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Cobalt cationic sites in ferrierites: QM/MM modeling

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Abstract

Cobalt(II) sites in ferrierites are already well-known from their catalytic activity, their speciation and properties, however, the knowledge are far from completeness. The following paper presents the first in literature combined QM/MM study to elucidate the structure of these sites. With this end force-field parameters describing Co interactions with ionic shells in zeolite have been tested and the cell size for various Al distributions and Co positioning has been determined. Oxide-type Buckingham parameters are shown to perform better than the carbonate ones. Moreover, Co(II) ions stability in α and β sites with various Al distribution indicates at T1T1 Al substitution in β-site as that the preferred Co(II) siting. DFT results show that the quartet spin state of Co(II) is more stable than the doublet one.

Keywords: Cobalt(II) site; Ferrierite; QM/MM; NO SCR; Buckingham potential

1. Introduction

Transition metal-exchanged zeolites are active catalysts for a variety of chemical reactions [1–4]. Notable examples include the decomposition of NO and N_2O, the selective oxidation, ammoxidation, or aromatization of hydrocarbons, and the selective catalytic reduction of nitrogen oxides (NOx). Among the many factors that may control catalytic activity are the type of metal, the metal–zeolite coordination, the location of the metal in the zeolite, and the zeolite topology. Ferrierite is a particularly active zeolite for many catalytic reactions and any fundamental description of the catalytic ability of these materials must begin with the understanding of the metal active sites nature. Extraframework Co(II) sites in ferrierites are of special interest since they show enhanced activity in NOx reduction by hydrocarbons in the presence of excess oxygen, a highly desirable process in the case of lean-burn engines. Nevertheless, speciation and properties of Co(II) sites in ferrierites is still not well known. Therefore theoretical modeling has been used to elucidate the structure of the site, however, only limited number of works can be found in the literature and no final consensus has been met.

More recent DFT calculations on model cobalt–ferrierite clusters have shown that the relative arrangement of aluminum substitutions in addition to the position of the site within the zeolite determine the observed cobalt infrared, UV–vis or EXAFS signature [5,6]. Nevertheless, even if an assignment of e.g. infrared signature to extraframework site may be observed, cluster DFT calculations clearly show that the overall dependence is more complex and requires the modeling that would take into account extended framework environment of the site. A convenient method, which enables taking into account the influence of periodic lattice on catalytic center is a combined QM/MM technique. Within this approach the nearest surrounding of Co site built of several tetrahedral Si or Al units is described at accurate QM (preferably DFT) level while the periodic framework is treated by less computationally expensive approximate force-field methods. On top of that, prospective modeling of the interaction of cobalt sites with adsorbed molecules of various types additionally justifies the need of devising extended QM/MM methodology. In the present work we apply a variant of QM/MM called combined quantum mechanics/interatomic potential (QM-Pot) functions method [7]. The QM-Pot has been widely tested and shown to provide good description of copper sites in MFI or FER type zeolites and their interaction with adsorbed molecules (for example see Ref. [8–11] and references therein). However, cobalt sites in zeolites have not yet been treated by this

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methodology; hence specific parameters for the interaction of Co(II) with zeolite framework are not available in the literature. Therefore the following paper addresses two problems. Firstly, the appropriate set of cobalt parameters should be selected and tested for performance with respect to properties of Co–ferrierite sites. Force-field parameters for Si, Al and O atoms are available from the precise parameterization [12]. On the other hand, parameters A_{kl} and ρ_{kl} in van der Waals Buckingham-type potential (Eq. (1)), describing short-range repulsion of Co cations with anionic shells, should be determined aiming at final QM/MM model:

$$V_{\text{short-range}} = \sum_{k,l} A_{kl} \exp(-r_{kl}\rho_{kl}^{-1}) - \sum_{k,l} C_{kl} r_{kl}^{-6} \qquad (1)$$

Assessment of Buckingham parameters requires force-field and QM/MM calculations for many types of cobalt sites in ferrierite (Co(II) positioning and Al contents) thus, in addition, our calculation results form a fairly good basis for qualitative analysis of site speciation and properties. Therefore the second goal of the paper is the assessment, description and ranking of cobalt sites in ferrierite.

2. Models and methods

The ferrierite structure (*Immm*) taken from the Cerius^2 [13] database was the basis of the models. There are four types of T-atoms. For each individual site all possible ways of substituting T-atoms with Al have been taken into account. It allowed then to analyze the influence of the distribution of aluminum on cobalt(II) stability and properties. Following Kaucky et al. [14] we have nominated three positions of cobalt cation, namely α, β and γ (Fig. 1). Al atoms were placed only in T-positions which were in the nearest neighborhood of Co(II) hence the models mimicked high Si/Al ratio. This procedure produced 9 models to be tested.

For transition metal ions dispersion term in Eq. (1) can be usually neglected [8]. Hence only Buckingham parameters A_{kl} and ρ_{kl} describing short-range Pauli repulsion were considered while aiming at final QM/MM model. As a trial testing parameters two sets available in literature have been used. The first one (BI) has been optimized for cobalt oxide: $A_{kl} = 684.9$ eV and $\rho_{kl} = 0.3327$ Å [15], while the second (BII) for carbonate: $A_{kl} = 1095.6$ eV and $\rho_{kl} = 0.2863$ Å [16]. Because Co(II) ions always appear inside QM cluster and the strongest interaction with the nearest neighbors are covered by QM calculations less accurate force-field parameters can be used for cobalt cations than for remaining lattice atoms. The main criterion of the choice of parameters for cobalt cation in zeolite was the similarity of geometry obtained with the same set of force-field parameters at MM alone and QM/MM levels, in conjunction with criterion taken by Nachtigallová et al. [9]. Parameters for other atoms (Si, Al, O, H) were adopted after Sierka and Sauer work [12].

To estimate cell parameters we performed constant pressure MM simulation for all models considered in this work and selected the cell size for the most stable one as valid for all other

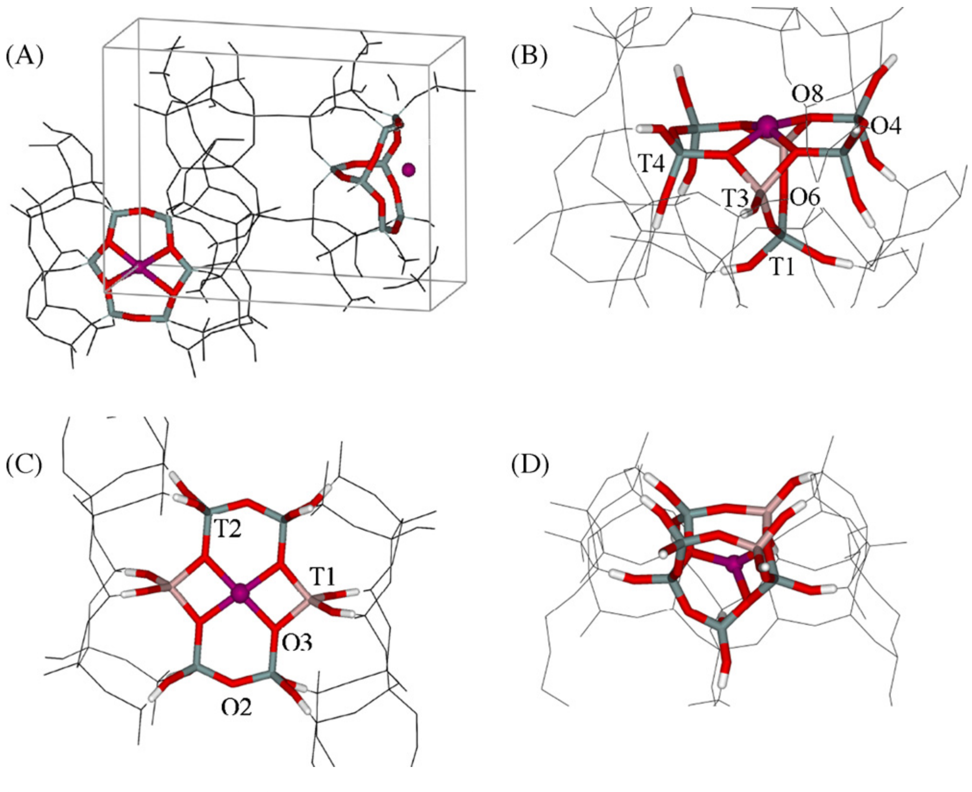

Fig. 1. (A) Positioning of α and β Co sites (relevant for further modeling) in the ferrierite, QM clusters depicted with sticks and balls; (B) α-site; (C) β-site; (D) γ-site (proposed cluster).