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An Analysis of Commercial Zeolite Catalysts by Multinuclear NMR

by

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INTRODUCTION

This work involves studying two commercial hydrocracking catalysts by solid state multinuclear NMR with the goal of developing a method of determining the fraction of zeolite in the catalysts. The zeolite fraction is known to be one of the faujasite zeolites type X or Y. The clay matrix of the catalyst is assumed to be kaolinite.

Since 1933 when it was shown that silica supported alumina was a catalyst with acidic properties, there has been increasing use of aluminosilicates as catalysts.¹ Later the acid sites were determined to be the catalytically active centers. Natural aluminosilicate clays were found to be active catalysts but they deactivated readily at the high temperatures used for catalytic cracking of hydrocarbons.² Natural faujasite zeolites have catalytic activity more than a thousand times that of the clays. With the advent of synthesized faujasite zeolites, catalytic selectivity and activity were further enhanced.

Zeolites are used in a wide variety of applications including catalysis of hydrocarbon reactions, separation of hydrocarbons, and removing carbon dioxide from natural gas. Crystalline zeolites have been used in cracking catalysts since the early 1960s and now are used to produce several million barrels of oil per day. Commercial cracking catalysts usually contain 10 to 20 wt% of the faujasite zeolites X or Y in a clay matrix.³

The unit cells of zeolites X and Y consist of a three-dimensional framework of 192 MO_4 tetrahedra linked by shared oxygen bridges with M representing Si or Al. Substitution of Al^{3+} for Si^{4+} in the tetrahedra

must be charge compensated by additional cations usually Na^+ . The formula for a unit cell of a typical zeolite X is $\text{Na}_{86}[(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \cdot 264 \text{ H}_2\text{O}$. A typical zeolite Y might contain $\text{Na}_{56}[(\text{AlO}_2)_{56}(\text{SiO}_2)_{136}] \cdot 250 \text{ H}_2\text{O}$. Faujasite zeolites with Si/Al ratios of 1 to 1.5 are designated X type; those with ratios of 1.5 and above are designated Y type. The faujasite framework is shown in Figure 1.

The primary unit of the faujasite framework is the MO_4 tetrahedron. The secondary unit is the sodalite cage, a truncated octahedron. The final unit is composed of four sodalite cages arranged tetrahedrally around a fifth sodalite unit. Throughout the framework, the ordering of Si and Al follows Loewenstein's rule: no two Al^{3+} are connected to the same oxygen.⁴ Together these units produce a framework with large pores or supercages with internal diameters of $\sim 1.27 \text{ nm}$ connected by narrower channels. In the case of faujasites, the channels between supercages are restricted by rings which are $\sim 7.4 \text{ \AA}$ in diameter composed of twelve Si and/or Al atoms joined by oxygen bridges. Zeolites have a steric selectivity in the channels which limits the size of molecules entering the pores, hence their name molecular sieves.

While zeolites are synthesized in the Na form, to produce active catalysts it is necessary to decationate them by exchanging the Na^+ cations with NH_4^+ . After decationation, they are heated to drive off ammonia leaving the acid form of the zeolite which is more active and thermally stable than the parent form. They may also be partially cation exchanged with other cations. Often the zeolite is dealuminated as well to decrease acid strength and greatly increase thermal and hydrothermal stability. This is accomplished by the methods listed in

Figure 1. The building blocks of faujasite zeolites a) sodalite unit, b) five sodalite units connected by hexagonal prisms, c) formation of a supercage

Figure 2. Locations of five general types of cation sites (I, I', II, II', U) in zeolites X and Y

Table 1. Preparation methods of aluminum-deficient Y zeolites⁵

- I. Hydrothermal treatment of NH_4 Y zeolites
(formation of ultrastable Y zeolites)

 - II. Chemical treatment
 - A. Reaction with chelating agents
 - B. Reaction with CrCl_3 in solution
 - C. Reaction with $(\text{NH}_4)_2\text{SiF}_6$ in solution
 - D. Reaction with SiCl_4 vapors or other halides

 - III. Hydrothermal and chemical treatment
Reaction of ultrastable Y zeolite with:
 - A. Acids (e.g., HCl , HNO_3)
 - B. Bases (e.g., NaOH)
 - C. Salts (e.g., KF)
 - D. Chelating agents (e.g., EDTA)
-

Table 1.⁵ Dealumination initially removes framework Al associated with weak acid sites so the Al remaining produces strong acid sites.⁶⁻⁸ Framework Al removed thermally leaves the framework but remains inside the zeolite pore structure. Even with the other methods and repeated washings it is not always possible to remove the extra-framework Al created by dealumination.

Zeolites used as cracking or hydrocracking catalysts sieve the original feedstock and selectively crack the hydrocarbons. After the initial cracking, the products are briefly held inside the zeolite framework supercages and are therefore increasingly likely to undergo further reactions such as branching. Here it becomes apparent that the location of the cation sites within the framework may effect the reactions catalyzed. Zeolites X and Y have been found to contain roughly five types of cation sites which are depicted in Figure 2.⁹

Besides cracking, at least five other reactions can occur during catalytic cracking: isomerization, alkylation (the reverse of cracking, in equilibrium with it), disproportionation, hydrogen transfer, and coke formation. Coke is a highly carbonaceous nondesorbable material which coats the surface of the zeolite. It is formed by condensation and accumulation of reaction products onto the surface of the catalysts but not necessarily directly onto the active centers of the zeolite. Coke formation deactivates cracking catalysts requiring continuous regeneration by coke removal at a higher temperature than the cracking temperature. Normal temperatures required for cracking are in the range of 500 to 700 °C.

Hydrocracking combines hydrogenation with catalytic cracking, the purpose of which is to convert high boiling feedstock to low boiling products by cracking and hydrogenating aromatics. The use of hydrogen pressure of 1 to 10 MPa and temperatures ranging from 200 to 400 °C hydrogenates coke precursors thereby greatly extending catalyst life.¹⁰ Y zeolites which have been exchanged with divalent cations or loaded with palladium function as hydrocracking catalysts.

Catalyst formulations need to optimize the selectivity of the reactions catalyzed, the activity, and the life of the catalyst. Commercial catalysts typically contain a small fraction of zeolite, the active catalyst, in an inert matrix.¹¹ The matrix reduces catalyst loss by attrition, provides bulk and support for the zeolite, and serves as a sink for poisons in the feed.¹² It has been found that increasing the amount of zeolite in a cracking catalyst increases the yield of gasoline and light cycle oil, increases the aromatic content, increases the octane number of the gas produced, and decreases the amount of coke formed.¹³

Aluminosilicates have been studied by many methods. Their long range order can be characterized by X-ray and neutron powder diffraction, while high-resolution (transmission) electron microscopy (HREM), energy-dispersive analysis of x-rays (EDAX) and electron energy loss spectroscopy (EELS) can show local order of Al and Si.^{14,15} Infrared and Raman spectroscopies have also been used to characterize aluminosilicates.¹⁶

THEORY

The theory of nuclear magnetic resonance has been described in rigorous detail in many excellent books.¹⁷⁻¹⁹ Several useful technique oriented monographs and papers are also available as are books offering combinations of quantum theory and practice.^{20,21} The following is an overview of solid-state NMR.

The Zeeman Interaction and Basic Theory

An NMR active nucleus with spin I has a magnetic moment equal to $\gamma \hbar I$, where γ is the gyromagnetic ratio of that isotope and $\hbar$ is Planck's constant. The spins have degenerate energy levels until they are subjected to a magnetic field, B_0 , at which time they have $2I+1$ levels associated with the magnetic quantum number m . The equation for this interaction is the Zeeman Hamiltonian shown in Table 2.

In the case $I = 1/2$, there are two energy levels associated with spins aligning against (high energy) or with (low energy) the B_0 field. The low energy direction of the B_0 field is labeled the positive z axis by convention. Since there is no magnetic force in the x or y directions, the magnetization of an ensemble of spins in a magnetic field is caused by the slightly greater population of spins in the low energy direction, M_z , with the x and y directions cancelling. The magnitude of M_z is determined by Boltzmann distribution and the isotopic abundance of the nucleus.

The net moment precesses around B_0 with the Larmor frequency,

$$\gamma B_0 = \omega_0 \quad , \quad (1)$$

which is in the radiofrequency range for the magnetic fields used in NMR. The energy of each level is given by

$$E = -\gamma\hbar B_0 m_I \quad (2)$$

Therefore, the energy difference between m and $m+1$ levels is $-\gamma\hbar B_0$.

The application of a pulse of radiofrequency ω_0 , perpendicular to B_0 creates a field B_1 perpendicular to B_0 . The spins can then absorb energy from the B_1 field and enter the higher state. While the pulse is on, the spins precess around the B_1 field with frequency γB_1 . A pulse long enough to rotate the moment from the z direction down onto the y axis is called a $\pi/2_x$ pulse, where the $\pi/2$ indicates the fraction of a complete rotation and x indicates the direction of the applied B_1 field. The moment can be detected when it is in the xy plane. The signal of nuclei in one chemical environment exactly on resonance will resemble a Gaussian or Lorentzian decay called a free induction decay (FID). If the applied radio frequency was not exactly matched to the Larmor frequency, the FID will be a sinusoidal wave the envelope of which shows the same decay. The pulse and detection constitutes one scan of a single pulse experiment.

Usually an accumulation of scans is required which means waiting for the excited spins to relax back to the low energy state. This is accomplished by a transfer of energy to the system, called spin-lattice or longitudinal relaxation and characterized by a time T_1 . Nuclei in different chemical environments within the same compound can have widely

varying T_1 values. One must wait at least five times the longest T_1 between scans for quantitative data if a 90° pulse is used.

In addition, spin-spin or transverse relaxation also occurs, characterized by T_2 . The initial height of a FID will be attenuated if the time between scans is less than $5T_1$. T_2 affects the length of the decay especially in the case of solids which generally have shorter T_2 's than liquids and in the case of homogeneous magnets (inhomogeneity shortens the FID by non- T_2 mechanisms). A longer T_2 produces a longer FID.

NMR is essentially a measurement of the nuclear spin Hamiltonian experienced by a particular type of nucleus in a sample. That Hamiltonian is represented by

$$H = H_Z + H_{CS} + H_D + H_J + H_Q + H_{RF} + H_{SR}$$

where H_Z is the Zeeman interaction; H_D represents the dipole-dipole interaction; H_J is the indirect electron coupling between spins; H_Q is the quadrupolar interaction; H_{RF} is the interaction caused by applying an oscillating radio frequency field; and H_{SR} is the effect caused by the interaction of spins with the magnetic moment produced by the angular momentum of the molecule. For many solids H_{SR} and H_J can be neglected since the other interactions are orders of magnitude larger. The remaining Hamiltonians are shown in Table 2.

The magnitude of H_Z is determined by the magnet used and subtracted by the spectrometer hardware during detection of the signal. H_{RF} is under experimental control, being a factor of transmitter power, probe

Table 2. Hamiltonians of solid-state NMR

Interaction	Hamiltonian
Zeeman	$H_Z = -\gamma \hbar I_Z B_0$
Radio Frequency	$H_{RF} = -\gamma \hbar I_X B_1$
Chemical Shift	$H_{CS} = \hbar \gamma \vec{I} \cdot \vec{\sigma} \cdot \vec{B}$
Homonuclear Dipole-Dipole	$H_{D_{II}} = \hbar \sum_{i \neq j} \vec{I}_i \cdot \vec{D} \cdot \vec{I}_j$
Heteronuclear Dipole-Dipole	$H_{D_{IS}} = \hbar \sum_{i=j}^{N_I N_S} \vec{I}_i \cdot \vec{D} \cdot \vec{S}_j$
Quadrupole	$H_Q = \frac{eQ}{4I(2I-1)} \vec{I} \cdot \vec{V} \cdot \vec{I}$

Where γ is the gyromagnetic ratio of the nucleus

Q is the nuclear quadrupole moment

e is the charge of an electron

I_X , and I_Z are spin operators

B_0 is the static magnetic field

B_1 is the radio frequency field

quality factor, Q, and pulse length. The other Hamiltonians are determined by the nucleus under observation.

The Chemical Shift Interaction

The electrons surrounding a nucleus distort the field it experiences. In the range of magnetic fields typically used, the chemical shift anisotropy is represented by a symmetrical second rank tensor, σ , called the chemical shielding tensor, whose magnitude is described by σ_{xx} , σ_{yy} , and σ_{zz} . The chemical shift anisotropy tensor is represented graphically in Figure 3. The isotropic value of the tensor, the value observed with rapid molecular tumbling as of liquids, is

$$\bar{\sigma} = \frac{\sigma_{xx} + \sigma_{yy} + \sigma_{zz}}{3} \quad (3)$$

Two other parameters used to describe the tensor are

$$\text{the anisotropy, } \delta = \bar{\sigma} - \sigma_{zz}$$

and

$$\text{and the asymmetry, } \eta = (\sigma_{yy} - \sigma_{xx})/\delta.$$

A powdered solid sample experiences all possible orientations to the external magnetic field B_0 in a statistical distribution based on solid angles. Instead of producing a spectrum consisting of a single line at $\bar{\sigma}$, the solid produces a powder pattern. When a powdered solid sample is spun at the angle β to the magnetic field the average value of σ_{zz} for the whole system is

$$\langle \sigma_{zz} \rangle = (3/2)\bar{\sigma}\sin^2\beta + 1/2(3\cos^2\beta - 1) \sum_{j=1}^3 \sigma_{jj}\cos^2\chi_j \quad (4)$$

Figure 3. The chemical shift anisotropy tensor representation showing that different orientations of the molecule relative to B_0 experience different amounts of shielding and therefore produce a range of resonance positions for the same chemical species

a)

b)

Figure 4. The effects of differing asymmetry on the observed NMR powder pattern a) $\eta > 0$, unsymmetric, b) $\eta = 0$, axially symmetric

where χ is the angle between B_0 and each of the three principal axes.²² The effects on a powder pattern of different asymmetry parameters are illustrated in Figure 4.

The Dipolar Interactions

These result from the fact that NMR active nuclei act as magnets which can affect each other's magnetic fields. Inserting the appropriate values into the dipolar interaction tensor from Table 2 yields a homonuclear dipolar Hamiltonian with secular terms being

$$H_{D_{II}} = (1/2) \gamma_I^2 \hbar \sum_{i,j}^N r_{ij}^{-3} (I_{i1} I_{j1} - 3 I_{i2} I_{j2}) (3 \cos^2 \theta_{ij} - 1) \quad (5)$$

and a heteronuclear dipolar Hamiltonian with secular terms being

$$H_{D_{IS}} = \hbar \sum_{i,j}^N \gamma_I \gamma_S r_{ij}^{-3} I_{zi} I_{zj} (3 \cos^2 \theta_{ij} - 1) \quad (6)$$

in units of rad sec^{-1} . The γ values are gyromagnetic ratios, r_{ij} is the internuclear vector and θ_{ij} is the angle between r_{ij} and B_0 . From this equation one can see that the dipolar effect decreases strongly with distance. The effect can result from like or unlike nuclei, with abundant, nearby nuclei with high γ values showing the strongest effect.

The Quadrupolar Interaction

This applies only to nuclei with $I > 1/2$ all of which have an electric quadrupole moment, eQ . This interacts with an electric field gradient (EFG) equal to d^2V/dz^2 . The EFG is described by its three orientation coordinates and by the following:

$$\text{the magnitude, } eq = V_{zz}$$

and

$$\text{the shape, } \eta = (V_{xx} - V_{yy})/V_{zz} .$$

Quadrupolar nuclei experience more than one resonance frequency for a nucleus in a single chemical environment since $\nu_L = (E_{m-1} - E_m)/h$, m has values $I \geq m \geq -I$, and the quadrupolar interaction does not affect all m the same. The energy diagram illustrating this is shown in Figure 5. In the principal axis system of the EFG tensor, the Hamiltonian governing the interaction of the quadrupolar nucleus with the EFG is

$$H_Q = \frac{e^2 q Q}{4I(2I-1)} [3I_z^2 - I^2 + \eta(I_x^2 - I_y^2)] . \quad (7)$$

When perturbation theory is applied, sizable first and second order terms result. Defining the resonance frequency $\nu_m = \nu_L + \nu_m^{(1)} + \nu_m^{(2)}$, and denoting the order by superscript, the first and second order frequency shifts are:

$$\nu_m^{(1)} = (1/2) \nu_Q (m-1/2) (3\cos^2\theta - 1) \quad (8)$$

$$\nu_m^{(2)} = \frac{-\nu_Q^2}{16 \nu_L} (a - 3/4) (1 - \cos^2\theta) (9\cos^2\theta - 1) \quad (9)$$

with the following definitions

$$\nu_Q = \frac{3e^2 q Q}{2hI(2I-1)} \quad (10)$$

$$a = I(I+1) \quad (11)$$

$$\nu_L = \gamma B_0 (1 - \sigma) / 2\pi . \quad (12)$$

Figure 5. An energy diagram showing the effects of Zeeman, first and second order quadrupolar interactions on nuclear spins

For half-integer spin nuclei, such as ^{27}Al with $I = 5/2$ used in this work, only the $-1/2$ to $1/2$ transition is observed since the other transitions are too broad to observe given our bandwidths for broadcasting and reception. From equation 8 one can see that $\nu_m^{(1)}$ goes to zero when $m = 1/2$. The second order shift is not dependant on m and is inversely proportional to B_0 .²³

Magic Angle Spinning

In all of the preceding Hamiltonians, factors involving the angle between a tensor or vector and B_0 produce broad lines in a static powder spectrum since all angles are possible. Magic angle spinning (MAS) at the angle 54.74° to B_0 ideally sets the factor $3\cos^2\theta - 1$, which is present in the Hamiltonians of chemical shift anisotropy, dipolar and first order quadrupolar interactions, equal to zero. The spinning speed should be greater than or equal to the linewidth (in Hertz) caused by the interaction to be cancelled in order to avoid the problem of intensity loss in spinning sidebands for inhomogeneous broadening, and of residual broadening of homogeneous interactions. If spinning sidebands occur they are located at intervals equal to the rotation frequency from their central peak. Table 3 lists the factors which can affect the ultimate resolution possible with magic angle spinning.²⁴

Table 3. Factors affecting resolution in magic angle spinning²⁴

I. Instrumental Factors
inhomogeneity of magnetic field, B_0
imperfect adjustment of the magic angle
insufficiently fast spinning
bulk susceptibility effects
II. Residual Interactions
residual dipolar interactions
chemical shift distributions
intermolecular J couplings
antisymmetric tensor interactions
quadrupolar effects
higher-order multipole interactions
III. Motional and Relaxation Effects
spin-lattice relaxation
cross-relaxation
slow internal motions

SOLID STATE NMR OF ALUMINOSILICATES

Aluminosilicates are good subjects for study by solid state ^{29}Si NMR. Of the major constituents of zeolites and clays, ^{29}Si the only spin 1/2 nucleus is in 4.7% abundance, ^{17}O is spin 5/2 and only 0.037% abundant while ^{27}Al is 100% abundant but also a spin 5/2 quadrupolar nucleus. Therefore, dipolar relaxation mechanisms that can cause severe line broadening in solids are minimized by the fact that the closest possible abundant NMR active nucleus is ^{27}Al two bonds removed from ^{29}Si . The line broadening mechanisms that affect solid ^{29}Si in aluminosilicates are primarily the heteronuclear dipolar interaction between Si and abundant NMR active nuclei and the shielding anisotropy of ^{29}Si . Since ^{29}Si is a rare spin nucleus it suffers essentially no homonuclear dipolar broadening.

Both dominant broadening mechanisms have a space dependence of $1-3\cos^2\theta$ which can therefore be averaged to near zero by magic angle spinning at $\theta = 54.74^\circ$. In the case of ^{29}Si shielding anisotropy, the linewidth to be narrowed by spinning is generally 100 ppm (4372 Hz and 5962 Hz at the fields used for these experiments) or much less.²⁵

The isotropic chemical shift is responsible for relative peak locations. In aluminosilicates the ^{29}Si chemical shift is primarily determined by the number of Al atoms attached to the $^{29}\text{SiO}_4$ producing the peak. Figure 6 shows the possible ranges of chemical shifts in framework aluminosilicates where the detected Si is connected to four other tetrahedral units.²⁵ Similar ranges of shifts have been observed for Si connected to three other units (layer structures) but the entire

Figure 6. The range of chemical shifts (relative to tetramethylsilane) of ²⁹Si connected to four other tetrahedral units ²⁵

set occurs between -90 and -102 ppm relative to TMS with downfield shifts being positive.²⁶ The identity of the exchangeable cations present can account for the range of chemical shifts at a particular level of Al substitution. The final factor with an effect on chemical shifts is the Si-O-T angle between the ^{29}Si and the next tetrahedral unit with upfield shifts associated with increasing angle.²⁷⁻³¹

NMR active ^{27}Al is 100% abundant but since the dominant effect measured is the quadrupolar interaction, the primary information readily obtained from an NMR spectrum is the coordination of Al atoms that are in relatively symmetrical environments. A symmetrical, or nearly so, octahedral environment will produce a peak between +20 and -10 ppm from aqueous $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$. A peak at +50 to +80 ppm (downfield) is associated with a tetrahedral environment. Some aluminosilicates and their coordination numbers and isotropic ^{27}Al chemical shifts are listed in Table 4. To have accurate isotropic chemical shift locations one must consider the second order quadrupolar shift which is not cancelled by MAS.³² This second order effect decreases with increasing B_0 field making uncorrected chemical shifts at higher magnetic fields more accurate than at lower fields. Unfortunately, if one wants to keep spinning sidebands from occurring between -10 and 80 ppm, higher fields require spinning speeds that are unattainable with customarily available MAS probes. In the case of kaolinite and Y-type zeolites at 5.2 Tesla, the uncorrected experimental shift locations can still be used to indicate octahedral or tetrahedral coordination.

Table 4. ^{27}Al chemical shifts as a function of Al coordination number

Compound	δ_{CS} (ppm from $\text{Al}(\text{H}_2\text{O})_6^{6+}$)			ref
	Al(4)	Al(5)	Al(6)	
Al_2SiO_5 polymorphs ^a				
Sillimanite	64.5		4.0	33
Andalusite		36.0		34
Kyanite			7.5 5.0	35
Layer aluminosilicates ^a				
Pennine	72 $\pm$ 2		10 $\pm$ 1	
Muscovite	72 $\pm$ 1		5 $\pm$ 1	
Margarite	76 $\pm$ 3		11 $\pm$ 4	
Xantophyllite	76 $\pm$ 4		11 $\pm$ 1	
Framework aluminosilicates ^a				
Mordenite	55.8			36
Na X, Y zeolites	62.8			37,38
Aluminates ^b				
$\text{Mg}(\text{AlO}_2)_2$			22	
$\alpha\text{-Al}_2\text{O}_3$			5	
$\beta\text{-Al}_2\text{O}_3$	64		9	
Miscellaneous				
Barium aluminate glyconate		35.3		39
Hydrothermally de- aluminated zeolite	61.0	33.9	-0.4	40
Calcined kaolin	67.3	31.2	-0.3	40

^aExact chemical shifts calculated by Lippmaa et al.³²^bMeasurements taken at 6.4 Tesla, no correction of chemical shift.⁴¹

EXPERIMENTAL METHODS

Fresh, air-exposed commercial hydrocracking catalysts were provided by Phillips Petroleum.⁴² Sample 33351-86 was known to be a physical mixture of a Y zeolite and a clay matrix. The other catalyst, 33351-20, was composed of a faujasite zeolite grown within a clay matrix. Both were suspected of being about 20 wt% zeolite. Nothing is known about the state of pretreatment or cation exchange. A portion of each catalyst was calcined in a porcelain crucible in air at 500 °C for two hours with a two hour heating ramp preceding and a two hour cooling ramp following calcination.

A highly crystalline kaolinite, with formula $\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$, was used to represent the clay matrix in the model compound. In kaolinite there is a layer of octahedral aluminum joined to a layer of tetrahedral silicon as shown in Figure 7. The silicon layer features Si bonded to three other tetrahedral Si and one octahedral Al by oxygen bridges, so the clay has a layer not a framework structure. This sample was found to be 52.5 wt% SiO_2 , 39.3 wt% Al_2O_3 , and 0.54 wt% Fe_2O_3 by chemical analysis.⁴³

The Linde molecular sieve LZY-52, which has a Si/Al ratio of 2.37 according to the suppliers specifications, was examined in its Na-exchanged form, without dehydration. A model mixture was made from 79.8 wt% nondehydrated kaolinite and 20.2 % LZY-52 zeolite also non-dehydrated.

S115, a silicalite zeolite (lot #9574-6C Union Carbide Corp., Linde Div., Tarrytown, New York) which is about 99% SiO_2 was used for tuning.

Figure 7. The layer structure of kaolinite showing the aluminum atoms in octahedral coordination and the silicon atoms in tetrahedral coordination⁴⁴

Figure 8. X-ray powder diffractogram of calcined α -alumina

The silicalite, which produces a peak at -112 ppm (upfield) from TMS, was also used for spin counting and as an internal reference for the preliminary catalyst spectra. Thermogravimetric analysis revealed that the air-exposed S115 samples used are 7.24% water, a factor included in subsequent calculations.

Powdered α -Al₂O₃ was used as a standard for spin counting ²⁷Al. The alumina was calcined in air at 500 °C for two hours then kept in a dessicator. An X-ray powder diffractogram of the calcined alumina, shown in Figure 8, indicates the sample is essentially free of impurities.

Silicon NMR

Silicon at 43.72 MHz

Initial measurements were performed on a home-built NMR spectrometer which has been described elsewhere with the exception that quadrature detection capability has been added since then.^{45,46} The probe used was a home-built model capable of spinning large samples to 5 kHz with air drive.⁴⁷ The probe was tuned to 43.72 MHz for ²⁹Si and had a Q of 75. Although the ²⁹Si NMR signal from S115 can just be seen in one scan, ten scans were signal averaged while applying the pulse tuning sequences.⁴⁸

Spectra of catalyst 33351-86, calcined and uncalcined, were taken with recycle times varying from 4 to 200s to roughly determine when relaxation associated with the longest T₁ no longer affected relative intensities. The recycle time finally used was the one which gave the same lineshape as the next longer recycle time. The final parameters used were: 90° pulse, 22μs; recycle time, 50s uncalcined sample, 30s

Odd scans

Ringdown transient →

Accumulate: +

Even scans

Ringdown transient →

Figure 9. The pulse sequence used to reduce noise and pulse ringdown on experiments at 43.72 MHz

The pulse sequence used was one designed to minimize noise as well as pulse ringdown thereby decreasing the deadtime. The sequence used is shown in Figure 9. The pulse ringdown is the same phase and amplitude after each 90°_x pulse whereas the NMR signal inverts between alternating scans. The negative of the even scans is added to the odd scans thereby adding the NMR signal but cancelling much of the noise and pulse ringdown.

Silicon at 59.62 MHz

All of the quantitative ^{29}Si data were obtained with a Bruker MSL-300 with a multinuclear probe capable of routinely spinning 0.2 g samples at 4 kHz. The final parameters used were: 90° pulse, 6 μs ; recycle time, 100s all samples; dwell, 13 μs ; spinning speed, 4 kHz; pulse sequence, single 90° pulse CYCLOPS; linebroadening, 100 Hz.

Aluminum NMR

All ^{27}Al data were gathered on the homebuilt spectrometer with aqueous $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ resonating at 57.37 MHz. The probe used for the lower field silicon work was designed to be adaptable to the higher resonance frequency and faster spinning speeds needed for aluminum in the same field. As an ^{27}Al probe it uses smaller diameter rotors which hold less sample but spin up to 10 kHz with air drives. Signal to noise, S/N, is not a problem with Al since it is abundant and has a short T_1 . Pulses of 1 μs (less than 15° flip angle on the liquid) were used to produce quantitative data.⁴⁹ Alternating x and -x pulses were used with detection always along the +y axis and subtraction of alternate scans to improve S/N. The pulse sequence from Figure 9 could not be used because the π pulse would make it nonquantitative for Al

species with differing quadrupolar coupling constants. The final parameters used for ^{27}Al were: carrier frequency 57.319 MHz; recycle time, 0.6s; dwell, 5 μ s; spinning speed, 8 to 8.2 kHz; filter, 100 kHz; quadrature detection; 2000 scans. In addition, to insure quantitative data, the transmitter was left on and no cables were moved until all experiments were finished.

It is known that the maximum Al signal detected from all transitions in pulse mode will be a fraction, ~ 0.38 , of what would be detected from the same number of nuclei if the sample were liquid.^{20,50} Usually only the central ($m=1/2$ to $m=-1/2$) transition is easily seen so this fraction is even smaller. Often quantitative data are obtained by using a liquid sample as a standard, observing the solid samples at varying pulse lengths and using the central transition fraction to calculate the number of spins in the unknown. It seemed reasonable that using a powder of known composition for the spin counting standard would eliminate the need to know the exact fraction of the liquid signal which corresponds to the central transition. It was also found that a liquid Al sample detuned the probe and substantially changed the probe Q making quantitative comparisons especially difficult.

RESULTS AND DISCUSSION

The initial ^{29}Si spectra of uncalcined catalyst 33351-86 taken at 43.72 MHz shows one easily resolved peak and a broad line of unresolved peaks with reasonable S/N in 4100 scans (Figure 10a). The calcined sample produces a spectrum consisting of a broad skewed peak after about 15,000 scans (Figure 10b). Spectra taken of the catalysts with Si15 mixed in as an internal reference placed the resolved peak of the uncalcined catalyst at -91 ppm thereby moving the peaks 6 ppm upfield from where they seem to be with an external reference (Figure 11).

The spectrum of the uncalcined sample shows a peak at -91 ppm which largely disappears upon calcination at 500°C for two hours. It has been reported that uncalcined kaolinite exhibits a peak at -91.5 ppm^{51,52} although a shift of near -93 ppm has also been reported for natural kaolins.⁵³ The kaolinite peak reportedly loses intensity upon calcination at 550 to 600°C as a broad peak centered at -101 ppm builds in. The latter peak is attributed to metakaolinite.⁵⁴⁻⁵⁶ Although the -91 ppm peak of the 33351-86 catalyst lost intensity at a lower temperature than reported in the literature, it is still likely that the peak represents kaolinite since that clay is frequently used as a binder.

The spectrum intuitively expected from the catalyst was one with the familiar group of 4 or 5 peaks representing the zeolite fraction from which the Si/Al ratio can readily be calculated and a much broader peak indicating the presence of an amorphous clay. Instead the clay fraction produced the only readily identifiable peak.

Figure 10. Initial ^{29}Si spectra of catalyst 33351-86 at 43.72 MHz a) uncalcined, b) calcined

Figure 11. ^{29}Si spectra of calcined 33351-86 with S115 internal reference a) uncalcined, b) calcined

The ^{29}Si spectrum of the uncalcined sample was deconvoluted into one peak of kaolinite, five relatively narrow peaks for the framework zeolite, and one broader peak to represent Si in interstitial locations in the zeolite. Two possible deconvolutions which show the amount of zeolite to be arbitrary when determined by this method are presented in Figure 12. Neither deconvolution was obtained with a fitting program because each still leaves a portion of the spectrum unaccounted for, and our fitting routines will produce unreasonable peaks (e.g., negative) to fit the whole spectrum. Of course deconvoluting the spectrum into more peaks will produce a better fit, but then the explanation of the origin of the peaks becomes increasingly tenuous.

One problem with the deconvolutions was the lack of unambiguous peaks. Another problem was the possibility of peaks with different widths. The presence of a peak that is much wider than the others means the quantitation of nuclei producing the various peaks will be affected. Because of the Fourier transform relationship between the time domain in which data are recorded and the frequency domain in which the components are quantified, short FID's transform into broad peaks and long FID's yield narrow peaks. The area under a peak in the frequency domain is equal to the initial intensity of that peak's component of the corresponding FID. The deadtime, from the middle of the rf pulse to the first good data point, which must be subtracted from the start of the FID removes proportionally more intensity from a short than from a long component of a FID. For these reasons, two conclusions were drawn. Si NMR alone cannot be used to distinguish zeolite fraction from matrix fraction of even the catalyst with the more resolved spectrum.

Figure 12. Two possible deconvolutions of the uncalcined 33351-86 catalyst showing the relative areas of the zeolite peaks to be equivocal by this method

Furthermore, the ^{29}Si spectrum of the catalyst should be collected again using a spectrometer with a better S/N and shorter deadtime.

The experiments were repeated on the Bruker MSL-300. The spectra of the pure Na-Y zeolite, LZY-52; the intergrowth catalyst, 33351-20; the physical mixture catalyst, 33351-86; the model mixture of zeolite and kaolinite; and kaolinite are shown in Figures 13 and 14. The uncalcined 33351-86 catalyst spectrum taken at the higher field still does not show the separate peaks typical of crystalline faujasite zeolites even after 11,140 scans (Figure 15). In fact, the earlier spectrum had less true structure and more noise than originally thought. For this reason deconvolution of the spectrum into 4 or 5 peaks for the zeolite fraction and 1 or 2 for the clay fraction is likely to produce arbitrary results as before.

It was originally thought that after data manipulation to remove the clay component, the remaining spectrum could be deconvoluted and used to calculate Si/Al of the zeolite. The ^{29}Si spectrum of kaolinite shows the usual peak at -91 ppm but a broad upfield shoulder as well. Although the upfield shoulder indicates that this sample may not be pure kaolinite, the X-ray powder diffraction data show it to be highly crystalline (Figure 16) and it is unlikely to be less pure than the clay added to commercial zeolite catalysts. With the shoulder, the kaolinite spectrum cannot be fitted with one peak. This means deconvoluting the spectrum of a catalyst or model mixture into one peak for the clay component and several for the zeolite part probably will not work well especially in the case of the model mixture which is made with the same kaolinite.

Figure 13. The quantitative ^{29}Si MASNMR spectra with abscissa ppm relative to TMS, 64 scans each a) LZY-52, b) uncalcined catalyst 33351-20, c) uncalcined 33351-86, d) the model mixture of zeolite and kaolinite, e) kaolinite

Figure 14. Quantitative ^{29}Si MASNMR spectra with abscissa ppm relative to TMS, 8 scans each a) LZY-52, b) uncalcined 33351-86, c) the model mixture of zeolite and kaolinite, d) kaolinite

Figure 15. ^{29}Si MASNMR of catalyst 33351-86, 11,140 scans, recycle 6 s (partially saturated)

Figure 16. X-Ray powder diffractogram of kaolinite

The alternative of subtracting the kaolinite spectrum from that of the catalyst or model mixture is also problematical. The difference spectrum is adjusted subjectively on the spectrometer assuming that it should look like a distribution as in Figure 17a rather than two separate peaks as in Figure 17b. However, further fine adjustments can affect the size and location of apparent peaks in the final spectrum. For these reasons the difference spectra were not deconvoluted no matter how obvious the peak locations seemed. It is obvious that these subtractions will allow no clear demarcation between the Si of clay and of zeolite and will affect the experimental Si/Al ratio of both the clay and zeolite fractions. Even for the model compound made from the kaolinite, the process of spectrum amplitude adjustment for subtracting the kaolinite spectrum is largely subjective.

By contrast, cut and weigh integration technique used on the resolution enhanced ^{29}Si spectrum of LZY-52 using the known formula for calculating Si/Al from peak intensities,⁵⁷

$$\text{Si/Al} = \frac{\sum_{n=0}^4 I_{\text{Si}(n\text{Al})}}{\sum_{n=0}^4 (n/4) I_{\text{Si}(n\text{Al})}}, \quad (13)$$

where $I_{\text{Si}(n\text{Al})}$ stands for the intensity of the peak caused by Si connected to $n \text{ AlO}_4$ units, yielded a value of 2.37, exactly matching the supplier's specifications.

The ^{27}Al MAS-NMR spectra of the samples are shown in Figure 18. Figure 19 is the spectrum for the spin counting standard in the same

Figure 17. Spectra created by subtracting an amplitude adjusted kaolinite spectrum from the spectrum of catalyst 33351-86 a) adjusted to look like a statistical distribution of intensities, b) adjusted to remove the entire peak at location of kaolinite resonance

Figure 18. Quantitative ^{27}Al MASNMR spectra 2000 scans a) LZY-52, b) kaolinite, c) model mixture, d) uncalcined catalyst 33351-86

CALCINED ALPHA AL₂O₃ SPIN SPEED 8.2 KHZ 200 SCANS

Figure 19. 200 scans of α -alumina in the same absolute intensity scale as Figure 18

AL2O3 SPIN SPEED 8.5 KHZ 2000 SCANS 0.1013 G

Figure 20. 2000 scans of α -alumina showing the sideband manifold of the outer transitions which is at least as wide as the spectral bandwidth, and the central transition with one set of sidebands

Figure 21. A qualitative comparison of ^{27}Al spectra of α -alumina showing approximately the same linewidth under a) static conditions, b) MAS conditions

absolute intensity mode as Figure 18. From these one can see that pure zeolite has only Td Al while kaolinite has only Oh Al. Also, although both alumina and kaolinite have Oh Al, the peak location of the alumina is shifted from that of all the other Oh peaks. Spinning sidebands (ssb) are present in the alumina and kaolinite spectra, and to a lesser degree in the other spectra having Oh peaks. When intensities are measured, all ssb are counted as part of the octahedral peak since they occur 8 kHz from it.

When using a solid of cubic symmetry as the spin counting standard, one must consider whether transitions other than the central transition are small enough to ignore. In particular, Al in a highly symmetric Oh environment may have other transitions narrow enough to see when spinning exactly at the magic angle.⁵⁸ The reference alumina in fact shows this effect when 2000 scans are collected; the linewidth of the manifold of outer transitions is greater than the spectral bandwidth used (Figure 20). From weighing cutout peaks, other transitions were determined to account for 4.4% of the total intensity of the center peak and the first set of sidebands. The extensive manifold of sidebands from noncentral transitions was not evident in the 200 scans used for spin counting; only the central peak and a sideband on either side were visible. ²⁷Al spectra of the samples with clays are not as symmetrical and are not expected to show this effect. The Al intensities were not corrected for this effect in the standard sample since the error is within the normal uncertainty of NMR measurements and the resulting Si/Al ratios are more reasonable without the correction. Linewidth comparison between the spectra under static (Figure 21a) and MAS (Figure

21b) conditions confirms that the reference spectrum includes only the central transition.

The tabulated peak locations of both the Al and Si MASNMR are presented in Table 5. Since there is strong evidence that kaolinite, with Si/Al ratio of at least 1.1 (theoretically 1 but not likely to be a more perfect clay than our sample kaolinite), is the binder in the 33351-86 catalyst, the amount of Si in the clay fraction is considered to be equal to 1.1 times the amount of Oh Al in the catalyst. After spin counting total Si and determining the Si in the zeolite fraction by difference, the Si/Al ratio of the zeolite fraction of the catalyst can be calculated. The original quantitative Si data of 8 scans each, integrated with the spectrometer hardware (including sidebands) produced numbers which seemed to fit this model.

When the Si measurements were repeated with 64 scans, there was a slight probe tuning problem with the zeolite sample making that value low, but more importantly, the moles Si/g sample calculated from the spectrometer integrated intensities differed by more than expected from the values corresponding to 8 scans. A spectrum with sidebands and only moderate S/N is often more accurately integrated by manually drawing the baseline and weighing paper cutouts of the peaks. This method was tried for both the 8 and 64 scan spectra. The results from these weighings as well as the spectrometer integrations are shown in Table 6 along with the average value for each sample. The latter was calculated as

$$[8(\text{cut}_{64} + \text{int}_{64}) + \text{cut}_8 + \text{int}_8] + 18 , \quad (14)$$

where subscripts denote number of scans, "int" means from spectrometer integration, and "cut" means from paper cutouts.

Table 5. Silicon-29 and aluminum-27 peak locations

Sample ^a	²⁹ Si δ(ppm) from TMS	²⁷ Al δ(ppm) from [Al(H ₂ O) ₆] ³⁺
S115	-112	
αAl ₂ O ₃		8
Kaolinite	-91,+ upfield shoulder	-13
LZY-52	-88.5, -93.7, -99.3, -104.9	56
Model mixture	-91, -91 ^b to -110	59, -13
33351-86	-91, -91 ^b to -120	60, -10
33351-20	-80 ^b to -120	

^aAll samples except alumina uncalcined.

^bBroad peak.

Table 6. ^{29}Si Silicon spin counting - moles Si/gram sample ($\times 10^3$)

Sample	cut & weigh 64 scans	integrate 64 scans	cut & weigh 8 scans	integrate 8 scans	average value ^a
Kaolinite	5.99	6.41	5.03	5.59	6.10
Zeolite	7.02	7.03	7.10	7.67	7.07
Model	6.41	6.19	5.79	6.02	6.26
Catalyst-86	6.15	6.43	5.01	5.42	6.17

^aThe error is estimated to be 8%.

Table 7. Results of silicon and aluminum MASNMR spin counting

Sample ^a	moles Si/g [*] (x10 ³)	moles Al/g ^{**} (x10 ³)	Si/Al ^{***} calculated	Si/Al True value
Kaolinite	6.1	5.4	1.1 ±.1	1.135 ^b
Zeolite	7.1 ^c	3.3	2.0 ±.3	2.37
Model mix	6.26			
clay ^d	4.77	← 4.34	set = 1.1	1.135
zeolite ^e	1.49	0.699	2.1 ±.3	2.37
Catalyst-86	6.17			
clay	3.00	← 2.73	set = 1.1	?
zeolite	3.17	0.698	4.5 ±.6	?

^aAverage values from equation 13 were used for Si data.

^bValue from chemical analysis.

^cThis value is low since the probe had a lower Q for this sample.

^dOctahedral Al assigned to clay, then Si in clay fraction set equal to 1.1 times that.

^eSi in zeolite by difference, Td Al assigned to zeolite.

* Error estimated to be 8%.

** Error estimated to be 10%.

*** Error estimated to be 13%.

Researchers are currently debating under which conditions Al can be quantitatively detected in solid aluminosilicates. Others have performed quantitative Al NMR experiments on static samples to avoid dealing with spinning sidebands. At high magnetic fields with probes that can only spin to 4 kHz, this is absolutely necessary unless one deconvolutes ssb since the ssb are located between the principal Oh and Td peaks and cause considerable overlap. In our 5.2 T field with 8 kHz spinning speed ssb are placed well away from both of the central peaks.

As mentioned earlier, for quadrupolar nuclei the peak intensities are proportional to the number of atoms only for small flip angles, $\pi/12$ of a liquid. At larger angles the intensities of nuclei with larger quadrupolar frequencies are damped relative to those of nuclei with relatively small quadrupolar frequencies and none of them maintain a strictly proportional relationship to the intensity of nuclei in a liquid.⁵⁰

Knowing that the maximum signal for the central transition of the solid occurs at a pulse length, t_p , equal to $1/3$ of the $\pi/2$ pulse for a liquid in the spin $I = 5/2$ case,²⁰ one can adjust the $\pi/12$ pulse length by taking $(1/2)t_p$ or a little smaller to be sure to be in the quantitative region of flip angles. The pulse length was adjusted in this way for this work without using a liquid since the liquid sample changed the Q of the probe. The final flip angle was estimated to be $\sim 8^\circ$ on a liquid using a probe with the same Q. Later a small, dilute $AlCl_3$ sample which did not detune the probe showed a 90° pulse to be 19 μs . The 1 μs pulses were well within the quantitative range.

Others have noted the necessity of plotting intensity of the Oh and Td peaks verses pulse flip angle and directly comparing initial slopes to quantitatively determine the Oh/Td ratio of a physical mixture of zeolite and alumina.⁵⁹ Calculating the ratio of the slopes from points at the same small flip angle effectively cancels the flip angles and one is merely comparing intensities. Essentially, the requirement is merely to measure at a small flip angle.

Table 8. Check on quantitation of ²⁷Al MASNMR

Zeolite

By Weight

$$(\text{g in Mix})/(\text{g Zeolite sample}) = 0.0136/0.0430 = 31.7\%$$

By NMR

$$(\text{Td Al in Mix})/(\text{Zeolite Al}) = 146/440 = 33.2\%$$

error 5%

Kaolinite

By Weight

$$(\text{g in Mix})/(\text{g Kaolinite sample}) = 0.0539/0.0689 = 78.2\%$$

By NMR

$$(\text{Oh Al in Mix})/(\text{Kaolinite Al}) = 907/1152 = 78.7\%$$

error 1%

The quantities of Al detected by NMR in the known mixtures are proportional to the amounts of sample present as shown in Table 8. However, it is acknowledged that this method of checking quantitation does not test whether Td and Oh Al in the same sample are detected equally well.

A further complication is the physical assignment of the Oh and Td peaks themselves. For the uncalcined zeolite and clay used as the model compound in this work, it is true that the Oh peak is produced solely by the layer structure Al associated with clay. Similarly the Td peak is uniquely from Al in the zeolite framework. However, the ^{27}Al NMR spectrum of calcined kaolinite is known to contain a peak in the Td position,^{40,53,54} and is reported to have a peak with penta-coordination as well.⁴⁰ In addition, ultrastable Y zeolites which have been formed by various dealumination treatments of Y zeolites are known to form non-framework Td Al as well as the usual nonframework Oh Al as the framework is dealuminated.⁶⁰⁻⁶² Not all of this extra-framework Al is removed by washing. Since the pretreatment of the catalysts of this study is unknown, one can only surmise that the samples have undergone some hydrothermal treatment. If some of the Oh Al is from dealumination, the amount of Al attributed to clay will be overestimated thereby resulting in a Si/Al ratio for the zeolite fraction and $\text{Si}_{\text{zeo}}/\text{Si}_{\text{clay}}$ ratio which are too low.

Another assumption is that the binder of the physical mixture catalyst is purely kaolinite, with Si/Al equal to 1.1. It is much more likely to have other additives as well, perhaps with Si or Al

components. There is no way of knowing the actual Si/Al of the binder fraction.

One technique developed recently which can separate components of the peaks is quadrupolar 2-D nutation ^{27}Al NMR.^{63,64} With 2-DNMR a peak in the Td position was shown to have two components. The F_2 direction of the Fourier transformed spectra shows the chemical shift in ppm. In the F_1 direction, the lineshapes reflect differences in the ratio of quadrupole interaction constants to rf field strength. Al in a zeolite framework, which is a symmetrical environment, has a lower quadrupolar constant than does Td nonframework Al so the two types of Td Al appear separated on the F_1 axis. Since the pulse lengths are varied, this technique does not produce quantitative results, but it could be used to determine whether or not the Oh and Td peaks of the 1-D spectrum are one component peaks.

Another possibility is to try the lengthy process of washing the catalyst then repeating the ^{27}Al measurements. If some of the Oh Al is from dealumination of the zeolite, some of it may be removed by the washing, thereby increasing the apparent Si/Al ratio of the zeolite fraction as determined by this method.

SUMMARY

Two commercial hydrocracking catalysts were investigated by solid-state ^{29}Si and ^{27}Al MASNMR. When ^{29}Si MASNMR revealed that the catalyst which was a physical mixture of zeolite and binder seemed to contain kaolinite as the binder, a model mixture was used to test a method of quantifying the amount of zeolite in that catalyst mixture and determining the Si/Al ratio in the zeolite fraction. Using spin counting to quantify Si/g, tetrahedral Al/g, and octahedral Al/g, a method was devised which relies on the following facts: kaolinite has only Oh Al, kaolinite has a Si/Al ratio of ~ 1.1 , and zeolite frameworks have only Td Al. To the extent that the model represents the true catalyst, a lower limit of the fraction of zeolitic Si and of the Si/Al ratio of the zeolite fraction can be determined by this method.

In the second catalyst studied, which contained zeolite formed as an intergrowth of the clay, the kaolinite peak was not visible in the ^{29}Si spectrum. If kaolinite is the binder of that sample it has undergone sufficient hydrothermal treatment that it is likely to contain Al in Td as well as Oh environments which will produce more error in measurements by this method.

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