

Spatial Differentiation of Aluminium Siting by the Single-Atom Adsorption Sites in Zeolite by Electron Microscopy

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Over past years, the synthesis of cage-like porous zeolite frameworks has been frequently researched due to the size of their channels and cavities which are in the range of typical for small organic molecules of industrial interest (5–12 Å) reported. Over 230 types in this family have gained industrial importance owing to their outstanding properties such as high surface area, size and shape selectivity; controllable adsorption capacities; and stability. In the aluminosilicate framework, small quantities of trivalent aluminium (Al) atoms are incorporated into the silicate (Si–O) matrix at tetrahedral sites (T sites). Tetrahedrally coordinated by oxygen (O) atoms, this key aliovalent element Al introduces negative charge into the framework of zeolites. The H⁺ cation covalently binds to one of the oxygens of the AlO_{4/2}⁻ units, which sp²-hybridises to be one plane ≡Al–O(H)–Si≡, realising the polarizing effect of Si/Al. In this process, the charge balance of neutrality is achieved and a catalytically active acidic site (H⁺, Na⁺, NH₄⁺, etc.) bonded to oxygen is generated. This is also known as the Brønsted acid site (BAS) [1]. With the aluminium atoms siting in the framework of zeolite, these BASs can be used as an anchor point for the immobilisation of extra-framework single metal sites or controlled metal clusters. The orthorhombic unit cell of the zeolite ZSM-5 with possesses 12 distinct crystallographic T sites.

Thus, the H⁺ cations can be replaced by a metal ion through ion-exchange and as a result, form immobilised external single metal sites or controlled metal clusters [2–5]. Another way for foreign metal immobilization to take place is the formation of a covalent bond between the metal and oxygen via a dehydration step during synthesis. Since the accessibility and catalytic properties of zeolite depend on each BAS's local environment, it is important to know the exact locations of BAS and the number of BAS in these locations. However, research over time has reported the difficulty of locating BASs due to the randomness of aluminium atoms [6] which are affected significantly by Si/Al ratio and the synthesis conditions.

Recording high-resolution annual dark-field scanning transmission electron microscopy (ADF-STEM) was almost an impossible task because of zeolites' tremendous sensitivity to the electron beam [7]. Under the electron beam, a transition from crystal to amorphous structure is induced very rapidly. This results in damage caused by electron beam irradiation, as an accelerating voltage can cause subtle thermal and chemical change. With the goal to contribute to this field's long-lasting issue, the low-dose high-angle ADF-STEM and electron energy-loss spectroscopy can be applied to in-situ characterise the BASs by replacing them with silver (Ag) atoms.

I will present our discovery and technical detail regarding the single-metal sites, namely the use of STEM to image the atomic arrangement of zeolite framework and guest elements, and deducing Al–O's position and bond angle; it is approximately halfway between a tricoordinated and tetracoordinated

environment. Figure 1 demonstrates different contrast between pristine ZSM-5 and Ag-ZSM-5. It shows the highly crystalline microporous structure with isolated heavy silver-containing species near the sinusoidal channels. Moreover, the statistical analysis of local maximal peaks caused by the contrast of doped metal can be found by using a gaussian peak, there are silver sites located on another 10-membered ring adjacent to the specific BAS. STEM imaging and electron diffraction patterns are also consistent with the structural model which derived from synchrotron X-ray diffraction refinement. This finding of silver sites indicates that the distribution of aluminium surrounding these sites is periodical [8].

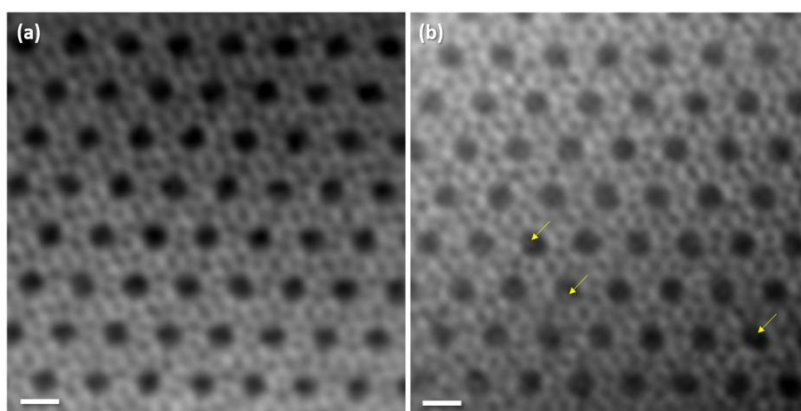


Figure 1. Aberration-corrected HAADF-STEM images of (a) Pristine ZSM-5 and (b) Ag-ZSM-5 along the [010] axis (scale bar: 10 nm).

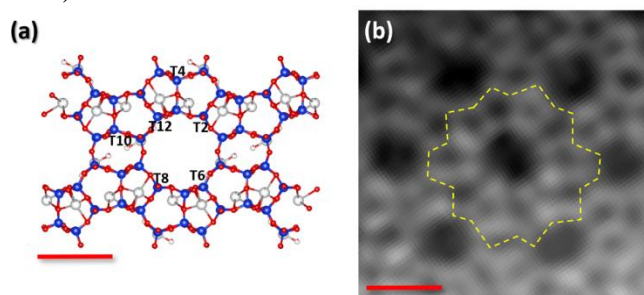


Figure 2. (a) A structural model based on SXRD refinement, blue: Si or Al atoms as the TO_4 tetrahedra, and grey: potential positions of silver ions. (b) Higher magnification of HAADF-STEM image of Ag-ZSM-5; yellow dotted line label as a cyclic annular (scale bar: 8.15 Å).

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[8] The authors acknowledge Mr Raymond Liang (Primax Electronics Ltd.), Dr Jianwei Zheng, Dr Guangchao Li, Mr Zhiyuan Ding (Oxford) and Mr Chu-Ping Yu (Antwerp) for valuable discussions and contributions to this work. P.-L.H is grateful for funding from the Swire Charitable Trust and Ministry of Education (Taiwan). This work made use of the resources of the David Cockayne Centre for Electron Microscopy and Diamond Light Source.