

STRUCTURAL PARAMETERS OF ZEOLITIC CATALYSTS (FAUJASITE NaX AND NaY) WITH CHEMISORBED METHYL GROUPS BY NEUTRON DIFFRACTION AND ¹³C MAS NMR

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Nature of acid or basic sites, their amount and distribution of their strength in the zeolitic lattice belong to the most important problem of surface chemistry. The aim of our study was to estimate the location of chemisorbed species in the lattice and to elucidate the role of lattice oxygen types in chemisorption. We have dedicated to carry out our experimental study on well-developed crystals of NaX and NaY with high content of sodium cations and with low content of defects and decationation. Distribution of chemisorbed methyl groups and sodium cations in the structure of NaX and NaY zeolites was studied by neutron diffraction and NMR technique. Chemisorbed methyl groups were prepared in the structure by chemical reaction of methyl iodide with reactive sodium cations available in SII and SIII position of faujasites. The polarized covalent bond of methyl carbon to lattice oxygen resembles methoxy compounds as demonstrated by ¹³C NMR signals of chemisorbed surface species at 54 and 56 ppm TMS for NaX and NaY, respectively. Changes in the distribution of structural sodium cations in the lattice after chemisorption of methyl cations has been detected. The location of methyl groups was also estimated. The location at O1 lattice oxygen type was found to be most probable for NaY. Nuclear densities of chemisorbed methyl groups were detected in NaX at O1 and O4 lattice oxygen.

Keywords: NEUTRON DIFFRACTION, ZEOLITES, CHEMISORBED METHYL GROUPS

THE DESIGN OF LIGANDS FOR METAL SURFACE ENGINEERING

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Ciba's Irgacor 419, 3-(4-methylbenzoyl)-propionic acid and related molecules are good corrosion inhibitors for steel. It has been proposed [1] that modification of surface properties by molecules of this type depends on 'multisite' attachment involving a combination of primary (metal-donor) and secondary (hydrogen) bonds between the ligand and oxide surface. High surface complex stability will result when the free energy associated with the conformation of the complexed ligand is similar to that of the 'free' molecule in solution.

In order to elucidate the modes of action of existing 'actives' and to design new surface ligands it is necessary to compare enthalpies of solution and surface conformers. The conformational structures of the free molecules have been investigated using the Cerius2 software and empirical forcefields such as COMPASS[2] and energy profiles have been calculated for torsional rotations. It is apparent that there is a strong correlation between the observed crystal structures of closely related molecules in the Cambridge Structural Database and the energy minima in the calculated profiles.

References

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A NEW OPEN-FRAMEWORK ALUMINOPHOSPHATE-OXALATE

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A new three-dimensional aluminophosphate-oxalate with the unit cell formula $[\text{NH}_3(\text{CH}_2)\text{CH}_3\text{NH}_3][\text{Al}_4\text{P}_6\text{O}_{20}(\text{OH})(\text{C}_2\text{O}_4)]\text{H}_2\text{O}$ has been synthesised as part of our studies of mixed organic-inorganic frameworks. It was prepared hydrothermally from an aluminophosphate reaction gel containing oxalic acid and 1,2-diaminopropane. Crystallisation was carried out in a Teflon-lined stainless steel autoclave at 170 °C under autogenous pressure for 4 days. A transparent prismatic single-crystal of 0.225 x 0.045 x 0.038 mm³ size was selected for room temperature intensity data collection on a Nonius Kappa CCD diffractometer with MoK α radiation (3571 unique reflections, R = 4.0%). The product crystallises in triclinic P1 space group with unit cell parameters a = 8.6112(2)Å, b = 9.0958(2)Å, c = 11.3706(2)Å, α = 104.8112(8)°, β = 111.3676(9)° and γ = 94.2482(9)°. The macroanionic $[\text{Al}_4\text{P}_6\text{O}_{20}(\text{OH})(\text{C}_2\text{O}_4)]^{+}$ framework consists of aluminophosphate layers with characteristic 8-member rings, which are linked together with bidentately bonded oxalate units. In each layer there are six crystallographically different PO₄ tetrahedra, two AlO₄ tetrahedra and two AlO₆ octahedra, the later two being connected through C₂O₄ group. Four of six PO₄ tetrahedra consist of three oxygen atoms, which are further bonded to aluminium atoms and one oxygen atom, which forms P = O bond. Two PO₄ tetrahedra have two bridging and two terminal oxygen atoms (P = O or P-OH groups). The structure is stabilised by doubly protonated 1,2-diaminopropane molecules and water molecules, which lie in the structure pores. They balance the negative charge of the framework and form strong hydrogen bonds with the framework oxygen atoms.

Keywords: INORGANIC ORGANIC HYBRID, ALUMINOPHOSPHATE, POROUS MATERIALS SYNTHESIS

TWIN BOUNDARIES: COMPATIBILITY, TWIN-DISPLACEMENT VECTOR, COHERENCY

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Twin boundaries are usually low-energy interfaces of good structural fit. Three important aspects: (i) The concept of compatibility was introduced for ferroelastic twin interfaces by Fousek and Janovec (1969) and Sapriel (1975). It is based on phase transitions obeying group-subgroup relations. Possible extension of this theory to growth twins (e.g. gypsum) and mechanical twins (e.g. calcite or cubic metals) is discussed. It would lead to a modification of Sapriel's classification of twin boundaries: W boundaries are now all rational or irrational interfaces parallel to a twin reflection plane or perpendicular to a twofold twin rotation axis, whereas W' boundaries are all other (usually irrational) twin interfaces. Example: Albite and pericline twins of triclinic feldspars. (ii) Twin displacement vectors are well-known for boundaries of merohedral twins ('fault vectors'). For non-merohedral twins, the 'first' twin displacement vector was postulated by Bragg (1937) for the (021) Baveno twin boundary of K-feldspars (twin glide plane). Calculations of the interface energies of (102) reflection twins of saccharine by Liebermann et al. (1998) lead to an energetic minimum for an irrational twin displacement vector. HRTEM examples will be given for the (112) reflection twins of anatase (Penn and Banfield, 1998) and others. (iii) Coherency: In the literature this term commonly stands for a boundary coinciding with a reflection twin plane free of twinning dislocations. It is, however, based on lattice aspects alone and therefore insufficient. The concept of coherency is reconsidered here under the aspects of compatibility, rationality, twin displacement vector and electrical constraints.

Keywords: TWIN INTERFACES COMPATIBILITY COHERENCY