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Spectroscopic studies of the stability of zeolitic deNO$_x$ catalysts

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Abstract

Cu-ZSM-5 is considered for selective catalytic reduction (SCR) of NO$_x$ in streams with ca. 10% H_2O which causes dealumination and activity loss. Multivalent Co^{2+}, Ni^{2+}, Pd^{2+}, Cu^{2+}, Ga^{3+}, Al^{3+}, Fe^{3+}, La^{3+} and Ce^{3+} ions were tried as stabilizers. MAS-NMR of tetrahedral ^{27}Al was the dealumination yardstick. Information was also obtained from NMR of ^1H, ^{23}Na and ^{29}Si. Some ions, La^{3+} and Ce^{3+}, suppress the dealumination but samples containing the active Cu^{2+} and the La^{3+} are not as stable as singly modified materials and not more active in SCR than non-modified Cu-ZSM-5. The Cu^{2+} was monitored in-situ by ESR under flow-through conditions. Steaming at 650°C or calcination at 850°C irreversibly changes the co-ordination of all square-planar Cu^{2+}. By incorporating ca. 5 wt% of La or Ce, a part of the copper (20–30%) preserves the active square-planar Cu^{2+} co-ordination even after 0.5 h at 850°C. This is reflected in a higher ethane oxidation activity.

Keywords: NO$_x$; Stability; Zeolitic catalysts; Reduction

1. Introduction

Attempts to implement Cu-containing zeolite-based catalysts for treatment of combustion exhaust gases have been tried for 15 years but not yet implemented in practice [1]. One reason is low durability in hot combustion gas streams containing water [2]. Water vapor, often ca. 10% of the stream, may depress the activity but this is reversible. The catalysts deactivate irreversibly if a certain temperature is exceeded. At the higher end of the T-range the structural collapse of the zeolite is accompanied by loss of the Cu out of the lattice and its agglomeration. At lower T's, say ca. 500°C, dealumination, i.e., removal of the tetrahedral Al^{3+} ions from the zeolite lattice has been suspected. Dealumination causes loss of isolated cupric ions of a defined co-ordination because these ions replace the protons which neutralize the excess negative charge associated with Al^{3+}. The 'dislocated' ions migrate to the exterior of the crystallites forming agglomerated copper oxide. In Cu-ZSM-5 a part of the activity is irreversibly suppressed by dealumination while another part is quite resistant [3]. High-T calcination at 700–850°C also affects the co-ordination and activity of the Cu^{2+}-ions. The aim is to stabilize the catalytic centers without impairing activity. Introduction of certain ions into ZSM-5 can be used to inhibit dealumination by steam [4,5]. We followed the dealumination by MAS-NMR of several nuclei in the zeolite and the state of the active cupric ion by ESR. Recently, workers

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at Toyota [6] explored the stability of Cu-ZSM-5 using the same methods.

2. Experimental

2.1. Preparation of samples

Two zeolites were used. Alcoa Na-ZSM-5 was used because it exchanges easily. XRF analysis gave (on an O and H_2O-free basis): Na 3.9, Al 3.9, Si 92 wt%. corresponding to 15% excess Na, external to the lattice and $SiO_2/Al_2O_3 = 46$. The exchange was from nitrate solutions at pH 5.5 and 85°C. After contacting for 2 h, the material was cooled to ambient, filtered, washed with water, dried in air at 140°C for 2 h and calcined for 2 h at 500°C. The solid was then recontacted with the mother liquor and the procedure was repeated. The added ions included Fe^{3+}, Co^{2+}, Ni^{2+}, Ce^{3+}, La^{3+}, Pd^{2+}, Cu^{2+}, Ga^{3+} and Al^{3+} [7]. Samples containing both the active Cu^{2+} and the stabilizing La^{3+} were also made. The LaCu-ZSM-5 was prepared by taking the finished Cu-ZSM-5 and exchanging the residual Na^+ with La nitrate solution in a similar manner. CuLa-ZSM-5, where the order of ion introduction was reversed, was also prepared. The analysis shows that 20 to 45% of the Na remained after the exchange and that the atomic ratio of the introduced ions to the available Al sites, accounting for the residual Na, was ca. 1 for divalent modifiers and ca. 0.5 for the trivalent modifiers. The poor crystallinity of the Na-ZSM-5 was thought to, perhaps, have an adverse effect on the stabilization. Hence, samples from NH_4-ZSM-5 from P and Q Corp. ($SiO_2/Al_2O_3 = 50$) were made. This comprised Cu-ZSM-5, La-ZSM-5 and specimens containing both Cu^{2+} and La^{3+} introduced before or after the cupric ion. These catalysts were made by incipient wetness followed by drying and calcination as it was found that after 500°C calcination there is no difference between these methods. The Cu loading in the second series was lowered to 1% because we used these materials also for ESR which requires isolated cupric ions for unambiguous results.

2.2. Nuclear magnetic resonance

MAS-NMR spectra were collected on a Bruker MSL-300 spectrometer. High power decoupling and ^1H CP (cross polarization with protons) were employed in some cases. The rotors were spun at 4.0 kHz. For silicon this removed all spinning side-bands. The spinning side-band intensities of other elements were small and well separated from resonances of interest. Reference materials to specify the resonances were employed for each nucleus and the data could be correlated quantitatively. The TOSS (total suppression of sidebands) method was used to remove sidebands of the tetrahedral Al resonance which interfere with the observation of octahedral Al resonances.

2.3. Electron spin resonance

The description of the apparatus was given earlier [8]. The ESR signals of Cu^{2+} were registered in the field region 2300–3800 G in 2 modes: (1) 5 scans with a sweep time of 21 s; (2) 10 scans with a sweep time 42 s. Resonances for microwave power 0.64–6.41 mW were recorded to verify the lack of sample saturation.

2.4. X-Ray diffraction

To obtain the XRD patterns the samples were dispersed on a quartz crystal and mounted in a powder X-ray diffractometer (Scintag X-1) without binder. The samples were scanned from 4° to 80° 2θ using a step scan of 0.02° with a preset counting time of 2.0 s. A Cu X-ray tube ($K\alpha = 1.5406$) operated at 45 kV, 40 mA of incident radiation was used. The relative crystallinity for each zeolite was determined by integrating the area encompassing the 5 strong peaks in ZSM-5 from 22.5° to 25.0° 2θ and comparing the integrated areas to a standard, fully crystalline ZSM-5.

2.5. Catalytic activity

In SCR, a powder sample of 0.15 g was loaded into a quartz reactor onto a frit and covered by quartz wool. The reaction mixture of 5% O_2, 550 ppm NO, 1120 ppm C_3 hydrocarbon ($C_3H_6/C_3H_8 = 2$) and balance He flowed through the frit and then the catalyst. The total flow was 0.5 l/min, corresponding to about 30000 h^{-1} space velocity for a typical monolith catalyst. The reactor was heated in a furnace and the temperature was controlled by a program. The NO_x conversion was measured at 300–600°C while ramping the temperature up or down. The heating/cooling rate was 12°C/min. Three cycles were performed at each set of conditions. In ethane oxidation 0.1 g of the catalyst was placed in a quartz reactor and conditioned at 500°C in flowing dry air for 5 h. The activity was measured at 280–500°C and ethane conversions from 6 to 90% in a reaction mixture of 90.6% He, 8.4% O_2, 0.96% ethane, which corresponds to a ca. 2.5-fold excess of oxygen. The space velocity was 20000 h^{-1}.

3. Results

3.1. Crystallinity

The crystallinity of NH_4-ZSM-5 (90%) is higher than that of the Na-ZSM-5 precursor (67%) and La^{3+} stabilizes the structure of the latter. Calcination of doubly exchanged samples at 500°C sharpens the structure. The samples from both precursors are less stable after steaming at 650° or calcining at > 850°C with the crystallinity decreasing to 40–50%. The structural stability of exchanged ZSM-5 depends in a complex way on the initial crystallinity, the composition of the exchanged ions, the treatment and preparation conditions. There are parallels between the stability of tetrahedral Al^{3+} as measured by MAS-NMR, and the XRD data.

3.2. MAS-NMR

CYCLOPS (cyclically oriented phase sequencing) spectra of ^{27}Al were registered. A value of 100% was assigned to the integrated peak of Na-ZSM-5 for comparison with the other samples. The integration bounds were between 85 and 20 ppm. We could not observe the Al removed from the tetrahedral sites although octahedral Al was clear in CYCLOPS and TOSS spectra of γ-alumina and the chemical shifts in γ-alumina agreed well with literature. We postulate that the missing Al signal is either present as a very broad pedestal in the spectrum indicating a highly disordered, amorphous material or that the dealumination products are perhaps in a state where the NMR signal is quenched. Fig. 1 compares spectra of precursor Na-ZSM-5 before and after steaming and after calcining and steaming, showing the drop in the tetrahedral Al. Calcining in air at 650°C sharpens the signal, but does not prevent dealumination by steaming. Fig. 2 shows the stabilization of the tetrahedral Al, after steaming, by the most effective additives La and Ce. A large amount of

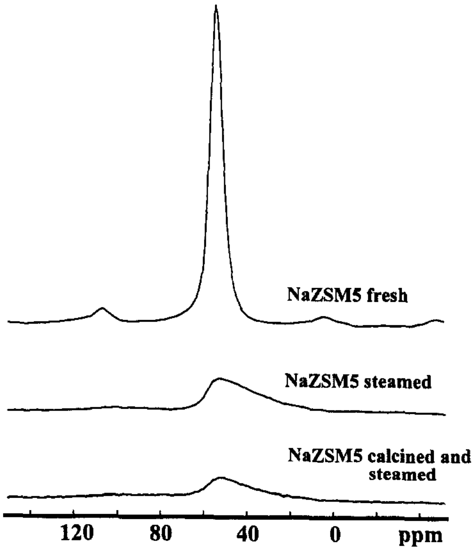

Fig. 1. ^{27}Al-MAS-NMR of Na-ZSM-5 precursor.

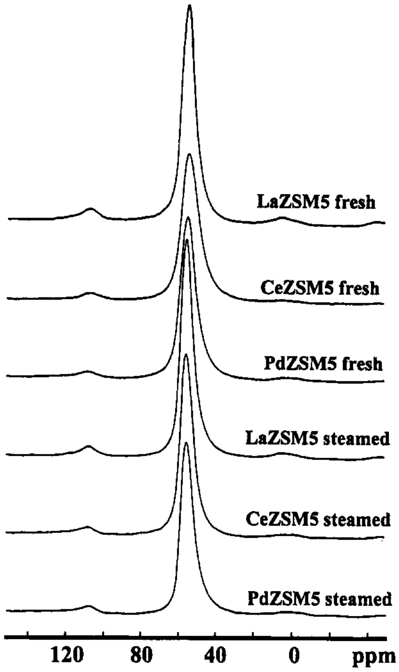

Fig. 2. ^{27}Al-MAS-NMR of fresh and steamed La-ZSM-5, Ce-ZSM-5, and Pd-ZSM-5 from Na-ZSM-5 precursor.

added Pd ions also stabilizes the tetrahedral Al. We have repeatedly noted that the exchange by Cu under slightly acidified conditions lowers the NMR ^{27}Al signal in a non-steamed material as compared with the precursor. Table 1 summarizes the results of the stabilization of the tetrahedral ^{27}Al by different ions.

Fig. 3 shows the ^{29}Si MAS-NMR of Na-ZSM-5 using both CYCLOPS and CP (cross-polarization) MAS. On the fresh sample the largest feature at -111 ppm represents the Q_4 site and the shoulder at -107 ppm represents a Q_4 site where one of the 2nd-nearest neighbors has been replaced by Al and its behavior mirrors that of the ^{27}Al peak in tetrahedral position. The feature at -100 ppm is a Q_3 site where the Si has a proton as a 2nd-nearest neighbor. All features in Na-ZSM-5 are strongly suppressed by steaming. This is corroborated by the CP MAS spectra which enhance the Q_3 signal by Si-proton CP. The CP MAS spectrum of the steamed Na-ZSM-5 also shows loss of all features. This material is very susceptible to steaming while in ZSM-5's with higher crystallinity the steaming affects the Si–O–Al linkages but not the majority of the Q_4 sites. Steaming of

Table 1
Relative intensities [a] of tetrahedral ^{27}Al-MAS-NMR signals

Sample	Treatment	^{27}Al
Na-ZSM-5	As received	100
Na-ZSM-5	Calcined	119
Na-ZSM-5	Steamed	44
Na-ZSM-5	Calcined/Steamed	46
Fe-ZSM-5	Fresh	86
Fe-ZSM-5	Steamed	43
Co-ZSM-5	Fresh	73
Co-ZSM-5	Steamed	82
Ni-ZSM-5	Fresh	112
Ni-ZSM-5	Steamed	86
Ce-ZSM-5	Steamed	105
La-ZSM-5	Fresh	111
La-ZSM-5	Calcined	121
La-ZSM-5	Steamed	115
Ga-ZSM-5	Fresh	101
Ga-ZSM-5	Steamed	66
Al-ZSM-5	Fresh	102
Al-ZSM-5	Steamed	82
Pd-ZSM-5	Fresh	104
Pd-ZSM-5	Steamed	97

[a] Intensities are referenced to fresh Na-ZSM-5.

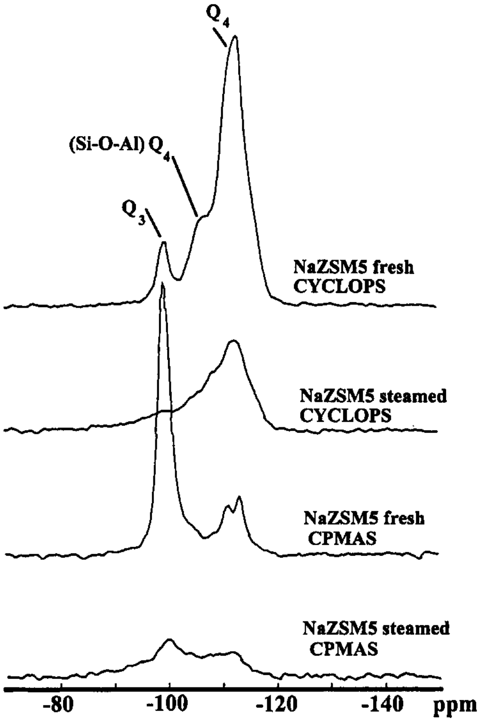

Fig. 3. ^{29}Si-MAS-NMR of Na-ZSM-5 precursor.

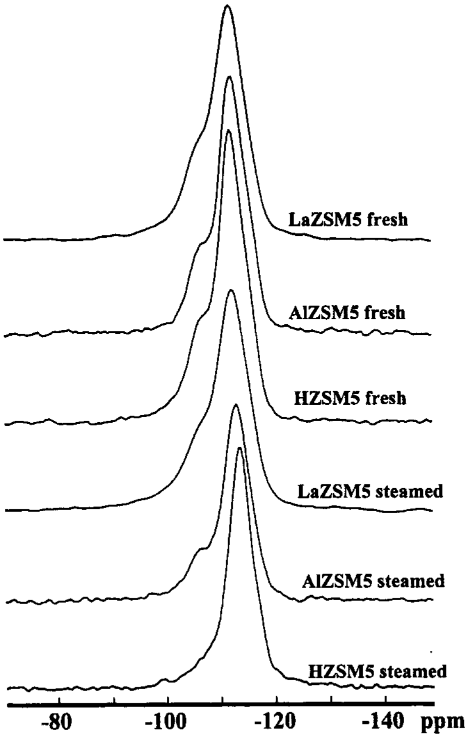

Fig. 4. ^{29}Si-MAS-NMR (CYCLOPS) of La-ZSM-5, Al-ZSM-5 and H-ZSM-5 from Na-ZSM-5 precursor.

substituted samples made from the Na-ZSM-5 precursors does not affect much the structural Q_4 sites. La ions or extra Al ions impede the destruction of the Si–O–Al linkages, i.e., dealumination (Fig. 4). The shoulder at -107 ppm associated with these linkages is absent in steamed H-ZSM-5 confirming stabilization by La noted in the ^{27}Al-MAS-NMR spectra. The integrated intensities of the Si signal indicate that La-modified -ZSM-5 best retains the structure. Table 2 gives the extent of stabilization of the ^{29}Si-MAS-NMR signal by La and excess Al. The NMR of ^{29}Si proves that La stabilizes the structure very effectively. To summarize, data for both nuclei, ^{27}Al and ^{29}Si, show stabilization, after steaming, of tetrahedral Al by additive ions, in particular, La and Ce. The crystallinity and ^{29}Si-MAS-NMR data show that the structure of the zeolite is stabilized as well.

Table 2
Relative intensities [a] of ^{29}Si-MAS-NMR signals

Sample	Treatment	^{29}Si (CP)	^{29}Si (CYCLOPS)
Na-ZSM-5	As received	100	100
Na-ZSM-5	Steamed	54	62
La-ZSM-5	Fresh	100	100
La-ZSM-5	Calcined	114	90
La-ZSM-5	Steamed	137	94
Al-ZSM-5	Fresh	100	100
Al-ZSM-5	Steamed	77	76

[a] Intensities of the treated samples are referenced to those of the fresh samples.

The ^{27}Al-MAS-NMR spectra of doubly exchanged ZSM-5 by Cu and La from Na-ZSM-5 show that the presence of Cu decreases the stabilization by La whether introduced before or after. Notwithstanding the higher crystallinity of NH_4-ZSM-5 and avoidance of acidic conditions, the stabilization of tetrahedral Al by La was lower than in samples from Na-ZSM-5. The stabilization of the tetrahedral Al in samples containing both Cu and La, after calcination or steaming is independent of the sequence of preparation and quite close to that registered before in samples from the Na-ZSM-5 precursor. Clearly, the simultaneous presence of the active Cu^{2+} and the ion La^{3+} impedes the effect of the latter on the stability of the Si–O–Al's.

Additional information is gained from ^{1}H-MAS-NMR. Several distinct protons are observed: terminal silanol protons at 1.2 ppm, Lewis acids from AlOH terminal hydroxyls at 3–3.5 ppm, Brønsted acids from bridging Si(OH)Al groups at 3.9–5.6 ppm, and protons from residual NH_4+ at 7.0–7.5 ppm. La addition affects the silanol and ammonium protons and promotes formation of Brønsted-like protons. Copper addition eliminates the silanols and broadens the ammonium proton resonance but does not eliminate it. Steaming of the Cu-exchanged sample also promotes the formation of Brønsted-like sites and the removal of residual NH_4^+. The spectra from the doubly promoted samples exhibit very broad resonances.

3.3. SCR activity

The SCR activity is compared in Table 2 with or without 10% H_2O in the stream. Calcination of samples from the NH_4-ZSM-5 was at 850°C for 1 h after ESR showed that this causes the Cu-ions to interact with the ZSM-5 framework. The activity measurement was reproducible without hysteresis when going up or down the temperature scale. Fig. 5 shows the effect of 10% H_2O on fresh Cu-ZSM-5 made from Na-ZSM-5. About half of the NO_x conversion is suppressed in comparison with dry conditions. After H_2O removal the activity recovers, i.e., the transient deactivation is associated with the co-ordination/adsorption of H_2O at reaction conditions. After steaming at 650°C the NO_x conversion, in the absence of water, is close to that on the fresh sample in the presence of 10% water. Water has little effect on NO_x conversion on the steamed sample. Thus, pre-steaming suppresses the same active centers that are reversibly deactivated by the transient presence of water. These vulnerable sites account for ca. 1/2 of the fresh activity and are associated with the square-planar configuration. Similar trends were noted in samples stabilized by La made from either precursor. Results for samples made from Na-ZSM-5 are shown in Table 3. The addition of La to Cu-ZSM-5 slightly improves the SCR activity of the fresh sample in a wet reaction stream but has no effect on the steamed sample either in a dry or wet stream.

Table 3
SCR NO_x conversion on catalysts prepared from Na-ZSM-5 precursor

Sample	State	H_2O (vol%)	T_{max} (°C)	Max. NO_x conv. (%)
Cu-ZSM-5	Fresh	0	430	73
		10	450	40
	Steamed	0	560	37
		10	480	35
CuLa-ZSM-5	Fresh	0	440	74
		10	460	46
	Steamed	0	530	15
		10	500	23
LaCu-ZSM-5	Fresh	0	440	74
		10	470	58
	Steamed	0	530	35
		10	460	35

The SCR activity of the sample where the La was introduced first is even more affected by steaming than the unmodified Cu-ZSM-5. For materials made from the NH_4-ZSM-5, the initial activity was somewhat lower and the Cu-ZSM-5 was more susceptible to steaming. Introduction of La, either before or after Cu, did not protect the 'fragile' sites and the activity of the steamed samples was the same in dry and wet streams. Thus, the overall effect of the stabilization of the Cu-ZSM-5 after steaming is small and the

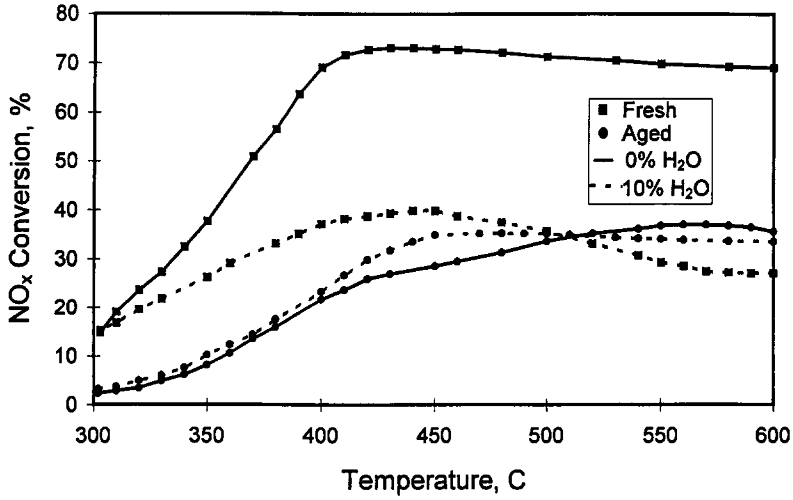

Fig. 5. Effect of H_2O on NO_x conversion over fresh and steamed Cu-ZSM-5 from Na-ZSM-5.

sensitivity of the more active fraction of the sites to steaming was not changed.

3.4. ESR studies

It was shown earlier that ESR monitors the isolated copper ions in Cu-ZSM-5. At 1% Cu in zeolites with the Si/Al ratio used in this work, the ESR signal is associated with all the Cu^{2+} present [8]. The isolated cupric ions preserve their oxidation state up to 500°C in the absence of hydrocarbons (or hydrogen) and in the presence of other polar and non-polar molecules. Here, ESR is used to follow the changes in the environment of the Cu^{2+} ion when steam-aged at 650°C or calcined up to 900°C in the absence/presence of a stabilizing additive. In the absence of stabilizers in Cu-ZSM-5 such treatments induce changes in the co-ordination of the cupric ion without agglomeration or encapsulation of the cupric ion [9]. Treatment in air up to 550°C for 4 h does not alter the ESR spectrum which changes only at T_{calc} = ca. 650°C. Stepwise heating in air at 750 and 800°C for 1 h and 900°C for 0.5 h induces a progressive change but without a decrease in the integral signal intensity. A decrease becomes measurable upon ≥ 1 h calcination of the sample at 900°C. Since the transformation, below 850°C, of the Cu^{2+} environment is not accompanied by a measurable intensity drop, all the Cu^{2+} ions remain isolated. This transformation is irreversible by re-hydration under hydrothermal conditions. The transformed sites behave differently in chemisorption and reduction. They do not adsorb NO, are not reduced by propene at ambient temperatures and are partially resistant to reduction even at 500°C. These observations are identical to those of Tanabe et al. [6]. While these authors maintain that the transformations are due to dealumination, we think that they occur before dealumination and are due to rearrangement of the local topography of the isolated Cu^{2+} sites. We interpret the transformation as a treatment-induced bonding change between the isolated Cu^{2+} ions and framework oxygens. These oxygens are linked in turn to the Al^{3+} ions. Such hypothetical elements of the structure are a part of the zeolitic framework but flexible enough to change symmetry upon additional ligand bonding. The high-T treatment irreversibly alters these elements. It is plausible that the loss of catalytic activity of CuH-ZSM-5 after treatment in the presence of steam, or even in its absence at higher T's, may be associated, in part, with the changes in the local topography of the isolated Cu^{2+}.

It was noted that the exchange of H^+ by Cu^{2+} in H-ZSM-5 has a small but observable stabilizing effect on the tetrahedral ^{27}Al-NMR signal after high-T steaming [3]. This is corroborated by ESR when comparing two steam-aged CuH-ZSM-5 samples differing by the sequence of the preparation steps: the first one was exchanged with copper and then steam-aged at 650°C; in the second case the pure H-ZSM-5 was steamed and then exchanged with copper. The ESR intensity of the first sample is 15 times higher. Thus the steaming of the H-ZSM-5 causes an almost total destruction of framework Al-sites where the isolated Cu^{2+} cations may be exchanged. The introduction of the Cu^{2+} before steaming preserves a part of these sites from total destruction, and only a transformation in local topography takes place. We examined by ESR samples containing copper and one other cation, La or Ce. Comparisons of spectra from samples containing Cu and La (1 or 5%) with those of Cu-ZSM-5 show their coincidence within experimental error. Here also, all the cupric ions in La-modified samples remain isolated and contribute to the signal. This is significant for the high-La sample, 1.06%Cu/5.4%La-ZSM-5, where the La^{3+}-ion was introduced ahead of Cu. It demonstrates that copper impregnated into 5.4%La-ZSM-5 migrates into the zeolite and occupies cationic positions during calcination, i.e., La does not block redistribution of Cu^{2+}.

In Cu-ZSM-5, ESR shows ions in two discrete coordinations, square-planar and square-pyramidal, in equal proportions. La, at the level

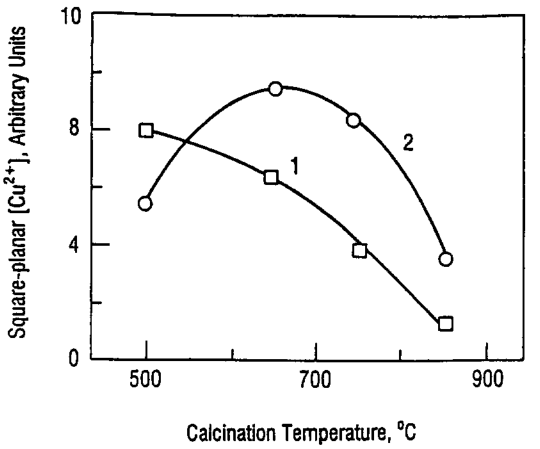

Fig. 6. Change in the relative concentration of the square-planar Cu^{2+}-ions after calcination of (1) 1.27%Cu-ZSM-5; (2) 1.06%Cu/5.4%LaH-ZSM-5.

of ca. 1%, does not change the coordination of the isolated Cu^{2+} ions in the zeolite. The ESR of 0.92%Ce/Cu-ZSM-5 calcined a 500°C for 5 h is also identical to the signal from Cu-ZSM-5. However, the sample with high La, 1.06%Cu/5.4%La-ZSM-5, differs in Cu^{2+} coordination from the other samples. The same two types of Cu^{2+} coordination are present but their ratio is different: the ratio of square-planar to square-pyramidal cupric ions decreases to ca. 30/70. The large amount of La in this sample influences the coordination of Cu^{2+} ions but not the number of isolated cupric ions. This points to modification of the local crystal field of the cupric ions by La. Calcination at 750°C lowers the concentration of square-planar Cu^{2+} in both the mono-cationic Cu-ZSM-5 and in 1%La/Cu-ZSM-5 but in 1%Cu/5.4%La-ZSM-5 the number of square planar cupric ions increases. Fig. 6 relates the calcination temperature and the concentration of the square-planar cupric ions. After calcination at 500°C the latter is higher for the mono-cationic sample but it falls monotonically with treatment T; addition of 5.4% La causes an increase in square-planar Cu^{2+} ions after treatment at 650°C but hotter treatment causes a gradual drop. Even after treatment at 850°C the sample with 5.4 wt% La retains 20-30% of square-planar Cu^{2+}. High La attenuates the high-T rearrangement of Cu^{2+} sites as compared with monocationic Cu-ZSM-5. Modification of Cu-ZSM-5 by 5 wt% Ce has a similar effect.

3.5. *Catalytic activity in ethane oxidation*

This reaction on pure H-ZSM-5 and 5.4%La-ZSM-5 is negligible up to 500°C. The active samples selectively catalyze complete oxidation. We extrapolated all the data by the Arrhenius equation to 330°C, at low conversion values, and plotted the specific activity vs. the stepwise T_{calc} for Cu-ZSM-5 and Cu/La-ZSM-5. The activity after calcination at 500°C is higher for the mono-cationic sample but it falls to a very low value with T_{calc}. For the sample with 5.4 wt%, La the activity rises initially with T_{calc} and a more severe calcination depresses the activity, but even after treatment at 800°C the 1%Cu/5.4%La-ZSM-5 specimen retains activity which exceeds that of the corresponding Cu-ZSM-5 by ca. 25. The activity follows closely the relative concentration of square-planar Cu^{2+} shown in Fig. 6. The effect of 5% Ce is not as pronounced but observable. After treatment at 800°C the activity of 1%Cu/5%Ce-ZSM-5 exceeds that of non-promoted Cu-ZSM-5 by a factor of ca. 10. The results confirm once more that the square-planar Cu^{2+} has high activity in the absence of water.

4. Conclusions

The activity drop of Cu-ZSM-5 under oxidizing atmospheres depends on many factors. In poorly crystallized materials steaming at high-T destroys not only the Si–O–Al linkages but collapses the structure. Dealumination by steam is likely initiated at protonic sites and the replacement of these by other ions, rare earths in particular, inhibits the dealumination. Trivalent ions do not exchange easily into the protonic sites in materials of high Si/Al ratio. The replacement of some protons by Cu itself inhibits somewhat the dealumination as observed both by MAS-NMR of ^{27}Al and ESR of Cu^{2+}. The presence of both Cu and La is less effective in inhibiting the dealumination by steaming than that of La only.

The La-stabilized Cu-ZSM-5 has no SCR activity advantage after steaming at 650°C. The active sites which are removed by steaming are the ones blocked by H_2O in the gas. High-T calcination induces an irreversible rearrangement of the square-planar Cu^{2+} into surface moieties which do not chemisorb NO and are not easily reduced by hydrocarbons. The rare-earth modifiers, La and Ce, attenuate this rearrangement during calcination. This stabilization of Cu^{2+} topography in ZSM-5 and of the Si–O–Al linkages by rare earth modifiers is not fully understood at present. The loss of catalytic activity in ethane oxidation under dry conditions of either Cu-ZSM-5 or Cu/La-ZSM-5 after high-temperature treatment correlates with the loss of the isolated Cu^{2+} sites located in the most reactive square-planar coordination.

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