



## Characterization of zeolitic intraframework molybdenum sites



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### ABSTRACT

An integrated experimental and computational study was carried out on molybdenum loaded BEA zeolite in order to scrutinize the most stable state of the molybdenum site at various oxidation and hydration states. After a two-step post-synthetic process, the incorporation of Mo ions into the vacant T-atom sites of the SiBEA framework zeolite as mononuclear Mo<sup>VI</sup> centers has been evidenced by combined use of XRD, FTIR and diffuse reflectance UV–vis spectroscopy. The consumption of OH groups upon Mo loading has been monitored by FTIR and adsorbed pyridine is used as probe molecules for characterization of Brønsted and Lewis acidity in SiBEA and Mo<sub>3,0</sub>SiBEA. Periodic DFT calculations in sodalite (SOD) framework indicate a trigonal-bipyramidal conformer at the Mo<sup>VI</sup> site with molybdenum being incorporated into the zeolite framework by four SiO– bonds and a Mo=O functionality under anhydrous conditions. Water splitting formally to O<sup>2–</sup> and 2H<sup>+</sup> is computed to be feasible in SOD cage, whereas it is strongly favored in MoBEA framework at the T1 position. Depending on the hydration state, it is shown that the Mo sites formed can exhibit two Mo=O functionalities in a trigonal-bipyramidal and a pseudo-octahedral arrangement.

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### 1. Introduction

Transition metal modified or substituted oxide materials have found many applications in catalysis. Zeolites, a typical group of materials used as support for heterogeneous catalysts are used for decades in industrial applications. The continuous search to improve or discover new catalyst has led to the chemical modification of the oxide support or zeolite in particular at atomic level [1,2].

In earlier work Dzwigaj et al. [3–5] have applied a two-step post-synthesis method to favor the incorporation of group VI metal, chromium, into the framework of the BEA zeolite and to obtain mononuclear chromium species. The transition metal intra framework site was characterized using a series of experimental techniques, followed by quantum chemical calculations by the Tielens

group [6]. A logic continuation of this study is the introduction of the other group VI elements, Mo, and W into the zeolite structure, in the same spirit as for the group V and group VI transition metals performed earlier: V [7–11], Nb [12], Ta [13], and Cr [14].

Molybdenum species grafted on silica have attracted considerable attention because of their relevance to a variety of catalytic reactions, including the selective oxidations of alkanes [15,16], alkenes [17], and alcohols [18,19]. Many research groups have reported methods of characterization and synthesis, which is supposed to generate specific surface molybdenum oxide species. It is well known that framework transition metal ions are considered to be active in selective oxidation reactions [20–23]. Nevertheless, the structure, stability and reactivity of Mo oxide functionalities encapsulated in zeolites are much less studied, especially as isolated mononuclear species.

To our knowledge no combined theoretical/experimental characterization studies are available on molybdenum oxide species inserted into zeolite frameworks. The most related material known to pure silica molybdenum zeolites is molybdenum oxide

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supported on silica surface. This material characterized by SiO–Mo linkages and has been thoroughly investigated, and molecular models have been studied theoretically [14].

The still growing computational power enables us to study models with increasing complexity and reliability. Until now, *ab initio* quantum chemical calculations have been performed on cluster models involving only dozen of atoms [24–26]. The present work follows the same spirit as those performed on the group V elements [27–29], and in particular Si substituted by Cr, characterized experimentally on BEA zeolite and theoretically using periodic DFT [6].

Different framework site models are proposed after a systematic theoretical study. The sites are characterized by structural parameters, vibrational frequencies, and (de)protonation energies. The results are in good agreement with the experimental findings.

## 2. Experimental details

### 2.1. Material preparation

A tetraethylammonium BEA (TEABEA) zeolite with a Si/Al atomic ratio of 17 provided by RIPP (China) was dealuminated by a treatment with nitric acid solution ( $c = 13 \text{ mol L}^{-1}$ ) at 353 K for 4 h, to obtain SiBEA with atomic Si/Al ratio  $> 1300$  and then washed several times with distilled water and dried at 368 K overnight.

SiBEA zeolite and molybdenum(II) acetate with a desired amount of Mo (3 Mo wt. % in Mo-containing SiBEA sample) were ground and mixed in agate mortar for 15 min. The obtained mixture was transferred to glass reactor and heated in flowing argon of  $150 \text{ mL min}^{-1}$  up to 773 K with heating rate of  $2 \text{ K min}^{-1}$  and left in this temperature for 12 h. After that, the gas flow was changed from argon to oxygen and the solid was calcined at 773 K for 3 h. As obtained, Mo-containing SiBEA was labeled  $\text{Mo}_{3,0}\text{SiBEA}$ .

### 2.2. Material characterization

Power X-ray diffractograms (XRD) of the prepared samples were recorded at room temperature on a Bruker D8 Advance diffractometer using the  $\text{CuK}_\alpha$  radiation ( $\lambda = 154.05 \text{ pm}$ ).

Analysis of the acidic properties of samples was performed by adsorption of pyridine (Py) followed by transmission FT infrared spectroscopy. Before analysis, the samples were pressed at  $\sim 1 \text{ ton cm}^{-2}$  into thin wafers of ca.  $10 \text{ mg cm}^{-2}$  and placed inside the IR cell.

Before Py adsorption/desorption experiments, the wafers were activated by calcination in static conditions at 723 K for 3 h in  $\text{O}_2$  ( $1.6 \cdot 10^4 \text{ Pa}$ ) and then outgassed under secondary vacuum at 573 K ( $10^{-3} \text{ Pa}$ ) for 1 h. These wafers were contacted at room temperature with gaseous Py (133 Pa) via a separate cell containing liquid Py. The spectra were then recorded following desorption from 423 to 573 K with a Bruker Vector 22 spectrometer (resolution  $2 \text{ cm}^{-1}$ , 128 scans). The reported difference spectra were obtained after subtraction of the spectrum recorded before Py adsorption.

Diffuse reflectance (DR) UV–vis spectra of  $\text{Mo}_{3,0}\text{SiBEA}$  were recorded at ambient atmosphere on a Cary 5000 Varian spectrometer equipped with a double integrator with polytetrafluorethylene.

### 2.3. Computational details

Periodic density functional theory (DFT) calculations were performed using *ab initio* plane-wave pseudopotentials implemented in the Vienna Ab Initio Simulation Package [30,31]. The gradient-corrected revised Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional [32,33] was chosen to carry out all

calculations. The valence electrons and their interactions with the ionic cores were described with the projector augmented-wave (PAW) method [34,35] and for valence electrons a plane wave basis set was applied.

A  $(3 \times 3 \times 3)$  k-point grid is used in the Brillouin-zone sums, and the partial occupancies are set for each wave function using the tetrahedron method with Blöchl corrections [36]. The convergence was reached when the total energy difference between the self-consistent field loops was less than  $10^{-4} \text{ eV}$ . To calculate the Hessian matrix each ion was displaced in all three Cartesian directions.

The sodalite structure (SOD, Fig. 1), commonly referred as the  $\beta$ -cage was used to perform a systematic study using periodic calculations. The use of the SOD cage as a model for a zeolite and in particular for BEA zeolite has been compared and justified in our previous study [11]. The unit cell has a regular network of tetrahedral sites (equal T-sites) and contains 36 atoms ( $\text{Si}_{12}\text{O}_{24}$ ). The use of such a small periodically repeated model makes the computationally very demanding calculations attainable. We also calculated, however, the most stable structures in BEA zeolite, to investigate the effect of the unit cell flexibility on the Mo insertion. The BEA unit cell contains 192 atoms ( $\text{Si}_{64}\text{O}_{128}$ ), and has 9 different T-sites. We verified our calculations in the  $\beta$ -cage in three different T-sites, namely T1, T2, and T9, which were previously shown for V, Nb, Ta inserted BEA zeolites to exhibit very different affinity to host metal ions [11].

Several configurations were systematically investigated to study the environment of the Mo site as the function of its oxidation state and its degree of hydration (Fig. 2). This study is a complementary work to our previous work on chromium-substituted zeolite [6]. We started from a hypothetical structure in which one silicon atom of the pure  $\text{SiO}_2$  framework is isomorphously substituted by one molybdenum atom, where the oxidation state of the transition metal is +4 (MoSOD). As a next step the metal center was reduced and oxidized by molecular hydrogen ( $\text{H}_2$ , right in Fig. 2) and oxygen ( $\text{O}_2$ , left in Fig. 2), respectively to form the parent  $\text{Mo}^{\text{III}}$  (B3) and  $\text{Mo}^{\text{VI}}$  (Mo6) sites. For both species, we added up to two water molecules (dissociated

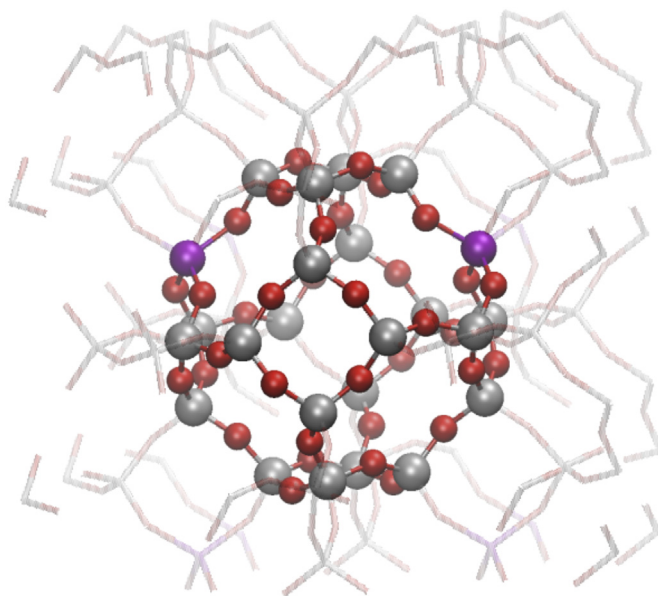


Fig. 1. Structure of model sodalite (SOD) cage in a supercell. (Mo substituted position is in purple). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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