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Theoretical and experimental insight into zinc loading on mesoporous silica

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ABSTRACT

Zinc oxide species grafted on mesostructured cellular foam (MCF) silica are investigated using a combination of experimental and theoretical techniques. MCF is modelled using a realistic amorphous silica surface model surface slab. The most energetically favorable complexes grafted on the silica surface were identified and characterized at the molecular level. The Zn metal center was found in tetrahedral coordination. Moreover, the Si-O-Zn-OH species is found to be stabilized in a 5 fold coordinated silicon with an unusual trigonal bipyramidal geometry. A mechanism for the grafting process of the metal species on the support is proposed.

1. Introduction

Zinc oxide is a modifier often used in silica and mesoporous silicas [1–5] for the generation of catalytic activity. In this perspective, zinc and copper, have been recently applied as modifiers to improve the catalytic activity of gold in AuCu-Zn/MCF catalyst [6]. It has been shown that zinc oxide loaded on MCF mesoporous silica strongly interacts with copper species, which leads to the incorporation of copper into the zinc oxide crystal structure. The easy penetration of copper into ZnO crystal lattice is explained by the similarity of the ionic radii of Cu^{2+} (0.73 Å) and Zn^{2+} (0.74 Å) [7,8]. Moreover, the replacement of zinc by copper in ZnO crystallites resulted in changes in the properties of AuCu-Zn/MCF catalyst. The interaction of zinc located in the support with reagents at one hand, and with the other modifiers, like gold or copper playing the role of active centers at the other hand, is strongly determined by the kind of favored (read the most stable) zinc species. Therefore the knowledge about such species is crucial. Usually ZnO crystalized in hexagonal wurzite structure (P63mc space group) is formed on the support surface. However, in many cases there are no diffraction peaks arising from ZnO in the XRD spectra of ZnO/SiO_2 catalyst indicating high dispersion of ZnO, or even isolated ZnO monomers on the surface [9,10].

ZnO is reported to show both basic and acidic properties and it can be called amphoteric [11]. Such solids usually display an interesting catalytic activity for dehydration or dehydrogenation reactions. However, upon catalytic reaction tests, ZnO was found to behave as basic catalyst [12,13]. It was proved that basic and Lewis acid sites as acid-base pairs on the ZnO surface are involved in basic heterogeneous catalysis (e.g. in the catalytic conversion of 2-methylbut-3-yn-2-ol (MBOH) [7].

It is also important to note, that ZnO is a typical n-type semiconductor with a relatively wide band-gap ($E_g = 3.24$ eV at 300 K). This feature, as well as, non-toxicity and low cost, makes ZnO one of the most popular photocatalysts active in UV photocatalytic degradation of organic pollutants [8].

The molecular structure of ZnO species and mononuclear species in particular are ideal systems to be studied theoretically even as is the case of extreme dispersion. Up till now, there are no

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computational studies on monomeric ZnO species acting on silica surface. In our group amorphous silica has been studied using DFT on models for the silica support [14–17], and transition metal oxide catalysts supported on our silica models have been studied [18–26].

In this study we investigate silica supported zinc oxide monomers using periodic DFT calculations, and confront the results with experimental ones. A mechanism for the grafting process and most favorable Zn species formed on silica surface is proposed.

2. Experimental

2.1. Preparation of catalysts

Mesostructured cellular foam (MCF) was prepared by the one-pot synthesis method proposed in Ref. [27]. At first, Pluronic 123 (Poly(ethylene glycol)-block-Poly(propylene glycol)-block-Poly(-ethylene glycol)-block) (8 g, 1.4 mmol) was dissolved in 300 g of 0.7 M HCl solution at 308–313 K. Then 1,3,5-trimethylbenzene (Aldrich) (12 g, 99.84 mmol) and NH_4F (Aldrich) (0.0934 g, 2.52 mmol) were added upon vigorous stirring. Following 2 h of stirring, TEOS (tetraethoxysilane; Fluka) (17.054 g, 81.99 mmol) was added. The final mixture was stirred at 308–313 K for 24 h and then transferred into a polypropylene bottle and heated at 373 K under static conditions for 24 h. The solid product was recovered by filtration, washed with distilled water and dried at room temperature. The template was removed from the as-synthesized material by calcination at 773 K for 8 h under static conditions.

For the preparation of Zn/MCF, a portion of MCF material was treated by incipient wetness impregnation with an aqueous solution of $Zn(NO_3)_2 .6H_2O$ (Aldrich) and then for 20 min in ultrasonic bath. The amount of metal nitrate used for the impregnation was calculated to achieve the loading of zinc equal to 10 wt %. The impregnated Zn/MCF were dried at 353 K and then calcined at 773 K for 5 h.

2.2. Characterization of catalysts

X-ray photoelectron spectroscopy (XPS) was performed on an Ultra-high vacuum photoelectron spectrometer based on Phoibos 150 NAP analyzer (Specs, Germany). The analysis chamber was operated under vacuum with a pressure close to 5.10^{-9} mbar and the sample was irradiated with a monochromatic Al Kα (1486.6 eV) radiation (15 kV; 10 mA). The binding energy scales of all samples were corrected to the Si2p, with the known binding energy in SiO_2 of 103.4 eV.

Infrared spectra were recorded on a Vertex 70 (Bruker) spectrometer (resolution 4 cm^{-1}). The samples were dispersed in KBr pellet (1 mg of the sample and 200 mg of KBr) with slight grinding. All spectra were recorded at room temperature in the range from 4000 to 400 cm^{-1}.

The test reaction of 2,5-hexanedione cyclization was performed using 0.05 g of catalyst activated for 2 h at 623 K under nitrogen flow (40 cm^3 min^{-1}). After the activation process 0.5 cm^3 of 2,5-hexanedione was passed continuously over the catalyst at 623 K. The substrate was delivered with a pump system and vaporized before being passed through the catalyst with the flow of nitrogen carrier gas (40 cm^3 min^{-1}). The reaction products were collected for 30 min downstream of the reactor in the cold trap (a mixture of 2-propanol and liquid nitrogen) and analyzed by gas chromatography (GC SRI 310C, DB1 column).

2.3. Theoretical study

2.3.1. Computational details

All geometry optimizations were performed using the ab initio plane-wave pseudopotential approach as implemented in VASP [28,29]. The Perdew–Burke–Ernzerhof (PBE) functional [30,31] was chosen to perform the periodic DFT calculations with an accuracy on the overall convergence tested elsewhere [14,19,20,24]. The positions of all the atoms in the super cell were relaxed until the total energy differences decrease below 10^{-4} eV. The atom positions as well as the unit cell parameters were relaxed.

Vibrational spectra were calculated for selected surface species within the harmonic approximation. Only the Zinc center and its first and second neighbors (O–Si and OH groups) were allowed to move, the support was kept fixed. The Hessian matrix was computed by the finite difference method followed by the diagonalization procedure. The eigenvalues of the resulting matrix lead to the frequency values. The assignment of the vibrational modes was made by inspection of the corresponding eigenvectors.

2.3.2. Model description

The hydrated 27 SiO_2 model [14] containing 13 (for models containing Si-O-Zn-OH species) and 12 water molecules (for models containing Si-O-Zn-O-Si species) were used to graft 1 ZnO per unit cell. These species were considered products of the following reactions:

$$\mathrm{surf_A{-}OH + ZnO \rightarrow surf_A{-}O{-}Zn{-}OH} \quad (1)$$

$$\mathrm{HO{-}surf_A{-}OH + ZnO \rightarrow surf_B{-}O{-}Zn{-}O{-}surf_B + H_2O} \quad (2)$$

where "$surf_A$" and "$surf_B$" stands for the $[(SiO_2)_{27}(H_2O)_{13}]$ surface and $[(SiO_2)_{27}(H_2O)_{12}]$ surface, respectively.

The silica model reproduces the experimentally established ring size distribution, Si–O–Si and O–Si–O angles, overall density of silanol groups and partition into several types (isolated, associated, geminate). The unit cell dimensions of the model are $11.89 \times 16.57 \times 25.53$ Å^3 as optimized for the mono-grafted Zn on the amorphous silica support having an hydroxyl group on the metal center with coordination number equal to 2 (Fig. 1, also see section 3.2, Fig. 4: **T c.n.** = **2**). For quality/cost reasons, those unit cell dimensions have been fixed during the optimization of the various different geometrical configurations of the ZnO species grafted on amorphous silica. It is computationally justified to compare the energy values of the unit cells of the same size. Due to the flexibility of the silica surface, other species can be easily accommodated. Furthermore, to get an insight into the impact of ZnO species on silica surface, the unit cell parameters were recalculated for the silica model alone. Then, the unit cell dimensions of the "pure" silica are $12.77 \times 17.64 \times 25.17$ Å^3. Such result is suggesting the slight contraction of the silica surface while ZnO species are grafted.

3. Results and discussion

3.1. Experimental evidence for the presence of Zn-OH species on the surface of mesoporous MCF silica

The experiments were performed using mesoporous cellular foam (MCF).

The MCF used as a support for zinc species possesses high surface area (608 m^2 g^{-1}) and pores with typical diameters of 16.8 nm for the windows and 37.2 nm for the cells. Mesoporous Cellular Foam possess the highest size of pores among mesoporous molecular sieves (e.g. MCM-41 – ca. 3–5 nm, SBA-15 – ca. 8–10 nm).