Poster

Determining Active Sites in Zeolite Structures Using Anomalous Diffraction at the Al K-edge

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The organization of Al atoms in zeolites, alongside their topology, is a critical parameter that defines the presence and behaviour of catalytically active centres. Al atoms introduce a negative charge in the zeolitic lattice, which needs to be balanced by extra- framework counter-ion species serving as active sites, including acid (protons) and redox (transition metal ions) sites [1]. In Al-rich zeolites, Al-O-Si-O-Al sequences dominate the structural organisation of a framework and are responsible for stabilizing divalent cations. In Si-rich zeolites, Al atoms can be present as single Al atoms, Al pairs, and close unpaired Al atoms. Single Al atoms can stabilize monovalent species, Al pairs, Al-$(SiO_2)_2$-Al sequences are balanced by bare divalent cations or provide proton proximity in acid sites [2,3]. When close Al atoms are present, Al-$(SiO_2)_3$-Al sequences can accommodate complexes of divalent cations. Regardless of the chemical composition of the sample, in the case of Si-rich zeolites (Si/Al > 10), the distribution of Al can be influenced by synthesis conditions. This offers a robust tool for customizing the zeolite structure, determining the prevalent type of desired active centres, and thus fine-tuning its catalytic properties.

The discrimination of aluminium from silicon in zeolite framework and recognizing T-site dependent reactivity of zeolites is a long- standing question in zeolite science. There is currently no general method that can identify directly which T sites in a zeolite framework structure are occupied by aluminium. The aluminum substitution for silicon is usually only partial (typical zeolite catalysts have Si:Al ratios larger than 5) and the scattering power of these two elements is very similar. Therefore we have developed anomalous X-ray powder diffraction (AXRD) methodology [4] across the Al K edge (1.56 keV), where the aluminum scattering factor changes drastically while that of silicon remains unchanged. Those changes in the scattering power highlight aluminum in the structure. While the spectroscopic methods are short-range probes and can report only on local environment around the aluminum position, AXRD can collect information of the long-range structural order of Al:Si distribution and consequently unambiguously pinpoint aluminum's position in the framework. Because the diffraction limit at 1.56 keV corresponds to a *d* spacing of only 3.98 Å, the data from a conventional measurement were combined with those at energies near the X-ray absorption edge to quantify the aluminum concentration at all T sites in the refined zeolite structure.

H-ZSM-5 zeolite framework holds 12 T-atoms in *Pnma* unit cell. The structure comprises 3D network of intersecting 10 ring straight and sinusoidal channels. Two samples with similar chemical compositions (Si/Al equals 18 and 15 respectively) but the different concentration of Al pairs (9% and 82%) and different catalytic properties could be determined quantitatively and unambiguously. The former sample display aluminum concentrated at the several T-sites located at the channel intersection that corroborates with the previous studies and synthesis conditions.

Latter sample is more active in propene oligomerization, since the proximity of protons controls the rates of adsorption and desorption steps, formation of intermediates, and the product release. Co-species that may be hosted by the second structure play a pivotal role in their exceptional catalytic performance in hydrocarbon SCR-NO_x reactions in the presence of water. The typical sites for bare divalent cations have been agreed based on spectroscopic studies to sit at the elongated 6-rings formed from two-folded 5-rings (α site) and at the deformed 6-rings (β site). α site corresponds to 25–40% of the total Co loading in the highly exchanged ZSM-5 and was suggested to be located at the wall of the straight channel while β site (50–70%) occupies the intersection of the straight and sinusoidal channels. The minor boat-shape γ site is formed from the 5- and 6-MRs in the sinusoidal channel. AXRD studies however revealed aluminum pairing in the straight channel that may be siting for β site. There finding show that the definition of cationic sites coined by spectroscopic studies is correct, however their situation in long-range periodic structure remain elusive. We believe that AXPD at the Al K edge may be right technique to reevaluate other zeolite framework structures hosting Al-paired distribution.

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