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[10] NH_2iPr (0.68 mL, 8.0 mmol) with $HClO_4$ acidification (pH 2.0) was added to a solution of $Na_8[Mo_{36}O_{112}(H_2O)_{16}]\cdot 58H_2O$, (0.4 g, 0.06 mmol) synthesized according to the method in reference [9], in H_2O (78 mL). Photolysis (two weeks; 500 W superhigh-pressure mercury lamp) of the resulting solution after degassing led to a deep blue solution. After cooling at 4 °C rhombohedral plate crystals of **1**, obtained as uniform crystalline material after 4 weeks, were collected by filtration and dried. Yield: 0.18 g (50% based on Mo), elemental analysis calcd (%): N 0.59, C 1.51, H 1.80; found: N 0.99, C 2.22, H 1.98. The higher N, C, and H values than expected from the given formula are presumably attributed to the high adsorption (corresponding to about six molecules per **1**) of $[NH_3iPr]ClO_4$ on the highly water-soluble crystalline material of **1**, as suggested by the presence of Cl in the elemental analysis. IR (KBr pellet): $\tilde{\nu} = 1.618$ (m, $\delta(H_2O)$), 972(m), 908(w), 746(s), 631(s), 555(s) cm^{-1}; λ(nm) (ε_M) = 747 ($1.3 \times 10^5\,L\,mol^{-1}\,cm^{-1}$), 1076 ($1.0 \times 10^5\,L\,mol^{-1}\,cm^{-1}$).
[11] Space group $P2_1/n$, $a = 32.316(1)$, $b = 18.021(1)$, $c = 58.618(2)$ Å, $\beta = 98.388(2)°$, $V = 33771(2)$ Å^3, $Z = 2$, $\rho = 2.34\,g\,cm^{-3}$, $\mu = 26.4\,cm^{-1}$, $F(000) = 22560$. Crystal dimensions $0.2 \times 0.1 \times 0.02$ mm. Crystal was coated with paraffin oil and mounted in a 20 micron nylon loop material. Intensity data were measured on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71071$ Å) at 103 K. Data collection using a ω scan at a scan width of 0.3° and $\chi = 45°$ in five runs (with 600 frames for each) of $-75.0° < \omega < 105°$, $\phi = 0°$; $-55.0° < \omega < 125°$, $\phi = 0°$; $-55.0° < \omega < 125°$, $\phi = 90°$; $-55.0° < \omega < 125°$, $\phi = 180°$; $-55.0° < \omega < 125°$, $\phi = 270°$. A crystal-to-detector distance was 95.35 mm. The detector swing angle for the first run was 15.5° and for other runs 35.5°. A total of 78689 reflections was collected of which 325154 unique reflections ($R_{int} = 0.098$) were used. Lorentz polarization factors were applied and an empirical absorption correction using equivalent reflections was performed with the program ABSCOR (T. Higashi, *Program for Absorption Correction*, Rigaku Corporation, Tokyo, **1995**). The structure was solved by direct methods and refined (1817 parameters) by using the TEXSAN software package (SHELXS97) to $R = 0.094$ for a full-matrix least-squares refinement procedure (29739 unique reflections with $I > 3\sigma(I)$). Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-171234.
[12] The X-ray powder diffraction (XRD) pattern of **1** shows (002), (010), and (200) peaks at $d = 30$, 18, and 16 Å respectively, and an intensive angle peak at $d = 28$ Å. The latter peak corresponds to one of the diameter spacings (35–23 Å) for the car-tire-shaped ring and seems to be characteristic of the mesostructured nature, since $Na_8[Mo_{36}O_{112}(H_2O)_{16}]\cdot 58H_2O$ as a starting material gives no low-angle peak at $2\theta < 5°$ ($Cu_{K\alpha} = 1.54056$ Å).
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Direct Evidence for the Nonrandom Nature of Al Substitution in Zeolite ZSM-5: An Investigation by ^{27}Al MAS and MQ MAS NMR[**]

Oc Hee Han,[*] Chang-Sam Kim, and Suk Bong Hong[*]

Many important properties of aluminosilicate zeolites, most notably their Brønsted acidity and hence catalytic performance, depend primarily on the framework Al content, that is, the extent of isomorphous substitution of Si by Al. However, even in materials with the same framework structure and composition, the location of catalytically active sites can differ according to the manner in which Al atoms are spatially distributed over the available tetrahedral sites (T-sites) in a given zeolite lattice. Therefore, detailed knowledge of the local ordering of Al atoms in these microporous materials is the starting point for systematically manipulating the distribution of acidic sites within the pore architecture.

Zeolite ZSM-5 (MFI topology) is one of the industrially most important zeolites. It typically crystallizes in the orthorhombic space group *Pnma*, and 12 crystallographically distinct T-sites with equal populations exist in the ZSM-5 framework.[1] A fundamental, recurring question regarding this type of zeolite structure is whether the acidic sites (that is, Al atoms on T sites) are spatially ordered. Recently, Olson et al.[2] carried out Rietveld refinement of synchrotron powder X-ray diffraction (XRD) data on a Cs-ZSM-5 zeolite with 5.8 Al atoms per unit cell (Si/Al = 15.6) and showed that Cs^+ ions are located in three different extraframework sites. They speculated that Al atoms may be unequally distributed over the 12 distinct T-sites of the ZSM-5 framework. However, because of the very similar scattering powers of Si and Al for X-rays and the difficulties in obtaining large single crystals, especially at high Al concentrations, it is very difficult, or even impossible, to directly locate Al atoms by conventional diffraction methods. Although many quantum chemical studies have also addressed this issue,[3] the nature of

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[*] Prof. S. B. Hong
Division of Chemical Engineering
Hanbat National University (HNU)
Taejon 305-719 (Korea)
Fax: (+82) 42-821-1593
E-mail: sbhong@hanbat.ac.kr

Dr. O. H. Han
Magnetic Resonance Team
Korea Basic Science Institute (KBSI)
Daejeon 305-333 (Korea)
Fax: (+82) 42-865-3419
E-mail: ohhan@comp.kbsi.re.kr

Dr. C.-S. Kim
Multifunctional Ceramics Research Center
Korea Institute of Science and Technology (KIST)
Seoul 130-650 (Korea)

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Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

the spatial distribution of Al atoms over the 12 ZSM-5 T-sites still remains unresolved, except that there is no strong energetic driving force for nonrandom Al distribution in the ZSM-5 structure. As was earlier indicated by Barrer,[4] on the other hand, zeolites are metastable phases that are synthesized hydrothermally under kinetic control. Therefore, if differences in the relative Al substitution energy for each of the 12 T-sites are not too large, the actual Al distributions in real ZSM-5 materials will be strongly influenced by the synthesis conditions. Here we present the results of ^{27}Al MAS and MQ MAS NMR measurements on a series of as-made ZSM-5 zeolites with 0.4–6.4 Al atoms per unit cell (Si/Al = 250–14) that provide the first direct evidence that the substitution of Al atoms on the T-sites of the ZSM-5 framework during the crystallization process occurs in a nonrandom manner.

Figure 1 shows the ^{27}Al MAS NMR spectra of a series of as-made ZSM-5 zeolites with different Si/Al ratios. All spectra consist of a two peaks at $\delta = 51.0-51.4$ and $52.9-53.9$. The same result was also obtained for the ^{27}Al MAS NMR spectra (not shown) of the corresponding calcined ZSM-5 samples, although these two peaks are shifted slightly downfield relative to the as-made samples. Hence, it is clear that the two peaks of each spectrum in Figure 1 result from the presence of at least two crystallographically distinct Al sites in the ZSM-5 framework, rather than arising from possible interactions between the framework Al atoms and encapsulated tetrapropylammonium (TPA) ions.[5, 6] Of particular interest is the observation that the intensity ratio of the two peaks for the as-made ZSM-5 samples increases continuously with decreasing Si/Al ratio in the zeolite (Table 1). This suggests that the extent of Al substitution on each of the 12 T-sites in ZSM-5 differs according to the Si/Al ratio of the zeolite synthesis mixture.

A logical next step would be to ascertain whether two or more crystallographically distinct Al sites really contribute to the intensities of the respective peak maxima of the six ^{27}Al MAS NMR spectra in Figure 1. To answer this question, we carried out ^{27}Al MQ MAS NMR experiments on all the ZSM-5 samples. Figure 2 shows the 2D ^{27}Al 3Q MAS NMR spectrum of an as-made ZSM-5 with Si/Al = 79. In general, the axis F_1 in MQ MAS NMR spectra after appropriate shearing consists of isotropic lines accompanied by second-order quadrupolar shifts for the central transition $\delta_{QS(1/2)}$, with their respective anisotropic quadrupolar features on the axis

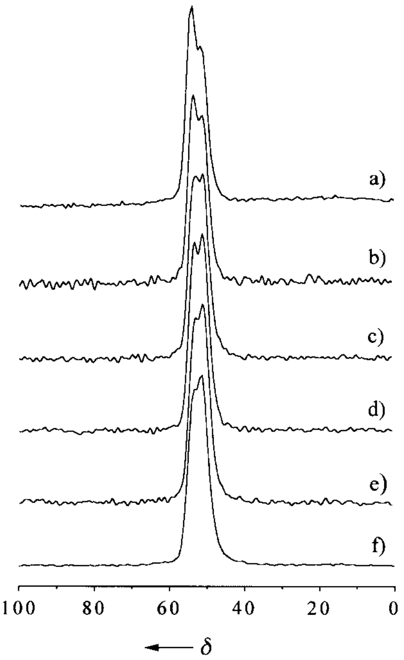

Figure 1. ^{27}Al MAS NMR spectra of as-made ZSM-5 zeolites with different Si/Al ratios: a) 250, b) 136, c) 79, d) 47, e) 27, and f) 14.

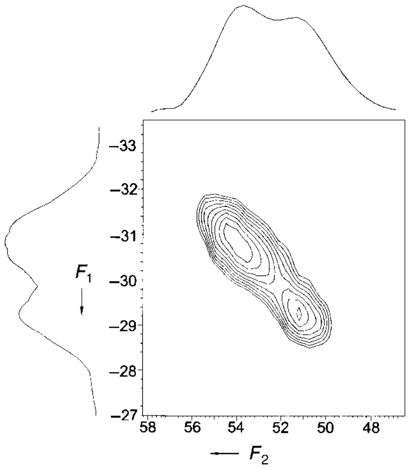

Figure 2. 2D ^{27}Al 3Q MAS NMR spectrum of an as-made ZSM-5 zeolite with Si/Al = 79 (1.2 Al atoms per unit cell). Two-peak maxima of tetrahedral Al atoms are clearly visible. The corresponding ^{27}Al MAS NMR spectrum is given at the top of the 3Q MAS NMR plot.

Table 1. ^{27}Al MAS NMR chemical shift data for as-made ZSM-5 zeolites with different Si/Al ratios.

Sample	Si/Al[a]	Al/uc[a]	Peak I			Peak II			Intensity ratio
			δ_{obs}[b]	δ_{iso}[c]	$C_{Q\eta}$[d] [MHz]	δ_{obs}[b]	δ_{iso}[c]	$C_{Q\eta}$[d] [MHz]	(A_{II}/A_{I})[e]
ZSM-5(I)	250	0.4	53.9	55.1	1.7	51.4	52.3	1.6	0.73
ZSM-5(II)	136	0.7	53.5	55.7	1.6	51.1	52.3	1.5	0.80
ZSM-5(III)	79	1.2	52.9	55.4	1.6	51.0	52.3	1.5	1.04
ZSM-5(IV)	47	2.0	53.1	55.5	1.6	51.0	52.3	1.5	1.11
ZSM-5(V)	27	3.4	53.0	54.8	1.7	51.0	52.2	1.6	1.20
ZSM-5(VI)	14	6.4	53.3	54.9	1.7	51.4	52.3	1.6	1.41

[a] Al atoms per unit cell, determined by elemental analysis. [b] Observed chemical shifts at 9.4 T; the error range is ±0.3 ppm. [c, d] Isotropic chemical shifts and second-order quadrupole effects, respectively, estimated from the experimental ^{27}Al MQ MAS NMR data (for example, see Figure 2). The error range for each δ_{iso} is ±0.3 ppm, and that for $C_{Q\eta}$ ±0.2 MHz. [e] Determined from curve deconvolution of the ^{27}Al MAS NMR spectrum of each ZSM-5 sample by using the Origin curve-fitting software.

F_2. This allows us to estimate the distribution of isotropic chemical shift δ_{iso} and second-order quadrupolar effect ($C_{Q\eta} = C_Q(1 + \eta^2/3)^{1/2}$) from the spectra, where C_Q and η are quadrupole coupling constant and asymmetry parameter, respectively.[7] A close inspection of the tilted, ellipsoidal contours in Figure 2 reveals that their slopes have some distribution, but the average is close to a factor of $-17/31$ (for $I = 5/2$).[7b] This clearly shows that the ^{27}Al 3Q MAS NMR spectrum in Figure 2 consists of overlapped signals from the many sites, whereby differences in δ_{iso} rather than in $C_{Q\eta}$ are the critical factor governing the spectral pattern. Essentially the same result was observed for the other five as-made ZSM-5 zeolites with different Si/Al ratios. To date, there is one ^{27}Al MQ MAS NMR study on ZSM-5 that showed tilted contours similar to those in Figure 2.[7a] However, the interpretation of the spectra differed from our analysis.

Although structural data on as-made ZSM-5 zeolites are not currently available in the literature for the entire Si/Al range studied here, the detailed crystal structures of two as-made samples with Si/Al = 86 and 11.9 were determined by single-crystal X-ray diffraction.[8] Since the Si/Al ratios of these two zeolites are similar to those of ZSM-5(III) and ZSM-5(VI), respectively (Table 1), we attempted to simulate their ^{27}Al 3Q MAS NMR spectra using the reported crystallographic data and compared the results with the experimental spectra of ZSM-5(III) and ZSM-5(VI). Table 2 lists δ_{iso}, C_Q, and η for the 12 possible Al sites in an as-made ZSM-5 with Si/Al = 86, calculated from the crystallographic data of Olson et al.[8a] by using the equation of Lippmaa et al.[9] and the point-charge model.[10] The $C_{Q\eta}$ and $\delta_{QS(1/2)}$ values calculated from C_Q and η[7b] are also given in Table 2. With the δ_{iso} and $\delta_{QS(1/2)}$ data, in turn, shifts of center of gravity on the axes F_1 and F_2 (δ_{CG1} and δ_{CG2}) were determined,[7b] and the 3Q MAS NMR spectrum of an as-made ZSM-5 with Si/Al = 86 was finally simulated with the 12 sets of δ_{CG1} and δ_{CG2} data (Figure 3). The overall scattering pattern of the data and the chemical shift ranges in this simulated spectrum match well with those of the experimental spectrum (Figure 2) of the ZSM-5(III) sample with Si/Al = 79. A quite similar result was obtained for the comparison of the simulated 3Q MAS NMR spectrum of as-made ZSM-5 with Si/Al = 11.9 and the experimental spectrum of ZSM-5(VI) (see Supporting Information). Figure 3 also shows that the expected intensities are not the same for the 12 possible Al sites with different $C_{Q\eta}$ values (Table 2), although they are assumed to have equal populations, since the intensity of MQ MAS NMR lines is a function of $C_{Q\eta}$.[7a, 11] Thus, the fact that the intensity pattern in Figure 3 differs from that in Figure 2 could be another indication of nonrandom Al distribution over the 12 ZSM-5 T-sites. If the 12 NMR lines indicated in the simulated spectrum are merged into two sets of contours like those found in the experimental spectrum, on the other hand, they can be divided into R and L groups, that is, sites T3, T4, T8, and T11 with a range of average T-O-T angles between 158.7 and 160.6° on the right, and the other eight T-sites, with a range of average T-O-T angles between 150.4 and 156.4°, on the left.[8a] From the $C_{Q\eta}$ values listed in Table 2, the average $C_{Q\eta}$ parameters for the R and L groups were calculated to be 1.19 and 1.21 MHz, respectively. These values are in reasonable agreement with the experimental values for the two peaks in the ^{27}Al MAS NMR spectrum of ZSM-5(III) (see Table 1), and this is further support for the reliability of the simulation. Since the intensity ratio of the two peaks in Figure 1 decreases with increasing Si/Al ratio in the zeolite,[12] the Al atoms in ZSM-5 samples with a lower Si/Al ratio (probably < 50) are preferentially located on T-sites with larger T-O-T angles, and vice versa in zeolites with higher Si/Al ratios.

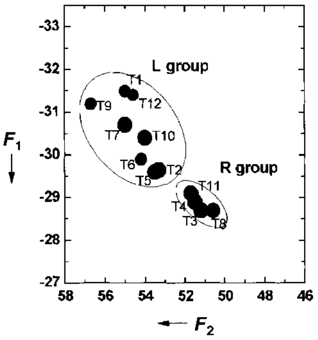

Figure 3. ^{27}Al 3Q MAS NMR spectrum of an as-made ZSM-5 sample with Si/Al = 86 (1.1 Al atoms per unit cell), simulated by using the calculated δ_{CG1} and δ_{CG2} values in Table 2. The dot sizes represent the expected intensity of the 12 possible Al sites with different $C_{Q\eta}$ values listed in Table 2, which are assumed to have equal populations.

Table 2. Calculated NMR parameters for Al atoms in the 12 distinct T-sites of an as-made ZSM-5 with Si/Al = 86 (1.1 Al atoms per unit cell).

Possible Al site	δ_{iso}[a]	C_Q [MHz][b]	η[c]	$C_{Q\eta}$ [MHz][d]	$\delta_{QS(1/2)}$[e]	δ_{CG1}[f]	δ_{CG2}[g]
T1	56.6	1.59	0.62	1.70	– 1.58	– 31.5	55.0
T2	53.8	0.88	0.49	0.91	– 0.46	– 29.6	53.3
T3	52.1	0.79	0.80	0.87	– 0.42	– 28.7	51.2
T4	52.3	1.14	0.51	1.20	– 0.78	– 28.9	51.5
T5	53.8	0.70	0.85	0.78	– 0.34	– 29.6	53.5
T6	54.4	1.55	0.47	1.60	– 0.21	– 29.9	54.2
T7	55.6	0.97	0.81	1.10	– 0.63	– 30.7	55.0
T8	51.7	1.35	0.40	1.40	– 1.06	– 28.7	50.6
T9	56.8	0.49	0.51	0.51	– 0.14	– 31.2	56.7
T10	54.9	1.23	0.44	1.30	– 0.89	– 30.4	54.0
T11	52.6	1.23	0.29	1.30	– 0.86	– 29.1	51.7
T12	56.3	1.61	0.82	1.80	– 1.75	– 31.4	54.6

[a] Isotropic ^{27}Al chemical shifts calculated from the average T-O-T angles of the 12 distinct T-sites in an as-made ZSM-5 with Si/Al = 86 (1.1 Al atoms per unit cell), reported by Olson et al.,[8a] by using the equation of Lippmaa et al.[9] [b] Quadrupole coupling constants calculated from the coordinates of the four nearest oxygen atoms of each T-site, given by Olson et al.,[8a] by using the point-charge model.[10] [c] Asymmetry parameters calculated by the same method described in [b]. [d] Second-order quadrupole effects ($C_Q(1 + \eta^2/3)^{1/2}$) calculated by using the C_Q and η values listed in this table. [e] Second-order quadrupolar shifts of the central transition calculated from $C_{Q\eta}$ in this table by using Equation 26c in ref. [7b]. [f] Shifts of center of gravity on the F_1 axis of a simulated 3Q MAS NMR spectrum, calculated from the $C_{Q\eta}$ and δ_{iso} values given in this table by using Equation 70 in ref. [7b]. [g] Shifts of center of gravity on the F_2 dimension of a simulated 3Q MAS NMR spectrum, calculated by using Equation 71 in ref. [7b].

In conclusion, we have demonstrated that the preference of Al atoms for particular T-sites in as-made ZSM-5 zeolites depends strongly on the framework Si/Al ratio, that is, the extent of Al substitution, although some differences could exist between zeolites synthesized in hydroxide and fluoride media in this respect. Further study is necessary to determine the underlying mechanisms of this intriguing behavior. However, the overall NMR results presented here strongly suggest that the substitution of Al atoms into the ZSM-5 framework during the crystallization process may be kinetically, rather than energetically, controlled. This led us to believe that the substitution patterns of other heteroatoms (e.g., B, Ga, Ti, etc.) in the ZSM-5 framework would also be nonrandom, although they may differ in manner from Al substitution. In fact, recent neutron powder diffraction studies on TS-1, the titanosilicate analogue of ZSM-5, showed that Ti atoms are not uniformly distributed over the 12 ZSM-5 T-sites.[13] Finally, it is of interest whether our concept can be applied to other important high-silica materials with multiple T-sites such as zeolites β and MCM-22.[1]

Experimental Section

Six ZSM-5 zeolites with different Si/Al ratios were synthesized by using NH_4F (+98%, Aldrich) and TPABr (98%, Aldrich) in fluoride media to minimize the possible influence of connectivity defects on the distribution of Al in the ZSM-5 framework, according to procedures described elsewhere.[14] The Si/Al ratio in the final product was varied by adjusting the amount of $Al(NO_3)_3 \cdot 9H_2O$ (99%, Wako) that was added to the synthesis mixture as Al source. Amorphous silica (Aerosil 200, Degussa) was used as Si source. All ZSM-5 zeolites prepared here were phase-pure and highly crystalline (powder XRD, Rigaku Miniflex, $Cu_{K\alpha}$ radiation). The Si/Al ratios of these six as-made samples were analyzed in the Analytical Laboratory of KIST. The absence of any detectable line at $\delta \sim 0$ in the ^{27}Al MAS NMR spectra (Figure 1) indicates that all the Al atoms in these samples are isomorphously incorporated into the T-sites of the ZSM-5 framework. Also, thermogravimetric and differential thermal analyses (TA Instruments SDT 2960) reveals that they contain 3.8–4.3 TPA cations per unit cell.

The ^{27}Al MAS NMR spectra were recorded on a Bruker DSX 400 NMR spectrometer that operates at a ^{27}Al frequency of 104.27 MHz and a spinning rate of 13 kHz. The spectra were obtained by acquisition of 300–400 pulse transients, which was repeated with a $\pi/12$ rad pulse length of 0.8 μs and a recycle delay of 1 s. The ^{27}Al chemical shifts are referenced to a 1 N $[Al(H_2O)_6]^{3+}$ solution. The 2D ^{27}Al 3Q MAS NMR spectra were recorded on a Varian INOVA 400 NMR spectrometer by the two-pulse z-filtered procedure with rotor synchronization[15] at a spinning rate of 10 kHz, with an excitation pulse of 6 μs and a conversion pulse of 1.8 μs for an rf field strength of 84 kHz. For each t_1 384 or 768 scans were accumulated, and t_1 was incremented 64 times.

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[12] We also considered the possibility that differences in the C_Q value for the specific Al sites in our ZSM-5 samples could produce significant changes in the intensity ratio of the respective ^{27}Al MAS NMR peaks in Figure 1. We calculated possible intensity variations for four ZSM-5 samples with Si/Al = 11.9–300 using the reported crystallographic data, according to a method available in the literature (for example, see D. Massiot, C. Bessada, J. P. Coutures, F. Taulelle, *J. Magn. Reson.* **1990**, *90*, 231–242). The extent of intensity variation was less than 3.5% in all four cases, and no correlation with the Si/Al ratio of the ZSM-5 samples could be observed. Thus, differences in the C_Q value for the specific Al sites have little effect on the intensity ratio of the respective two ^{27}Al MAS NMR peaks.

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A New Approach to Osmium-Catalyzed Asymmetric Dihydroxylation and Aminohydroxylation of Olefins**

Malin A. Andersson, Robert Epple, Valery V. Fokin,* and K. Barry Sharpless*

Osmium-catalyzed asymmetric dihydroxylation (AD) of olefins using cinchona alkaloid derived ligands is known for its exceptional scope and reliability across nearly the entire

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[*] Prof. V. V. Fokin, Prof. K. B. Sharpless, Dr. M. A. Andersson,
Dr. R. Epple
Department of Chemistry
and The Skaggs Institute for Chemical Biology, BCC-315
The Scripps Research Institute
10550 N. Torrey Pines Rd.
La Jolla, CA 92037 (USA)
Fax: (+1) 858-784-7562
E-mail: fokin@scripps.edu, sharples@scripps.edu

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