Computational studies of (mixed) sulfide hydrotreating catalysts

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Abstract

The important theoretical works that have been performed on hydrotreating catalysis within the last 10 years are reviewed. The active phase of these catalysts are generally constituted of MoS_2 crystallites, promoted by cobalt or nickel and deposited on large area supports such as alumina. It is well admitted that the active site of the catalyst is located on the edges of the MoS_2 particles. The review then focuses first on the sulfur stoechiometry of the edges of MoS_2 crystallites for both the promoted and unpromoted systems. It is shown, taking into account the gas phase surrounding the catalysts and the temperature, that on the metallic edge all the molybdenum atoms are saturated while on the sulfur edge they are in a four-fold tetrahedral coordination. This first part leads to propositions on the nature of the active surface that are confronted with experimental data. The influence of hydrogen on the stability of different surfaces is then discussed as well as H_2 activation and hydrogen mobility on the different edges. In a final part, results on the adsorption and on the determination of the desulfurization reaction pathways for different types of molecules such as thiols, thiophene and polyaromatic sulfur-containing compounds are presented and discussed.
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1. Introduction

The evolution of the legislation on the sulfur quantity allowed in the diesel fuel has induced an extensive work to improve the hydrodesulphurization (HDS) process. Different possibilities have been proposed to this purpose including extraction, absorption, biological process and/or modification of reactor design. These possibilities have been reviewed in details for example by Song [1] and Babich and Moulijn [2]. A more classical approach involves the improvement of the activity and the selectivity of the hydrotreatment catalyst itself. These catalysts are mostly composed of $Mo(W)S_2$ nanoparticles promoted by cobalt and/or nickel atoms deposited on a high specific area support like alumina [3]. A better understanding of the HDS reaction mechanism and of the exact nature of the catalytic site may be useful to further improve the catalytic activity and match the future environmental requirements.

The HDS catalyst – a complex material containing a large number of elements – can be obtained with a variety of preparation methods. A very important experimental effort has been performed in order to characterize precisely the nature and the morphology of the active phase (MoS_2), its interaction with the support and the location of the promoter atoms (Co, Ni) both on model and real catalysts. Results on these different points have been obtained by X-ray photoelectron spectroscopy (XPS) [4–6], transmission electron microscopy (TEM) [7–11], X-ray absorption spectroscopy (XAS) [12–14], scanning tunnelling microscopy (STM) [15–18] and vibrational spectroscopies [19–23]. All these techniques lead to the widely accepted Topsøe's catalyst model [24], in which the active site is supposed to be a sulfur vacancy on the edge of the MoS_2 active phase, the basal plane of the layered molybdenum (or tungsten) sulfide being inactive in HDS. However, the exact nature of the vacancy, the type of edge on which it is located, as well as the sulfur stoichiometry of the edge surface that will determine the active sites per molybdenum atom is generally not accessible experimentally under working conditions of the catalyst. Furthermore, the location of the promoter atoms is not determined precisely even if, according to the above-mentioned model, they should be on the edges of the catalyst in order to increase the number of vacancies by decreasing the strength of the metal-sulfur bonds [3]. This increase of the number of active sites is proposed to be at the origin of the increase in the catalytic activity, i.e. the so-called promoting effect. Another

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critical issue is the elucidation of the reaction mechanism by which the desulfurization of different types of molecules occurs. The dramatic decrease of the activity between light molecules, such as thiophene, and larger ones, like dibenzothiophene (DBT), suggests that different reaction pathways may occur on the catalyst when different molecules are involved. For sulfur-containing polyaromatic compounds like DBT and dimethyldibenzothiophene (DMDBT), two different mechanisms have been proposed, namely the hydrogenation route (HYD) in which one of the benzene ring is hydrogenated before desulfurization and the direct desulfurization route in which the molecule is desulfurized without hydrogenation [25]. There is still however a strong debate in the scientific community to know whether both routes occur on the same sites or on two distinct sites.

Hence, despite all these studies, a large number of questions are still open and some of them can be addressed by first-principle calculations. In the present review, after a brief presentation of the computational methods and of the model used in most studies, we will first focus the discussion on the determination of the stoichiometry of the MoS_2 particles edges, with and without promoter atoms, as a function of the temperature and of the gas phase composition and pressure. In a second part, the comparison between the theoretical results and the available experimental data will be performed in order to establish the validity of the theoretical models of the active site. Finally, we will summarize the results on the adsorption of the molecules on models of different catalysts (promoted or not) and the reaction path that can be obtained for the hydrogenation and the desulfurization of the small (thiol, thiophene) and large molecules (DBT, DMDBT).

2. Calculation models and methods

The application to heterogeneous catalysis of theoretical – and most especially of *ab-initio* – calculations has grown tremendously in the last 10 years, because of the introduction of density functional theory (DFT) methods in the chemists'

community and the concomitant massive increase of the computer power. It is now possible to perform *ab-initio* calculations on systems containing more than 200 atoms with the software usually used to model heterogeneous catalysis (VASP [26], Dacapo [27], CASTEP [28], ADF [29], Gaussian [30]). These calculations include geometry optimizations, systematic study of the adsorption modes and vibrational spectra simulations. The calculations of the activation energies of almost all the elementary reactions involved in a proposed reaction path are even possible. However, the accuracy of the calculations is an important parameter that must be taken into account especially for the comparison between theoretical and experimental results. Typically for DFT calculations using gradient corrected functionals (generalized gradient approximation, GGA), the calculated interatomic distances are very close to the experimental ones, the difference being smaller than 0.05 Å [31]. On the energetic point of view, it can be considered that the precision is of the order of 0.05 eV when comparing similar structures if the calculation parameters are carefully checked. The results are slightly less accurate for the vibrational wavenumber (20 cm^{-1}) [32] and the activation energies (typically estimated around 0.1 eV). However, the results obtained when first principle calculations are applied to heterogeneous catalysis are also, and mostly, dependent on the model used to describe the active phase. Two approaches are reported in the literature: the periodic and the cluster approach. Both have advantages and drawbacks: periodic calculations use the efficiency of plane wave basis set and deliver the results very quickly but they lead to high coverage and the modelling of defects can be difficult; on the other hand, the cluster approach provides efficient analysis tools for single molecule adsorption but is usually much slower and cluster termination can be problematic. Fig. 1 gives examples of MoS_2 models using both techniques. In the case of HDS catalyst, the results are generally similar for both models.

It is now accepted that the active sites are located on the (1 0 0) edge-surface of the MoS_2 nanoparticles. Using the crystallographic data, the two types of termination indicated in
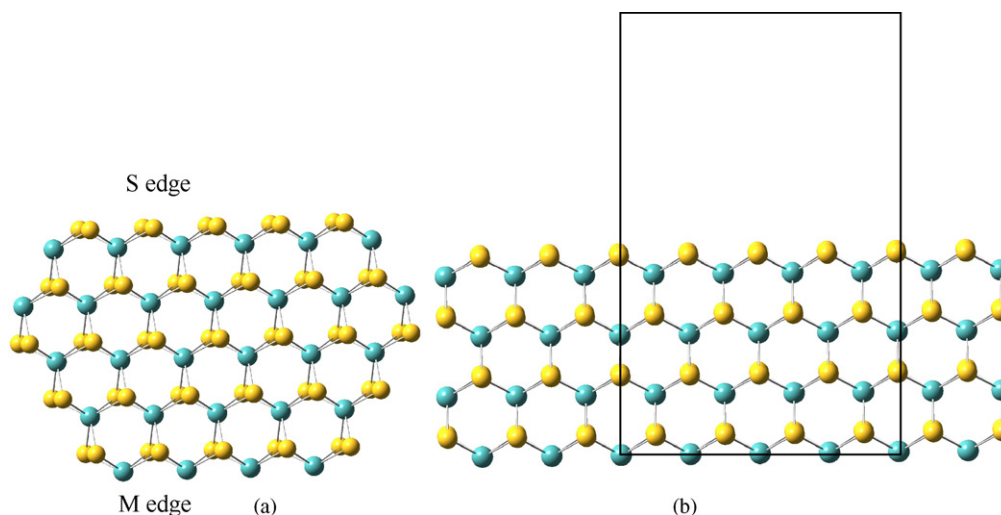

Fig. 1. Cluster (a) and periodic (b) MoS_2 models. S, yellow circle, Mo, blue circle.