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Selectivity effects of a new aluminum species in strongly dealuminated USY containing FCC catalysts

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We have hydrothermally prepared and characterized a catalytically active tetrahedral aluminum species in faujasite distinct from the normal framework aluminum. The new tetrahedral species is formed after a severe steam dealumination at 830°C and is characterized by a ^{27}Al MAS NMR shift of about 53 ppm compared to the 60 ppm shift observed for framework tetrahedral aluminum. DRIFTS experiments show that the 53 ppm species is associated with a Lewis rather than a protonic site. This species is associated with strong acidity and poor cracking selectivity compared to a conventional dealuminated faujasite at the same unit cell size. This site is very active and makes large amounts of gas and coke with poor gasoline selectivity compared to typical commercial FCC catalysts. After an appropriate sequence of hydrothermal dealumination and controlled pH washing steps, the 53 ppm species is the only species observed by NMR.

Keywords: Lewis site; tetrahedral; strong acidity; DEALY; faujasite; pyridine DRIFTS; ^{27}Al NMR; cracking; coke

1. Introduction

The activity of FCC catalysts is due primarily to faujasite, the zeolitic component. Deactivation of the FCC catalyst in the regenerator results in changes in the zeolite structure. It is well known that the zeolite can dealuminate as well as lose crystallinity. As the zeolite dealuminates, a variety of aluminum species are formed, some of which may have activity or may influence the selectivity of the catalyst. The occurrence of nonframework octahedral and pentacoordinate species with NMR ^{27}Al chemical shifts of ~ 0 and ~ 30 ppm is well known [1]. More recently, experiments have also demonstrated the existence of a tetrahedral aluminum species with a ^{27}Al MAS NMR shift of 53–54 ppm [2,3], lower than the 60 ppm shift observed for the framework species, but similar to shifts observed for framework species in beta and MFI zeolites. This species has been associated with superacidity and with an IR band at 3610 cm^{-1} [4] as well as with poor gas and coke selectivity [2,5]. Previous preparations of faujasite containing this species were obtained by dealumination with $SiCl_4$. Under these conditions there is the possibility that the species is formed by a secondary reaction between the $SiCl_4$ and the alumina removed from the zeolite during the dealumination. If this species is also formed during hydrothermal dealumination, then some of the changes in selectivity associated with further hydrothermal dealumination of low unit cell size faujasite (DEALY) may be a product of an acidic aluminum structure associated with the 53 ppm tetrahedral peak observed by ^{27}Al MAS NMR. These changes include increased coke and hydrogen and reduced gasoline selectivity associated with unit cell sizes below 2.427 nm. Since DEALY is in wide commercial use as the active component in cracking catalysts, hydrothermal deactivation mechanisms for this material are of significant interest, especially if the species formed as a result of the deactivation degrade selectivity.

In this paper we describe the preparation and characterization of a hydrothermally dealuminated faujasite containing predominately this species. The species is associated with a ^{27}Al chemical shift of 53 ppm and is a Lewis site. Catalysts containing these zeolites make large amounts of gas and coke and have poor gasoline selectivity compared to typical commercial FCC catalysts.

2. Experimental

The zeolites used in this work were prepared by repeated steam calcination with subsequent washing at a controlled pH to remove nonframework alumina without damaging the framework. The steam calcined zeolite was slurried with a ~ 10% ammonium sulfate solution. The pH was adjusted to 2.9 with sulfuric acid at 80°C and maintained for about 30 min. The sample was filtered, washed with hot water and dried. The zeolite samples listed in table 1 as well as the catalysts containing zeolites were characterized by crystallinity and unit cell size using standard XRD methods ASTM D-3906 and D-3942. ^{27}Al MAS NMR spectra were obtained on a Bruker instrument operating at a frequency of 104.263 MHz using a 2 μs pulse and a pulse delay of 100 ms. DRIFTS spectra were obtained on a Nicolet instrument at room temperature under a helium blanket. The sample was heated at 500°C in vacuum for 2 h, flowing pyridine was adsorbed at 150°C for 1 h, and the sample was evacuated at 200°C for 1 h before the spectra were taken.

Catalysts were prepared by mixing the zeolite with clay and an alumina chlorohydrol sol, drying, and grinding the dried material to a coarse powder. The catalyst contained 35% zeolite, 15% binder, and 50% clay. Activities and selectivities were measured as described in ASTM D-3907 and 4 C/O, 30 WHSV, and at a reactor temperature of 527°C. The effluent from the test run was analyzed by gas chromatography. The gas was collected in a gas bag and analyzed using an HP 5890 gas chromatograph equipped with a FID and a Poropack 7518 column. The liquid was analyzed by simulated distillation using a Supelco SP-2100 column on a HP 5880

Table 1
Properties of dealuminated zeolites

	Zeolite sample						
	USY	1	2	3	4	5	6
calcination (°C)		540	–	815	815	815	840
calcination time (h)	–	2	–	6	6	6	6
wash	no	no	yes	yes	yes	yes	yes
analysis							
%Na_2O	0.83	0.83	0.29	0.04	0.02	0.03	0.04
%Al_2O_3	23.61	23.61	17.45	6.45	4.04	3.26	2.86
%SiO_2	71.25	71.25	82.32	93.41	95.77	94.49	96.94
%Xtal	103	79	97	86	83	91	86
#Al/uc (chem)	51.9	51.9	34.9	14.4	9.1	7.5	6.0
^{27}Al NMR shift	–	–	–	60.7	56.2	53.9	53.0
uc (nm)	2.462	2.450	2.454	2.433	2.426	2.426	2.425
#Al/uc (XRD)	49.5	35.7	33.2	10.7	3.2	3.2	2.1

gas chromatograph. The selectivity and the activity of the catalyst was measured by a GC analysis of the product obtained from a standard microactivity testing unit.

3. Results

The preparation of the zeolites used in this work is summarized in table 1. A sample of steam dealuminated Y zeolite with the composition given was washed and steamed six times in succession ending in a final wash. The calcination procedure removes aluminum from the framework, and the washing procedure removes most of the nonframework alumina. The unit cell size of the faujasite may appear to increase slightly after washing. The framework aluminum content of the zeolite before washing (sieve sample No. 2, table 1) is estimated using the Breck correlation [6]. The framework aluminum content of the lower unit cell size washed (decationated) zeolite samples are estimated from the unit cell size using another recently developed correlation [7]. Both results agree well with the chemical analysis of the washed zeolite. The agreement indicates that the washing procedure removes most of the nonframework alumina but does not affect the framework. The washing procedure was repeated after each of the subsequent calcinations described in table 1.

After each washing the samples were analyzed and the species of alumina present was characterized by ^{27}Al MAS NMR. In each case after washing only the tetrahedral alumina peak is observed, fig. 1. The washing removes octahedral and pentacoordinated alumina responsible for peaks in the 0 and 30 ppm chemical shift region which would otherwise overlap with the peak in the tetrahedral region and

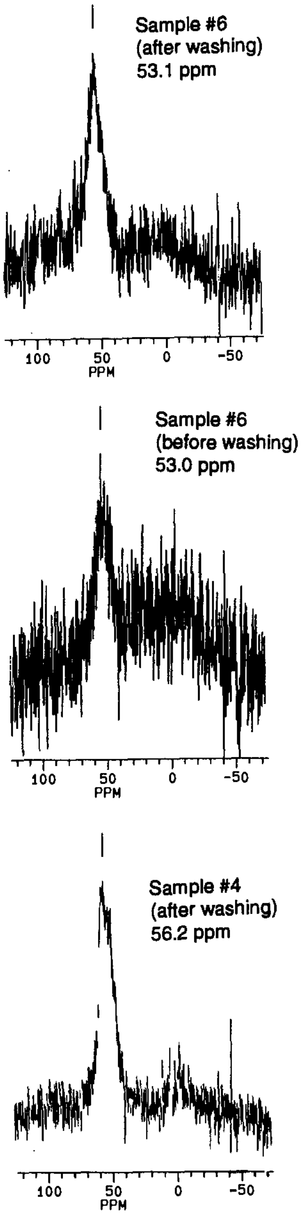

Fig. 1. ^{27}Al MAS NMR spectra of dealuminated faujasite samples from table 1. Included are (a) sample 4, (b) sample 6 before washing, and (c) sample 6 after washing.

make the measurement of the shift more difficult. Multiple aluminum species also can confuse the assignments of the pyridine DRIFTS spectra since other alumina species can be associated with Lewis acidity. The chemical shifts of the observed peak for each sample listed in table 1 show a progressive decrease with further calcination indicating a change in the character of the aluminum present. Although

NMR intensities cannot be used to measure in a quantitative way the amounts of the different aluminum species present, a systematic loss in intensity and the movement of the chemical shift to lower values indicates that the framework tetrahedral aluminum at ~ 60 ppm is progressively removed until it disappears. The ^{27}Al NMR spectra also show the occurrence of small amounts of other forms of nonframework alumina. After the final calcination/wash the tetrahedral peak appears with a low intensity at a chemical shift of 53 ppm. At this stage the zeolite is present in a highly crystalline form, about 90% crystallinity. Of the ~ 3% aluminum measured by chemical analysis, the only species observable by ^{27}Al NMR is in the 53 ppm form.

Diffuse reflectance spectra of adsorbed pyridine were obtained on the dealuminated zeolite samples Nos. 4, 5, and 6 of table 1. These spectra are shown in fig. 2. After calcination at 815°C and subsequent exchange, the sites formed on zeolites 4 and 5, table 1, were of primarily protonic character, at least after rehydration. However, the site formed after the higher temperature calcination did not rehydrate, zeolite sample No. 6. After the final calcination at 840°C and the subsequent washing the spectrum showed an increase in the relative intensity of the peak associated with Lewis sites [4]. The increase in intensity is either associated with an

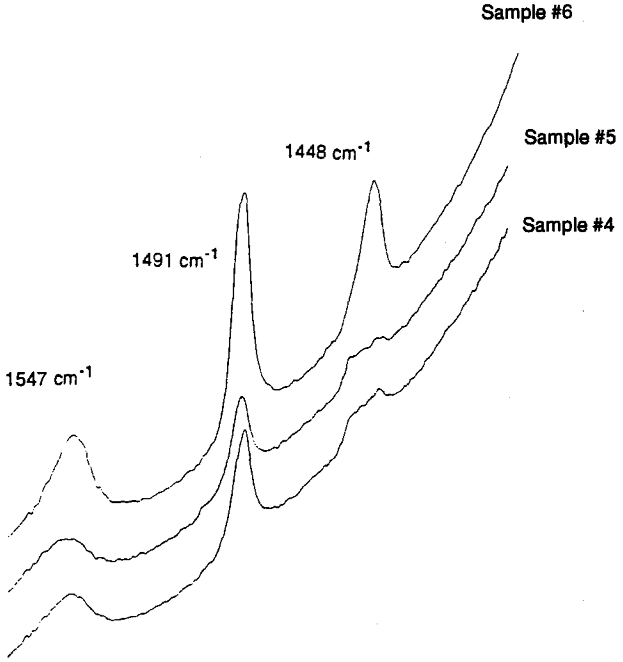

Fig. 2. DRIFTS (diffuse reflectance infrared Fourier transform spectra) of pyridine adsorbed on the zeolites prepared as in table 1. (a) Zeolite sample No. 4 and (b) zeolite sample No. 5, both steam calcined at 815°C, and (c) zeolite sample No. 6, steam calcined at 840°C. The peak at ~ 1450 cm^{-1} is characteristic of Lewis sites, the peak at ~ 1550 cm^{-1} is characteristic of protonic sites, and the peak at ~ 1490 cm^{-1} includes contributions from both.

increase in the amount of the site or an increase in strength. Since infrared intensities are proportional to the dipole moment of the measured species, the enhanced intensity may be a reflection of an increased charge separation associated with the electron transfer to the Lewis site.

A catalyst was prepared from zeolite sample No. 6, table 1, and was tested for activity and selectivity after calcination at 538 and 677°C as well as after steam calcination at 760°C. Calcination at 538°C removes water but does not dehydroxylate the surface, while calcination above 630°C typically dehydroxylates the surface [8]. Steam calcination at 740°C is typical of deactivation procedures designed to simulate a typical FCC regenerator deactivation. These catalysts were tested for activity and selectivity in a standard MAT evaluation procedure. The selectivity and activity results are compared in table 2 and fig. 3 to the results for a 40% USY catalyst steam deactivated, 100% steam, at 815°C for 2 h.

4. Discussion

Increased activity for paraffin cracking associated with thermal and hydrothermal dealumination of ZSM-5 [9] and faujasite [10–12] has been repeatedly observed. The site of the increased activity in faujasite has been associated with the occurrence of nonframework alumina. In both cases an activity increase for small paraffin cracking occurs as a result of relatively mild hydrothermal treatments. The excess activity is eliminated if the extra lattice alumina is removed by an acid treatment [11]. This differs from the present case where the observation of an acid

Table 2
Selectivities of catalysts prepared from conventional and deactivated zeolites

Final steam/calc.	Deactivated (#6, table 1)			Conventional		
%steam	0	100	0		100	
temperature (°C)	538	760	677		815	
%Xtal	30	30	25			
XRD relative intensity [a]	108	89	105		105	
uc	24.25	24.25	24.26		24.26	
catalytic selectivities (wt%)						
C/O	4.07	3.95	4.16	1.95	2.94	4.93
conv.	68.1	45.0	73.1	45.6	62.4	73.1
H_2	0.228	0.101	0.418	0.03	0.05	0.08
C_1	1.19	0.60	2.34	0.34	0.52	0.89
gasoline	42.0	30.8	38.5	33.7	43.7	46.5
gasoline sel.	0.62	0.68	0.53	0.74	0.70	0.64
coke	5.0	2.4	8.7	1.4	2.2	2.7

[a] Relative intensity of XRD peak at $2\theta \approx 24.5°$.

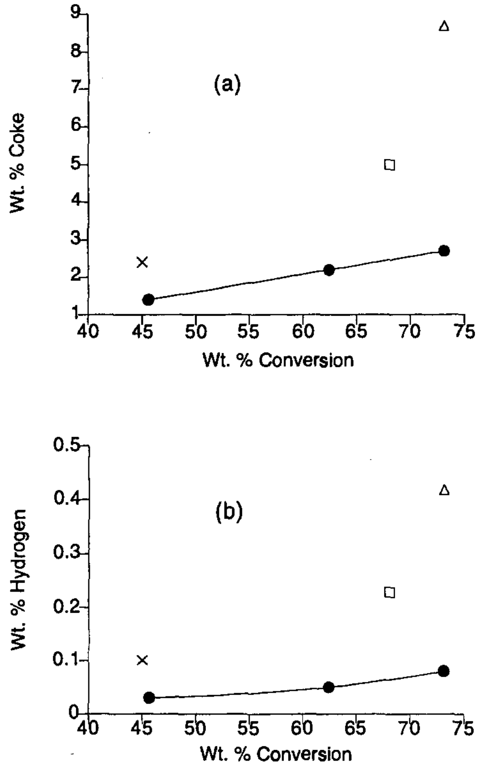

Fig. 3. Selectivities of conventional (○) and 53 ppm (●) cracking catalysts for (a) coke and (b) hydrogen from table 2. Gas oil cracking, 4 C/O, 16 WHSV, 527°C.

site of high activity follows a severe 830°C dealumination. Acid treatment does not remove the alumina responsible for this activity. The high temperature site is associated with Lewis character by the pyridine DRIFTS experiments, and appears in conjunction with an ^{27}Al shift of 53 ppm rather than the 60 ppm shift normally associated with tetrahedral aluminum in faujasite. The shift identifies the aluminum as having tetrahedral symmetry either in a distorted framework site or in a nonframework site possibly in association with the framework. It has been suggested that a nonframework alumina species with the structure AlO^+ can occupy exchange sites in faujasite [13]. This species might occupy any of several exchange sites and form partially covalent bonds to oxygens in the lattice. For example, occupation of a II or II' site on the face of a six ring would allow coordination to the three O_3 atoms, and a nonframework species of tetrahedral symmetry might be formed. Alternatively, a change in bond angles around a framework aluminum site associated with the distortion caused by bonding to cationic alumina may cause a change in the chemical shift as well as a related change in acidity. In any event, it is clear that a change in bonding around the aluminum site has occurred in these samples, and acidity is related to the bonding and the bond angles around the acidic oxygen [14]. A possibly analogous situation occurs in ZSM-5 exchanged with GaO^+. The cation GaO^+ forms a Lewis site believed responsible for increased activity for light paraffin cracking as well as increased aromatization activity [15,16]. In this case a strong Lewis site is formed at a relatively low temperature of 500°C. Lewis acidity has been identified in thermally treated ZSM-5 [17,18] as well as DEALY [17,19], presumably associated with a species of alumina formed during dealumination of the framework.

It has been observed that during the dealumination process a number of acidic protonic sites can form in hydrothermally treated DEALY [20]. The present work suggests that active Lewis sites are formed as well and that these sites can be expected to have different selectivities than the conventional sites in DEALY. The activities of these sites for making gas and coke are important in commercial cracking applications. While a commercial fluid catalytic cracking regenerator is not expected to exceed 760°C and the newly observed site only appears in significant concentration at 830°C, a cracking catalyst may remain in a commercial unit for a long time, in some cases several months. During this period of time catalytically significant amounts of this site may form and affect selectivity.

5. Conclusions

An active site associated with a ^{27}Al chemical shift of 53 ppm has been prepared by hydrothermal means. The difference in chemical shift between the aluminum in the conventional faujasite framework at 60 ppm and the aluminum formed after severe deactivation at 53 ppm implies chemical inequivalence. The 53 ppm shifted aluminum is either a tetrahedral nonframework species, or it is a framework species distorted by the formation of some non-framework structure. The new strong Lewis acid site is associated with the same detrimental selectivities, especially hydrogen make, that sometimes occur at low unit cell sizes after severe deactivation. Compared to the conventional USY based catalyst, the experimental catalyst containing the zeolite with very small amounts of the 53 ppm shift aluminum, in this case about 1% on the catalyst, is active, even after steam deactivation, but with poor selectivity for hydrogen, methane, gasoline, and coke.

These results combined with previous results suggest the following picture of deactivation. Faujasite rapidly dealuminates to a low unit cell size forming catalytically inactive predominately octahedral and pentacoordinate nonframework alumina. Selectivity and activity are determined by the isolation and strength of the framework sites. Under severe deactivation conditions, small amounts of very active tetrahedrally coordinated nonframework aluminum sites are formed with a significant Lewis character. These sites are responsible for the observed selectivity debits of USY catalysts and may be in part responsible for some of the selectivity effects previously ascribed entirely to unit cell size changes, especially increases in light gas and hydrogen production [2,21].

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