is certainly reduced on steam treatment [9]), then a reduction in the concentration of the strong acid sites as a result of lanthanum exchange might explain the stabilization observed. However, a corresponding stabilization was not found in CuCeZSM-5 catalysts. Further investigation of the CuLaZSM-5 catalysts is in progress to determine more precisely the specific role of lanthanum.

3.4. Conclusions

Steam induced lattice dealumination of CuZSM-5 zeolites is the primary cause of deactivation of these catalysts during NO_x reduction by hydrocarbons in the presence of water. The resulting loss of ion exchange capacity forces migration of Cu to the external surface of the zeolite. The presence of La inhibits the dealumination process and enhances the catalyst lifetime; further study is needed to determine if this is due solely to loss of acid sites, or if the presence of La imparts additional stabilization of the lattice analogous to that found in RE-Y cracking catalysts.

Acknowledgement

The ISS measurements were carried out in the laboratory of Professor J.H. Lunsford, Texas A & M University. His hospitality and the experimental assistance of Dr. Dingjun Wang are gratefully acknowledged. Financial support for this project came from the Australian Research Council and AIDAB.

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