Journal of Molecular Catalysis A: Chemical 307 (2009) 64–70

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

The interaction of vanadyl porphyrin with the HY zeolite surface

I.P. Zaragoza [a,*], R. Santamaria [b], R. Salcedo [a]

[a] *Departamento de Polímeros, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, D.F., C.P. 04510, Mexico*
[b] *Departamento de Física Teórica, Instituto de Física, Universidad Nacional Autónoma de México, D.F., C.P. 04510, Mexico*

ARTICLE INFO

Article history:
Received 31 July 2008
Received in revised form 4 March 2009
Accepted 6 March 2009
Available online 20 March 2009

PACS:
31.15.E
68.43.Bc
82.75.Qt
31.15.xv
71.15.Pd

Keywords:
HY zeolite
Vanadyl porphyrin
Zeolite cracking
Born-Oppenheimer molecular dynamics
Density functional theory

ABSTRACT

The interaction of vanadyl porphyrin with the acid sites of the HY zeolite surface is investigated. Structural changes, partial population charges and relative energies induced by the interaction between vanadyl porphyrin and the zeolite surface are estimated with recourse to the Born-Oppenheimer semiclassical molecular dynamics technique in conjunction with density functional theory. An energy optimization process indicates that bond lengths and charge populations of the acid sites are barely distorted when vanadyl porphyrin is adsorbed onto the zeolite surface. At the expense of surmounting a large energy barrier, a dynamic interaction results in the breaking of an OH bond of the surface acid site by the vanadyl porphyrin. Given the amount of energy involved in such a process, the destruction of the catalyst crystal structure by vanadyl porphyrin shows a low probability of occurrence.

1. Introduction

The refining process of the crude oil into gasoline and other useful products requires a large quantity of catalysts. Unfortunately, during this process undesirable reactions between the contaminants carried in the crude oil and the catalysts take place, seriously diminishing the quantity of activated catalysts, with consequent reductions in the production line of gasoline and other byproducts [1]. For instance, it is common to find metals like V, Ni, Fe, S, Cu, etc. capable of interacting with, deactivating and even damaging the catalyst [2]. In particular, there is evidence that vanadium complexes can produce the destruction of the HY zeolite, the main catalyst used in the fluid catalytic cracking (FCC) process [3,4], which in turn renders from a third up to a half of the total gasoline of a refinery [5]. Measurements indicate that about 50% of the catalyst surface area is lost for about 4000 ppm of vanadium [2]. Among the different organometallic contaminants containing vanadium, the best characterized are the vanadium oxide species and the vanadyl porphyrins. The characterization has been carried out by means of X-ray [6,7], high-resolution mass spectroscopy [8], electron spin resonance [9], temperature-programmed reduction [10], and electron paramagnetic resonance [11] techniques.

Several mechanisms have been proposed for the zeolite destruction in the presence of vanadium. For instance, the dehydrogenation products of benzene and olefins are preferentially formed on the vanadium sites, reacting further on the zeolite acid sites, which results in coke formation and the catalyst deactivation [1]. Another mechanism involves the formation of vanadic acid according to the reaction $VO_2^+ - (\mathrm{HY\ zeo}) + 2H_2O \rightarrow H^+ - (\mathrm{HY\ zeo}) + H_3VO_4$, thus destroying the zeolite by hydrolysis of the SiO_2/Al_2O_3 framework [12]. The existence of acidic species different to vanadic acid have been also suggested to be responsible for the catalyst deactivation in the FCC process. The acidic species would come from the SO adsorption on the catalytic surface, reacting with the strong acid sites of the zeolite, leading to the loss of crystallinity [13]. The effect of vanadium in the hydrothermal deactivation of the zeolite with and without the presence of rare earth elements has been also discussed. In particular, a lower zeolite surface area is observed for samples containing Ni and V when compared with samples containing only Ni or only V [3]. It has been observed that vanadium presents different oxidation states in the temperature range [300, 500]°C. However, at temperatures exceeding 500 °C, the V(v)

---

* Corresponding author.
E-mail addresses: ipzaragoza@iim.unam.mx (I.P. Zaragoza), rso@fisica.unam.mx (R. Santamaria), salcedo@servidor.unam.mx (R. Salcedo).

1381-1169/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2009.03.011

species is highly dispersed and is probably in the form of a framework surface species such as $(Si–O)_3V–O$ [14]. On the other hand, by using thermal techniques and complementing with other spectroscopic analysis, Pompe et al. [15] concluded that vanadium is able to pull out oxygen from the zeolite, thus destroying the catalyst. Clearly, the existence of several detrimental pathways of the HY zeolite points out the complexity in understanding at the molecular level its destruction, together with the role that vanadium compounds play in the zeolite destruction.

The effects of vanadium oxides (such as VO, VO_2, V_2O_3 and V_2O_5) on the internal acid sites of the zeolite have been also investigated at the theoretical level [16]. It is found that the breaking of an OH bond of the acid site, with the hydrogen ion escaping from there, permits the interaction between the vanadium atom of the oxides with the catalytic acid site. The response of the support in this interaction is a non-localized charge redistribution that seems to account for the oxidation of vanadium molecules.

The vanadium oxides are not the unique compounds containing vanadium and capable of permanently damaging the zeolite. For instance, it has been found that the vanadium porphyrins being abundant, can reach the catalyst surface [5] and may reduce the catalytic activity of zeolites [15]. Nevertheless, the large size of the vanadyl porphyrins (compared with the small dimensions of the zeolite pores) prevents the vanadyl porphyrins from penetrating the zeolite. As a consequence, the interaction of vanadyl porphyrin with the zeolite occurs at the zeolite surface. Salcedo et al. [17] have investigated the effects that different lateral chains of vanadyl porphyrinates have in their properties, as well as their solubility in different types of polar solvents. Their results indicate that the reactivity of the complexes is increased with substituents, more strongly polluting the catalyst than the molecule without them.

Since the reaction mechanism between vanadyl porphyrin and the acid sites on the zeolite surface is hard to observe with microscopic detail in the laboratory, the aim of the present work is to find the possible reaction mechanism of vanadyl porphyrin with the HY zeolite. In the first stage, the investigation establishes the adsorption of the organometallic molecule on the catalyst surface. In the second stage, the way in which vanadyl porphyrin is adsorbed onto the zeolite is considered as an indicator of a preferential approach of vanadyl porphyrin towards the zeolite surface. We use the Born-Oppenheimer molecular dynamics method to obtain the trajectory of the vanadium ion in its interaction with the aluminum acid site, when the vanadyl porphyrin molecule is given a large initial momentum. This is a model artifact to overcome the potential energy barrier imposed by the repulsion forces of the interacting compounds, without regard to a physical temperature. Given the large size of the porphyrin, we assume that vanadyl porphyrin pushes waters out of its path, directly impacting over the zeolite surface. In this context, the calculations are performed in the absence of water (our results on the interaction of vanadyl porphyrin with water support to some extent such a hypothesis). The dynamics exhibits a destructive reaction in which the vanadium portion of porphyrin tears the OH bond out of the acid site, producing drastic structural and electron changes of the zeolite surface at the expense of surmounting a large energy barrier. In the final stage, the reaction products consist of a porphyrin whose vanadium atom has captured an OH group of the zeolite, and a locally deformed zeolite without its OH group. Our investigation complements other studies in which small vanadium oxides (like V_2O_5) are able to penetrate the internal structure of the zeolite and, under the appropriate thermodynamic conditions, collapse the zeolite [15].

2. Model

Relevant features of the structure and composition of the HY zeolite are known by means of infrared and mass spectroscopy combined together [18,19]. The zeolite consists of a network of nanopores, through which under appropriate conditions of pressure and temperature, small or linear hydrocarbons may diffuse [20]. Tetrahedral (T) silicons (SiO_4) conform the rings that build the nanopores. It is common to find rings made of 12 T sites, with diameters of approximately 0.8 nm [21]. The Al sites of HY zeolite are commonly identified as the acid sites because it is at these places where a deficiency of electron charge occurs, with the consequent catalysis of hydrocarbons at such places. The acid sites located at the external surfaces of the HY zeolite also react with hydrocarbons, which can be larger than the ones traveling in the nanopores. However, the catalytic sites at the external surface exhibit a great propensity to be neutralized, deactivated or damaged by the contaminants carried in the crude oil like Ni- and V-porphyrins, Ni- and V-naphthenates, etc. [15].

In order to simulate the interaction of an exposed catalytic site with vanadyl porphyrin, we chose a crystallographic portion of the HY zeolite surface reported by Parise et al. [22]. It consists of 16 T sites as depicted in Fig. 1. In four arbitrarily chosen T sites the silicon atom was replaced with aluminum, in such a way that the zeolite composition was $(SiO_4)_{12}$ $(AlO_4)_4$, with a Si:Al ratio of 3, in agreement with experimentally observed and stable Y zeolites [22]. In each oxygen bridge linking the Al and Si atoms, a hydrogen atom was attached to compensate the local charge perturbation produced by the replacement of Si by Al. The terminal oxygens were saturated with hydrogens to avoid possible reactivities attributed to dangling bonds. Since the surface model represents the Y branch that conforms the HY zeolite unit cell, there exists a great probability for vanadyl porphyrin interacting with the zeolite surface, as illustrated in panels (a) and (b) of Fig. 2.

The zeolite surface shall be made to interact with a vanadyl porphyrin, a compound commonly found and isolated from the crude oil [9]. In our simulation, the vanadyl porphyrin corresponds to an oxovanadium porphyrin whose stable molecular structure was determined by X-ray crystallographic experiments reported in Ref. [23] (Fig. 1). In the oxovanadium porphyrin structure, the vanadium atom is coordinated with four nitrogens and one terminal oxygen, in such a way that this part of the structure is shown as a square pyramid [24] (Fig. 2). It is the vanadyl group which presumably causes the lack of planarity. The oxovanadium molecule with lateral aliphatic substituents exhibits terminal methyl groups in the different corners [23] (Figs. 1 and 2). Our vanadyl porphyrin is recognized as deoxophylloerythroetioporphyrin vanadium(IV) in the literature. In principle, the vanadyl compound is bigger than the zeolite surface model. Nevertheless, the catalysis exhibits a highly local character in such compounds making the size difference (whenever the surface model is not that small) of second importance. On the other hand, the vanadyl porphyrin reactivity has been investigated in different solvents with low, medium and high values of the dipole moment [17]. The results show that vanadyl porphyrin with aliphatic substituents is soluble in all these solvents. Still, we are not aware of any work describing from a theoretical perspective the reactivity of vanadyl porphyrin with the HY zeolite surface and, from an experimental perspective, most studies have been concerned with the combined effect and synergy of various primary feed contaminants [25,26].

3. Method

We apply density functional theory (DFT) to investigate the interaction between vanadyl porphyrin and the zeolite surface as it is appropriate to determine structural and electronic property changes of large compounds with relatively high accuracy, at a low computational cost. However, the method requires the proposal of an exchange-correlation energy functional in terms of the electron density, as well as basis sets for the molecular orbital rep-