Computational Modelling of the Acid Sites in Zeolite ZSM-5.

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The requirements for computational methods to reproduce the properties of the acid sites of zeolite ZSM-5 are determined. Then the selected method is used to model the structural, energetic and spectroscopic (IR and ^{1}H NMR) properties of the acid sites of zeolite ZSM-5. The results of calculations point to the heterogeneity of acid sites due to different aluminium sites in zeolite lattice, and due to several probable locations of acid sites around aluminium atoms. The analysis of experimental IR and ^{1}H NMR spectra in combination with our calculations suggests that the experimentally observable mean acidity of zeolite ZSM-5 depends on temperature.

Introduction

Zeolite ZSM-5 is an important shape-selective solid acid catalyst. Information about the location of the catalytically active centres (bridging hydroxyl groups) and their distribution over different possible crystallographic positions has a great importance in understanding the catalytic processes deeper. Unfortunately, the experimental techniques that are usually used to determine the structures of solids (X-ray diffraction) are not well suited for characterisation of the local structure of the acid sites in zeolites. Therefore, the precise location of bridged hydroxyl groups in zeolite ZSM-5 is not known. On the other hand, infrared (IR) and ^{1}H MAS NMR spectroscopy can be used for direct study of the acidic hydroxyl groups in zeolites – different types of hydroxyl groups can be identified and their amount (concentration) can be determined. But still, because the spectral lines consist of signals from a number of different hydroxyl groups coexisting in zeolites (hydroxyl groups in different geometric environments), the properties of the single acid sites are not sufficiently resolved.

Detailed information about the system at the microscopic level can be obtained from computational modelling. Comparison of the modelled results with the experimental data permits the verification of the underlying model, and if the model appears to be valid, an interpretation of the experimental data can be provided.

Methods

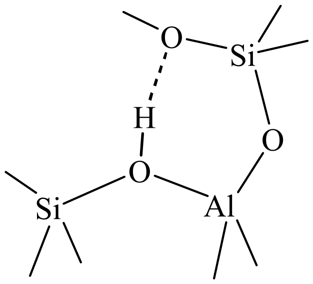
In the orthorhombic form of zeolite ZSM-5 there are 12 crystallographically distinct tetrahedral sites (T-sites) occupied by Si or Al atoms. In the current work, two different aluminium atom locations (at the T6 and the T7 site) were chosen, and all four acid sites that form when protons are attached to one of the oxygen atoms bonded directly to the aluminium atom were studied.

The rational choice would be to model the catalytically active centres in zeolites with ONIOM method [1-3]. The ONIOM method is a type of hybrid method where different levels of sophistication of the quantum chemical description are combined so that the material is modelled with higher accuracy in the region of interest than in regions further away.

Results

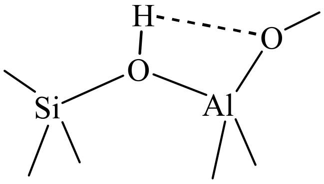
We used the ONIOM method to model the structural, energetic and spectroscopic (IR and ^{1}H NMR) properties of the acid sites in the different crystallographic positions in zeolite ZSM-5. We have made systematic test calculations to examine the performance of the ONIOM method to reproduce the properties of the acid sites of zeolite ZSM-5. The results of our calculations show that the ONIOM method (using HF/6-31G* or B3LYP/6-311+G** method for describing the model system and MNDO method for describing the real system) can differentiate between the crystallographically different acid sites. For reproducing the properties of the acid sites of zeolite ZSM-5 accurately, the size of the model system should extend at least to eight T atoms. It is also important that the computational methods used take into account electron correlation and the anharmonicity of stretch motion of the bridged hydroxyl groups [4].

We have shown also that both types of bridged hydroxyl groups (type 1 and 2) are represented among the studied acid sites in zeolite ZSM-5. In the case of the second type of Brønsted acid site, the hydrogen of the bridged hydroxyl group forms a hydrogen bond with one of the lattice oxygen atoms (Scheme 1).



Scheme 1. Schematic representation of the hydrogen bond formation in case of the second type of Brønsted acid site.

In the case of the first type of bridged hydroxyl groups, the distortion of the local environment around Al indicates that hydrogen atoms in the first type of bridged hydroxyl groups are also influenced by an electrostatic interaction (primarily) with nearby oxygen atoms (Scheme 2).



Scheme 2. Schematic representation of an electrostatic interaction between hydrogen atom in the first type of bridged hydroxyl group and the nearest oxygen of zeolites framework.

The results of calculations point to the heterogeneity of acid sites due to different aluminium sites in zeolite lattice, and due to several probable locations of acid sites around aluminium atoms. The analysis of experimental IR and ^{1}H NMR spectra in combination with current calculations suggests that the experimentally observable mean acidity of zeolite ZSM-5 depends on temperature as the occupancies of protons at various oxygen sites are kinetically controlled and thermodynamic equilibrium is reached at high temperatures [5,6].

References

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