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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.

Keywords: HDS; HDT; MoS_2; CoMo; NiMo; DFT; *Ab-initio*; Molecular modeling

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

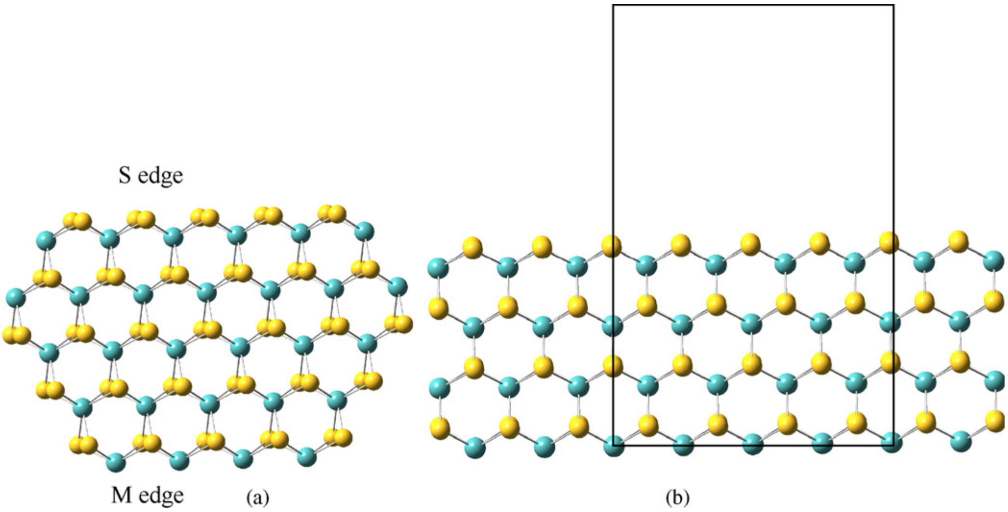

Fig. 1. Cluster (a) and periodic (b) MoS_2 models. S, yellow circle, Mo, blue circle.

Fig. 1 are possible for this surface: one exposes unsaturated molybdenum atoms and is called the metallic edge; the other one is constituted of sulfur atoms in bridging positions between two Mo atoms and is called the sulfur edge. The coordinations of the Mo atoms on these edges are respectively, 4 and 6. In order to improve the correlation between the theoretical results and the experimental ones, it is crucial that the theoretical model describes the catalytic system in realistic conditions of pressure and temperature. For example, the H_2S partial pressure will have a large effect on the number of vacancies on the edge of the catalyst. The introduction of statistical thermodynamic tools in the *ab-initio* calculations, taking into account the chemical potential of the gas phase molecule in the determination of the stable surface [33], makes possible the calculation of the sulfur coverage of the surface. However, approximations are generally used in the calculations; for example, the entropy of the adsorbed molecules (internal as well as configurational) is usually neglected. Furthermore, the translation of the calculated chemical potential into real partial pressure is not straightforward and the approximations included in the calculation may displace the boundaries between the stability domains. The results are nevertheless in good agreement with the experimental results [34] as far as the comparison is possible. The relation between the crystallographic termination and the stable surfaces in the catalytic conditions is discussed hereafter (Section 3).

3. Description of the active phase

3.1. Non-promoted systems

The description of the active phase and of its edge surface will be correct only if the calculations on well known systems are able to reproduce the experimental data. The first calculations [35,36] have been carried out on the whole range of bulk transition metal sulfide (TMS) in order to demonstrate the ability of DFT to describe their electronic and geometrical structures. For MoS_2, the calculated equilibrium volume and interatomic distances match the experimental ones and the system is correctly described as a semi-conductor, even if the band gap is underestimated as expected from DFT calculations [37]. The electronic properties of the edge of MoS_2 particles, which are important for the catalysis, have then been studied [38–44] in detail. On bare metallic edges Raybaud et al. [38] have demonstrated the existence of low energy empty states inducing a Lewis acid character for the molybdenum atoms. On the opposite, Bollinger et al. [45] have characterized a conducting band on the same edge terminated by sulfur dimers. This surface band has been observed experimentally [16] demonstrating the suitability of the model used in the calculations. None of these terminations will however be stable in catalytic conditions (see below) and they may not be important in the catalytic process.

The determination of the sulfur coverage of the edges has been the subject of a great number of studies [46–48]. The authors have shown that the addition of sulfur atoms on the metallic edge is an exothermic reaction. However, the determination of the most stable edge depending on the gas phase pressure and temperature can only be achieved by the introduction of the gas phase chemical potential of sulfur in the following equilibria (1, 2 or a combination of 1 and 2).

$$\text{Surface} + H_2 = \text{Defective surface} + H_2S \quad (\text{vacancy formation}) \tag{1}$$

$$\text{Surface} + H_2 = \text{H-Surface-H} \quad (\text{hydrogen adsorption}) \tag{2}$$

Various approaches have been proposed to take these equilibriums into account either on periodic models [47,49], or on cluster ones [50] but they all draw rather similar pictures of the particle edges. On the metallic edge, the stable surface in the catalytic conditions is saturated by bridging sulfur atoms (Fig. 2a). The coordination of the molybdenum atom is 6 and the adsorption of a molecule on the stable edge will be limited to small ones because of the steric repulsion between the adsorbed molecule and the sulfur atoms present in the surface. The creation of a vacancy will be needed before the desulfurization reaction even for light molecules like thiophene. The reaction leading to a vacancy formation is endothermic (−1.2 eV) and the number of vacancies present on the edge will be very small. The hydrogen adsorption has been studied using the same methodology [45,51] and does not change significantly the conclusions. To summarize, adsorption and reaction on this edge seem highly improbable. Experimental evidences of such vacancies (if they exist at all) will be

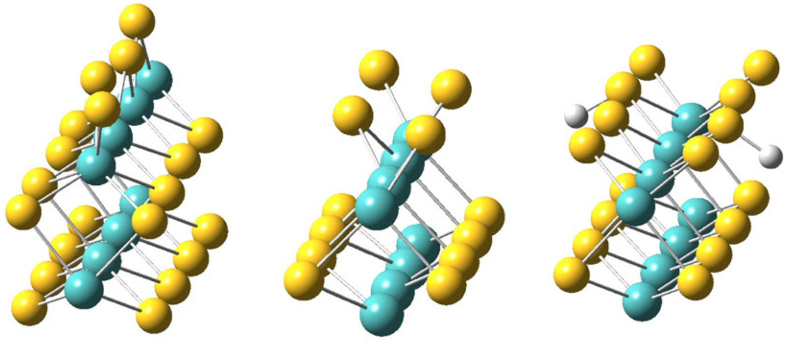

Fig. 2. Stable surface in the catalytic conditions: molybdenum edge (a) and sulfur edge (b) and (c) according respectively to refs. [49,45]. H, white circle.

very difficult to obtain because of their very low density at the surface of the active phase.

The same calculations have been carried out on the sulfur edge. Depending on the experimental conditions taken into account, two surfaces may be stable. On the one hand, according to Raybaud et al. [47] and Cristol et al. [49,51], the stable surface in the catalytic conditions is formed by removing half of the bridging sulfur atoms from the crystallographic edge (Fig. 2b). The coordination of the molybdenum atom is reduced to 4 and only very few hydrogen atoms will be adsorbed on the surface. On the other hand, Bollinger et al. [45] found that the stable surface is formed by adding a hydrogen atom on half of the sulfur atoms in bridging position for the crystallographic surface (Fig. 2c). The hydrogen adsorption on the crystallographic sulfur edge is indeed an exothermic reaction and stabilizes the edge with two sulfur atoms in bridging position. The molybdenum atoms are in this case six-fold coordinated and the removal of one sulfur atom will be needed before desulfurization reactions. The discrepancy between the two models is relatively small and on both studies, the catalyst conditions are close to the border of two surface stability domains. In this case, the removal of one H_2S molecule from the surface with stable S–H groups (Fig. 2c) as well as the addition of an H_2S molecule on the first surface (Fig. 2b) will have a small positive Gibbs free energy. The addition of these two steps in the catalytic cycle will lead to similar energy profiles.

Using a cluster model, Wen et al. [50] have proposed an intermediate model with five-fold coordinated molybdenum atoms. However, the effect of the hydrogen adsorption is not considered in this study. Finally, the sulfur chemical potential will influence the surface energy of the two types of edges and as a consequence, the shape of the particles as it has been mentioned by Raybaud [47,52] and confirmed experimentally [53]. These conclusions will be valid in the case of a thermodynamical control of the active phase formation.

In order to assess the reliability of these theoretical results, comparisons with experimental results have been performed. The evolution of the EXAFS spectra [13] with gas phase composition is consistent with the surface sulfur coverage determined by the theoretical model. This evolution as well as the relaxation of the edge (dimerization) explains the difficulty to use the molybdenum–molybdenum coordination number to determine the size of the MoS_2 particle [12,54–56]. The comparison of calculated and experimental vibrational wavenumber of a probe molecule such as CO [57–59] is probably the most straightforward test as this method probes only the surface outermost layer. Experimentally, the adsorption of CO molecule on HDS active phase gives rise to a broad band [57,20] at 2110 cm^{-1} and to a weak component [58,23] at c.a. 2070 cm^{-1}. The band at 2100 cm^{-1} is attributed to CO molecules adsorbed on the six-fold coordinated molybdenum on the metallic edge. The distance between the neighbouring sulfur atoms is large enough to allow a top adsorption of a small molecule like CO. The adsorption energy is however small due to the steric repulsion between the adsorbed molecule and the sulfur atoms of the saturated surface The CO adsorbed on sulfur edge is responsible of the broad band below 2070 cm^{-1}. Travert et al. [57] explained theoretically the evolutions of these bands under reducing and sulfiding conditions by evolution of the sulfur coverage. Zeng et al. [58,59] have studied the CO adsorption on a cluster model of the active phase. They have proposed another interpretation of the experimental spectra, and suggested the formation of dicarbonyl species on the corner of the particles. However this interpretation does not seem to be compatible with the results obtained using isotopically labelled carbon monoxide [60].

3.2. Promoted system

The addition of cobalt or nickel atoms to the MoS_2 system greatly increases the activity of the catalyst. In order to explain these promoting effects, different models [61–63] have been proposed in the literature. STM images [64] have demonstrated that the most probable model is the decoration model, in which the promoter atoms are located in substitution of the molybdenum ones on the edges of the catalyst. The calculations [46,65–68] on cobalt promoted systems have been carried out simultaneously with the calculations on the non-promoted systems. On the basis of systematic calculations, Raybaud et al. [69] have shown that the most favourable configuration is indeed the substitution of molybdenum atoms on the edges of the catalyst by the promoter atoms. These studies were performed for different promoter/molybdenum atoms ratio on the edges of the catalyst but the conclusions are qualitatively the same whatever the considered ratio. The main effect of the introduction of the promoter on the edge of the catalyst is a reduction of the average M–S bond strength, as the Co–S and Ni–S bonds are weaker than the Mo–S ones. This decrease, which has been observed experimentally [70], will induce the formation of stable vacancy on the edge of the catalyst under catalytic conditions. The number of vacancies of course increases with the number of promoter atoms located on the edges. Formally, one substitutes one $(MoS)^{2+}$ entity by a Co^{2+} or Ni^{2+} one [68]. On the metallic edge, when all the molybdenum atoms are substituted by cobalt or nickel atoms, the most stable surface in the catalytic conditions is composed of four-fold coordinated metallic atoms in a geometry close to the square planar one (Fig. 3a). When the promotion is only partial, the sulfur atoms in bridging positions between the promoter atoms and its neighbouring molybdenum atoms are removed leading to five-fold molybdenum atoms and square planar four-fold cobalt atoms on the edges of the particle (Fig. 3b). As a consequence, the alternate substitution of half the molybdenum atoms leads to the migration of the sulfur atom in apical position above the Mo. The effect of substitution of molybdenum by the promoter on the sulfur edge is smaller and the metallic atoms are four-fold coordinated with sulfur atoms in bridging position (Fig. 3c). The substitution of molybdenum atoms will change the energy of the edge of the catalyst, by changing the sulfur coverage in given conditions. If the growth of the particle is controlled thermodynamically, these energetic modifications will have an effect on the shape [71] of the particle and on the edge [67] on which the substitution will occur. A critical difference between the nickel and the cobalt atoms is the type of edge on which they will be located. The cobalt atoms are

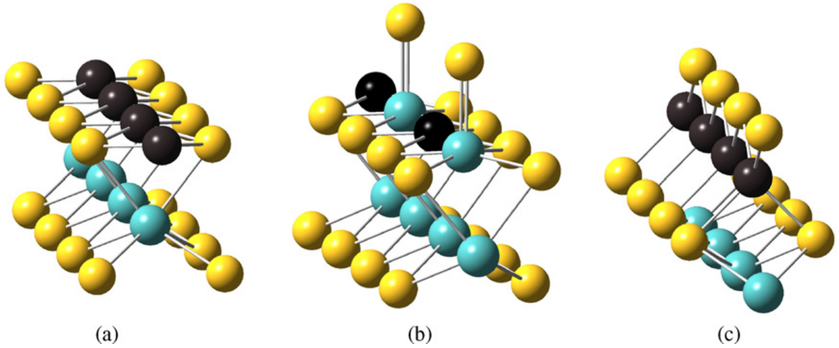

Fig. 3. Stable edges in presence of promoter atom: (a) molybdenum edge fully promoted, (b) molybdenum edge partially promoted, (c) sulfur edge partially promoted. Co, black circle (adapted from ref. [67]).

more stable on the sulfur edge while the nickel atoms will be present on the two edges. This difference may have an influence on the reaction path favoured by the two promoter atoms [66]. Experimental evidences on the preferential location of the promoter atoms are scarce. Vibrational spectra of adsorbed CO exhibits band at 2070 cm^{-1} for the cobalt promoted system and at 2120 cm^{-1} for the promotion with nickel that are both due to CO molecule in close proximity to the promoter. Theoretical calculations of the CO stretching [72] wavenumber should then give an indication on the relative localization of the CO molecule and of the promoter atoms. The results indicate that the promoter atoms (Co and Ni) are located on both edges, and that the promotion is partial, in contrast to the theoretical predictions. However, the theoretical conclusions are based on pure thermodynamical considerations of fully promoted edges while kinetic effects occurring during the sulfidation of the active phase may influence strongly the localization and the number of the promoter atoms on the edges.

A systematic evaluation of the number of sulfur atoms (and then of the number of vacancies) on the edges of the particles for each type of promoting atom and each Mo/promoter ratio would be helpful to propose new catalytic formulations. However, the number of calculations to perform for such a systematic study would be very large and to our knowledge, it has not been done so far. In order to reduce the number of calculations, Raybaud and co-workers [73,74] have proposed to use a global description based on the transition metal–sulfur bond energies computed in the bulk structure. This approach may raise valuable informations but is somehow frustrating: as a global descriptor, it does not define the catalyst site on which the reaction may take place.

4. Reaction mechanisms

First principle calculations have also been extensively applied to study the adsorption of molecules and the HDS reaction paths. The mechanisms usually proposed in the desulfurization reaction involve the adsorption of the organic molecule on a sulfur vacancy on one of the edges of the active phase. This molecule will react with hydrogen atoms (proton or hydride) that will induce the cleavage of the C–S bonds and the hydrocarbon desorption, leaving the sulfur atoms on the surface. The site is then regenerated by reaction with the hydrogen present in the gas phase. This global mechanism has been confirmed for large molecules such as DBT on non-promoted and promoted catalyst [75,76]. In agreement with this mechanism, the theoretical studies have focused first on the interaction of the hydrogen with the surface and on the vacancy formation both on the non-promoted and promoted systems. The second important subject has been the adsorption of molecules such as thiol, thiophene, DBT and DMDBT on the edges of the MoS_2 crystallites (in general, the non-promoted ones). These adsorption modes are used as starting point for the reaction mechanism. In the last few years, based on *ab-initio* calculations of the whole reaction (calculations of the energy variation and activation energy of the elementary step), new mechanisms have been proposed.

4.1. Hydrogen adsorption

The hydrogen adsorption on the non-promoted surface can be summarized in a simple way. The adsorption on the stable metallic edge [49,51,68,77–79] with sulfur atoms in bridging position (Fig. 2a) is slightly exothermic (Eads = 0.3 eV) and leads to the formation of two S–H groups. The activation energies computed for this reaction are close to 1.0 eV. It should be mentioned that the displacement of the hydrogen atom on the edge requires much lower activation energy and will be fast once hydrogen has been activated. The transformation of one S–H group into one Mo–H group is an endothermic reaction ($\Delta E = 0.3$ eV) and the activation energy is close to 0.4 eV. These values indicate that the proportion of hydride and proton on the edge of the particle will be equilibrated and that the two species can participate to the reaction mechanism even if the proportion of S–H groups will be larger than the one of hydrides [80–83]. The adsorption on a vacancy [51] or on the crystallographic edges [84,85] (i.e. on the bare surface) is exothermic, though not enough for the hydrogen adsorption to stabilize the formation of vacancies.

On the sulfur edge, the hydrogen adsorption has been studied for two sulfur coverages: one or two sulfur atoms in bridging position. For a H_2/H_2S ratio between 1 and ca. 10 two sulfur atoms are present per edge molybdenum atom and the adsorption is exothermic [42,46,49,51,68] (Eads = 1.4 eV) and leads to the formation of S–H groups. Depending on the experimental conditions, the hydrogen coverage can be as high as one S–H group per Mo atom. In more reducing conditions, only one sulfur atom is located in bridging position between two molybdenum atoms, H_2 adsorption is athermic yielding one S–H group and one hydrogen atom in bridging position between two molybdenum atoms. In this case, the activation energy is also close to 1.0 eV but the hydrogen displacement will be much slower. Indeed, the activation energy is also close to 1.0 eV. Taking into account the loss of translational entropy due to the adsorption, the number of hydrogen atoms on the surface will be very low.

The substitution of molybdenum by cobalt or nickel has obviously also a large effect on the hydrogen adsorption on the surface. On the metallic edge, for the promotion by cobalt, the hydrogen adsorption is exothermic, forming one Co–H and one S–H group. The adsorption energy depends on the number of substituted atoms [68]. Furthermore, the activation energy is reduced to 0.6 eV. Hence another effect of promotion by cobalt is to increase the amount of hydrogen atoms present on the surface of the catalyst. The same effect has been obtained by Nelson et al. [77] on the sulfur edge. The substitution increases the adsorption energy up to 0.9 eV for the formation of two S–H groups and the activation energy is reduced to 0.6 eV. The displacement of the proton from one sulfur atom to the following is highly activated (1.0 eV) indicating that the hydrogen atoms are again less mobile on the S-edge than on the metallic one. The results for the full promotion by nickel atoms are quite different [78]. The most stable adsorption mode on the metallic edge is a molecular adsorption on top of one nickel atom (adsorption energy 0.2 eV) but the following dissociation of the H_2 molecule will be endothermic. The hydrogen coverage of the Ni promoted metallic edge will then be very low. This last result is surprising as the promotion by nickel is found experimentally to favour the hydrogenation. The computation of the adsorption energies as well as dissociation pathways on the Ni-promoted S-edge are still lacking and are required to draw final conclusions.

4.2. Adsorption of reactive molecules

The adsorption and reaction on the surface of sulfur-containing compounds have also been studied theoretically, following the pioneering work of Neurock and Van Santen [86] who studied the adsorption and decomposition of thiophene on a small Ni_3S_x cluster. Studies range from the simplest molecules like methane–thiol or ethane–thiol to thiophene and polyaromatic compounds as well as nitrogen-containing molecules.

4.2.1. Thiols

The adsorption and reaction of thiols on the metallic edge of the catalyst have been extensively studied by Todorova et al. [87,88]. According to the authors, the reaction mechanism involves the participation of the surface sulfur atoms to activate the S–H bond, and the reaction will be slower on the crystallographic metallic edge than on single vacancy on the stable metallic edge. The computed activation energy is close to 1.1 eV for CH_3SH and C_2H_5SH on monovacancy. For the ethanethiol, the formation of ethene has also been considered, but the activation energies are larger (1.6 eV), indicating that the hydrogenolysis of the C–S bond is favoured with respect to the elimination mechanism. The value of the activation energy of the thiol desulfurization is similar to the activation energy for the hydrogen activation and for the vacancy formation on the non-promoted metallic edge [89]. From the theoretical point of view, it is therefore difficult to determine the rate-determining step of the reaction. When one molybdenum atom is substituted by nickel or cobalt, the activation energy is slightly reduced to 0.9 eV.

4.2.2. Thiophene

Thiophene adsorption has been investigated on the crystallographic metallic edge [90–95] which presents coordinatively unsaturated sites (CUS). Since the coordination of the molybdenum atoms is low, the adsorption is highly exothermic. The most stable adsorption mode (Eads = 2.8 eV) is a flat adsorption on two molybdenum atoms. One bond is created between the thiophene sulfur atom and the first molybdenum atom, while the two double bonds of the cycle are in interaction with the second molybdenum atom. A vertical adsorption with the sulfur atom of the molecule lying in a bridging position is possible but less exothermic (Eads = 1.1 eV). In both cases, the C–S bond length is enlarged, and the thiophene molecule activated. The adsorption on the crystallographic sulfur edge is also exothermic (Eads = 0.4 eV) due to the conducting character of the edge. However, from a thermodynamic point of view, these surfaces are highly improbable and the adsorption on more realistic surface or CUS must be considered [92]. The adsorption is not possible on the stable metallic edge and it is necessary to remove one of the bridging sulfur atoms to create a CUS, which is an endothermic step ($\Delta E = 1.2$ eV [89]). The adsorption on the CUS is exothermic (Eads = 0.71 eV) (Fig. 4a). The adsorption mode is parallel to the surface in a geometry similar to the most stable mode on the unsaturated surface.

Thiophene adsorption on the stable sulfur edge is possible (Fig. 4b) [92]. The adsorption is slightly endothermic but induces the activation of the C–S bonds. In this case, it is not necessary to create the vacancy in a first step and the regeneration of the catalytic site is exothermic even on a non-promoted catalyst. Finally, thiophene adsorption on the basal plane (Fig. 4c) has been proposed by Lauritsen et al. [18] in order to explain STM images of MoS_2 on which thiophene has been adsorbed. In fact the adsorption takes place on the side of the basal plane – the thiophene molecule interacting with a surface band – and is sensitive to the nearby edge as well as its sulfur coverage. The computed adsorption energy is 0.2 eV on the fully sulfurized metallic edge. This value is larger than the computed one on the stable sulfur edge and should then be considered as a starting point in the reaction mechanism. Furthermore, this value is probably underestimated as DFT does not include van der Waals interaction [96] that might be important for such a configuration. The result can probably be

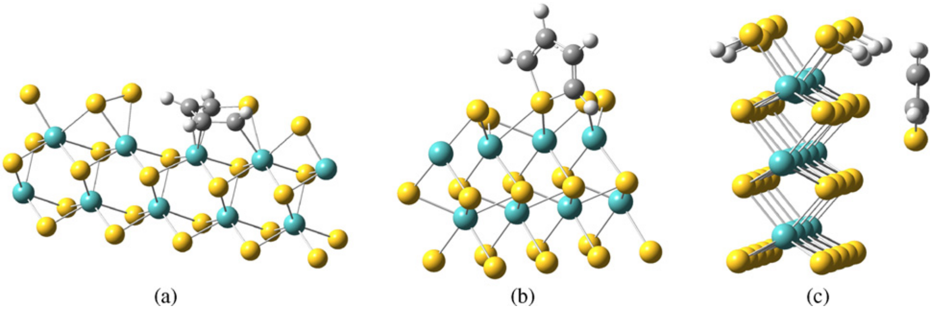

Fig. 4. Thiophene adsorption; (a) on a vacancy on the molybdenum edge; (b) on a stable sulfur edge; (c) on the basal plane. C, grey circle (adapted from refs. [92,18]).

extended to the sulfur edge taking into account the result of benzene adsorption on this edge [97,98]. To our knowledge, the effect of the promotion has not been studied extensively. An adsorption energy of 0.5 eV is computed by Sun et al. [99] for metallic edge fully promoted by nickel, a smaller value than the adsorption on the molybdenum atom in agreement with the evolution of the M–S bond strength between molybdenum and nickel. Such an evolution has also been mentioned by Itho and co-workers [94]. The thiophene reaction mechanism has been studied by Raybaud et al. [93] and Jiao and co-workers [95] but the active site used in these studies is constituted of molybdenum atoms of the unstable bare metallic edge, which excludes comparisons with experimental data.

4.2.3. Polyaromatic compounds

Because of their importance in deep desulfurization, adsorption and reaction of dibenzothiophene and dimethyldibenzothiophene on MoS_2 particles have been studied by different groups. The adsorption on the bare metallic edge is strongly exothermic [100,101]. The DBT adsorption is 3.3 eV for the flat adsorption on the crystallographic metallic edge. In this case, the adsorption energy is almost not influenced by the presence and the position of the methyl groups on the aromatic ring. The adsorption is even slightly stronger (3.5 eV) for the 2,8-DMDBT in agreement with the electron-donor properties of the methyl group. The perpendicular adsorption through the sulfur atom is also possible for all the DBT derivatives but less exothermic (1.3–1.5 eV). The hydrogenation of the benzene rings reduces the adsorption energy: 3.4 eV if one ring is hydrogenated and 1.75 eV if both are. On the basis of comparisons between DBT and its substituted derivatives, the authors conclude that the direct desulfurization (DDS) occurs through a $\eta 1$ adsorption mode by the sulfur atom even though the study is based on highly unsaturated clusters leading to surface models that are unlikely to be present in HDS conditions. The same proposition has been made simultaneously by Cristol et al. [102] but in this last study the molecular adsorptions have been studied on more realistic vacancies. The major differences between the DBT and the 4,6-DMDBT are obtained for the vertical adsorption by the sulfur atom. Because of the steric interaction between the methyl groups and the sulfur atoms of the basal plane, this adsorption mode is not possible on the metallic edge. The $\eta 1$ mode is however possible on the sulfur edge in the case of stacking defect of the MoS_2 particles (Fig. 5). Hence the number of adsorption sites for $\eta 1$ adsorption of DMDBT is far lower than the one for the adsorption of DBT. This difference is assumed to be at the origin of the very large differences in the DDS route between those two molecules.

The DDS of the DBT and DMDBT have been studied by the same group [103]. They calculated the activation energy of the DDS for a mechanism involving an electrophilic aromatic substitution for a fully cobalt promoted catalyst. The activation energy calculated for a reaction on the sulfur edge is estimated to be 1.0 eV (Fig. 6) in good agreement with the experimental value. Thus, based on theoretical calculations, it has been possible to propose an active site and a reaction mechanism for the DDS pathway (S-edge containing one sulfur atom per

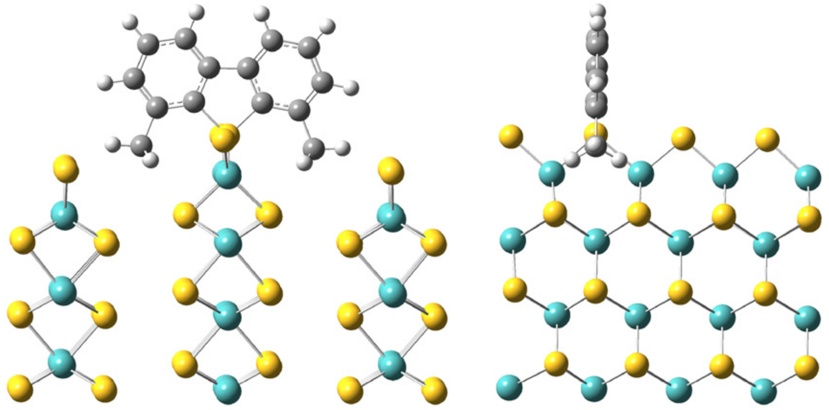

Fig. 5. 4,6-DMDBT adsorption on vacancy on the sulfur edge in case of stacking defect (adapted from ref. [102]).

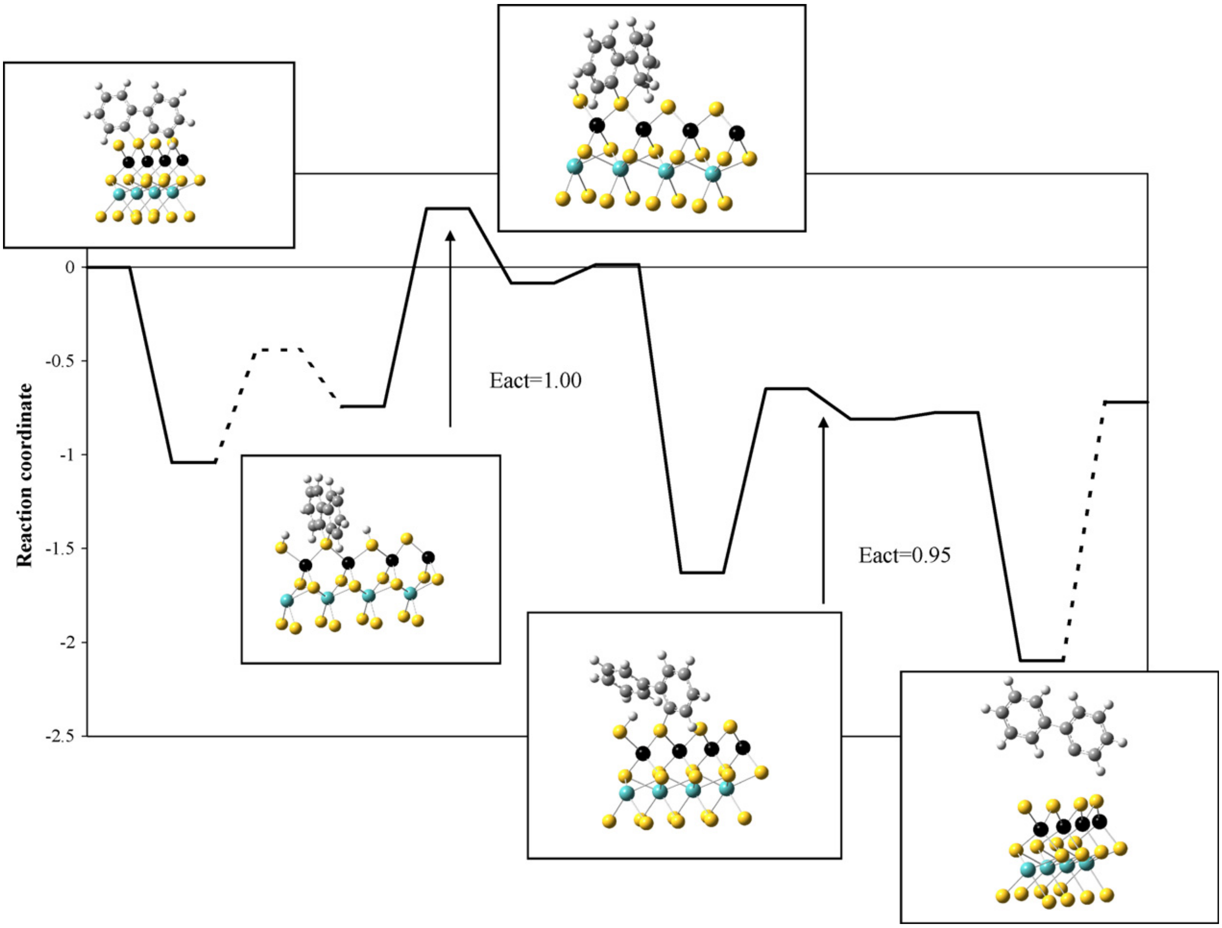

Fig. 6. DDS reaction pathway on fully promoted sulfur edge (adapted from ref. [103]). The dashed lines correspond to steps for which the activation energies have not been computed.

metallic atom). The hydrogenation site is however not well defined yet. For non-promoted catalysts, a flat adsorption by one of the benzene rings is possible on the bare surface as well as on a large vacancy [102] but the number of these types of sites will be very limited since their formation is highly endothermic ($\Delta E = 2.1$ eV). Furthermore, H_2S present in the gas phase will adsorb readily on such vacancies and would lead to a reduced catalyst activity. Another possibility has been proposed by Logadottir et al. [97] who computed the adsorption of benzene and pyridine on the edge of the basal plane. The computed values are very small but van der Waals interactions, which are not included in the DFT calculations, should have a major effect in such adsorption modes. These adsorption modes should be considered as possible starting points for the hydrogenation but, to our knowledge, the activation energies and reaction pathways have not been computed.

4.2.4. Nitrogen-containing compounds

The adsorption of nitrogen compounds has also been theoretically investigated mainly because of their strong inhibiting effect on the hydrogenation. Studies were carried out on the non-promoted catalyst [97] and on the Ni promoted one [99,104,105]. On the non-promoted catalyst, the adsorption of basic nitrogen molecules is possible on the edge of the basal plan, especially in presence of S–H groups which have acidic properties, the proton being transferred to the nitrogen atom (Fig. 7). Hence, the basic properties of these molecules will allow them to displace the sulfur-containing molecules adsorbed by the aromatic rings. This fundamental property may explain the strong inhibiting effect of this type of compounds on the hydrogenation properties of the catalysts. On the nickel promoted surfaces, the most favoured adsorption mode on the metallic edge is a vertical one through the nitrogen

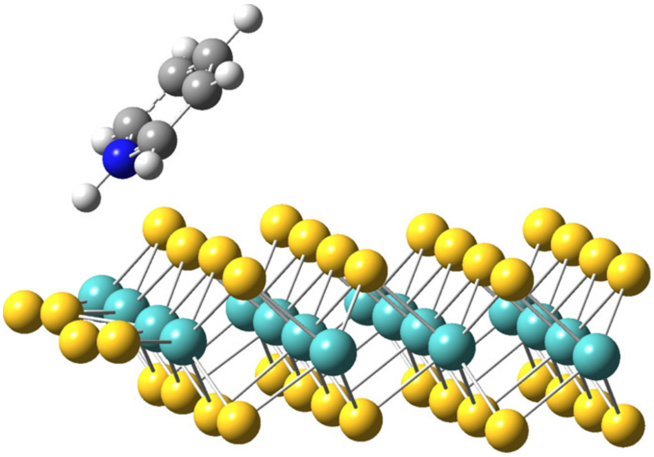

Fig. 7. Pyridinum adsorption on the basal plane (adapted from ref. [97]).

atom for a basic compound such as pyridine and flat by the aromatic ring for pyrrole. The hydrogenation reaction paths of these molecules have been investigated by Sun et al. [104]. The reaction path will depend on the reaction conditions. In presence of adsorbed H_2S molecule, the hydrogen is transferred from the H_2S group while it will come from Ni–H if the H_2S pressure is too low to allow the H_2S adsorption. It must be added that the calculations have been performed on a fully promoted edge. In the case of a partial promotion, the remaining sulfur atom on the stable surface may act as source of protons.

5. Conclusion

Within the last 10 years, *ab-initio* calculations performed on the HDS catalyst, either promoted or non-promoted, have given new insight in the catalyst reaction The main results can be summarized by the three following points.

First, the location of the promoter atoms have been studied in great details and the substitution model is now widely admitted on the basis of both experimental and theoretical studies.

Second, the sulfur coverage of both edges has been investigated. The results indicate clearly the non-promoted metallic edge is covered by bridging sulfur atoms and that the coordination of the molybdenum atoms is six, the adsorption of molecules being almost impossible. It is then mandatory to introduce a vacancy formation in the catalytic cycle. This step is endothermic and highly activated. On the sulfur edge, some discrepancies still exist in the results from different groups. However, it is possible to propose some general conclusions. The reaction conditions used to perform the reaction are close to the border of the sulfur coverage proposed in both models. The regeneration of the active site will then be a step with an equilibrium constant close to one. The ability to the metallic atoms to present different coordinations (here, 4 or 6) as well as different oxidation states is similar to what can be found in homogeneous catalysis. It is then possible to propose that the desulfurization can proceed on the sulfur edge. The effect of the promoter atom is clearly to reduce the M–S bond strength and to increase the number of vacancies on the stable edges of the MoS_2 particles. Furthermore, according to thermodynamic calculations, the cobalt atoms will mostly be localised on the sulfur edge while the nickel ones are located on both edges. This difference may be at the origin of the experimental differences between the two types of promoter atoms.

Finally, the calculations gave new indications on the possible reaction paths on the catalyst. Hydrogen activation is a key step in the reaction path, the activation energy being close to the experimental value obtained for the whole catalytic cycle on the non-promoted catalyst. The promoter atoms reduce the activation energy of this dissociation and increase the number of hydrogen atoms on the active phase. The adsorption of a great number of molecules has been studied. The results suggested a new reaction mechanism for refractory molecules such as the DMDBT, both for the hydrogenation and direct desulfurization reaction pathways. The starting point of the hydrogenation may be a flat adsorption on the rim of the basal plan, while the DDS is thought to be due to a vertical adsorption of the molecule through the sulfur atom. It must be added that the results on the promoted systems are less common, at least nowadays, and that the reaction mechanisms have not been fully calculated.

References

[1] C. Song, Catal. Today 86 (2003) 211.
[2] I.V. Babich, J.A. Moulijn, Fuel 82 (2003) 667.
[3] H. Topsøe, B.S. Clausen, F.E. Massoth, in: J.R. Andersen, M. Boudart (Eds.), Hydrotreating Catalysis. Science and Technology, vol. 11, Springer, Berlin, 1996.
[4] A.D. Gandubert, C. Legens, D. Guillaume, E. Payen, Surf. Interface Anal. 38 (2001) 206.
[5] I. Alstrup, I. Chorkendorff, R. Candia, B.S. Clausen, H. Topsoe, J. Catal. 77 (1982) 397.
[6] S. Kasztelan, J. Grimblot, J.P. Bonnelle, E. Payen, H. Toulhoat, Y. Jacquin, Appl. Catal. 7 (1983) 91.
[7] Y. Araki, K. Honna, H. Shimada, J. Catal. 207 (2002) 316.
[8] E.J.M. Hensen, P.J. Kooyman, Y. van der Meer, 1.M. van der Kraan, V.H.J. de Beer, J.A.R. van Veen, R.A. van Santen, J. Catal. 199 (2001) 224.
[9] A. Carlsson, M. Brorson, H. Topsøe, J. Catal. 227 (2004) 530.
[10] M. Brorson, A. Carlsson, H. Topsøe, Catal. Today 123 (2007) 31.
[11] K.P. de Jong, L.C.A. van den Oetelaar, E.T.C. Vogt, S. Eijsbouts, A.J. Koster, H. Friedrich, P.E. de Jongh, J. Phys. Chem. B 110 (2006) 10209.
[12] M.J.W. Crajé, S.P.A. Louwers, V.H.J. de Beer, R. Prins, A.M. van der Kraan, J. Phys. Chem. 96 (1992) 5445.
[13] G. Plazenet, S. Cristol, J.-F. Paul, E. Payen, J. Lynch, Phys. Chem. Chem. Phys. 3 (2001) 246.
[14] C. Geantet, Y. soldo, C. Glasson, N. Matsubayashi, M. Lacroix, O. Proux, O. Ulrich, J.-L. Hazeman, Catal. Lett. 73 (2001) 95.
[15] J. Kibsgaard, J.V. Lauritsen, E. Lægsgaard, B.S. Clausen, H. Topsøe, F. Besenbacher, J. Am. Chem. Soc. 128 (2006) 13950.
[16] S. Helveg, J.V. Lauritsen, E. Lægsgaard, I. Stensgaard, J.K. Nørskov, B.S. Clausen, H. Topsøe, F. Besenbacher, Phys. Rev. Lett. 84 (2000) 951.
[17] J.V. Lauritsen, S. Helveg, E. Lægsgaard, I. Stensgaard, B.S. Clausen, Topsøe, F. Besenbacher, J. Catal. 197 (2001) 1.
[18] J.V. Lauritsen, M. Nyberg, J.K. Nørskov, B.S. Clausen, H. Topsøe, E. Lægsgaard, F. Besenbacher, J. Catal. 224 (2004) 94.
[19] N.-Y. Topsøe, H. Topsøe, J. Catal. 84 (1983) 386.
[20] J.B. Peri, J. Phys. Chem. 86 (1982) 1615.
[21] F. Maugé, J. Lamotte, N.S. Nesterenko, O. Manoilova, A.A. Tsyganenko, Catal. Today 70 (2001) 271.
[22] B. Müller, A.D. van Langeveld, J.A. Moulijn, H. Knözinger, J. Phys. Chem. 97 (1993) 9028.
[23] J. Bachelier, M.J. Tilliette, M. Cornac, J.-C. Duchet, J.-C. Lavalley, D. Cornet, Bull. Soc. Chim. Belgium 93 (1984) 743.
[24] R. Prins, V.H.J. De Beer, G.A. Somorjai, Catal. Rev.-Sci. Eng. 31 (1989) 1.
[25] M. Breysse, G. Djega-Mariadassou, S. Pessayre, C. Geantet, M. Vrinat, G. Pérot, M. Lemaire, Catal. Today 84 (2003) 129.
[26] http://cms.mpi.univie.ac.at/vasp/.
[27] http://wiki.fysik.dtu.dk/dacapo.
[28] http://www.accelrys.com/.
[29] http://www.scm.com.
[30] http://www.gaussian.com.
[31] W. Kock, M.C. Holthausen, A Chemist's Guide to Density Functional Theory, Wiley-VCH, 2001.
[32] R.J. Meier, Vib. Spectrosc. 43 (2007) 26.
[33] D. Loffreda, Surf. Sci. 600 (2006) 2103.
[34] M. Digne, P. Sautet, P. Raybaud, P. Euzen, H. Toulhoat, J. Catal. 211 (2002) 1.

[35] P. Raybaud, G. Kresse, J. Hafner, H. Toulhoat, J. Phys. Condens. Matter 9 (1997) 11085.
[36] P. Raybaud, G. Kresse, J. Hafner, H. Toulhoat, J. Phys. Condens. Matter 9 (1997) 11106.
[37] J.P. Perdew, M. Levy, Phys. Rev. Lett. 51 (1983) 1884.
[38] P. Raybaud, J. Hafner, G. Kresse, H. Toulhoat, Surf. Sci. 407 (1998) 237.
[39] M.V. Bollinger, J.V. Lauritsen, K.W. Jacobsen, J.K. Nørskov, S. Helveg, F. Besenbacher, Phys. Rev. Lett. 87 (2001) 196803.
[40] Y. Aray, J. Rodrıguez, J. Mol. Catal. A: Chem. 265 (2007) 32.
[41] J.A. Spirko, M.L. Neiman, A.M. Oelker, K. Klier, Surf. Sci. 542 (2003) 192.
[42] V. Alexiev, R. Prins, T. Weber, Phys. Chem. Chem. Phys. 2 (2000) 1815.
[43] H. Orita, K. Uchida, N. Itoh, J. Mol. Catal. A: Chem. 195 (2003) 173.
[44] Y.-W. Li, X.-Y. Pang, B. Delmon, J. Phys. Chem. A 104 (2000) 11375.
[45] M.V. Bollinger, K.W. Jacobsen, J.K. Nøsrskov, Phys. Rev. B 67 (2003) 085410.
[46] L.S. Byskov, B. Hammer, J.K. Nørskov, B.S. Clausen, H. Topsøe, Catal. Lett. 47 (1997) 177.
[47] P. Raybaud, J. Hafner, G. Kresse, S. Kasztelan, H. Toulhoat, J. Catal. 189 (2000) 129.
[48] G. Wu, K. Fan, B. Delmon, Y.-W. Li, J. Mol. Catal. A: Chem. 247 (2006) 189.
[49] S. Cristol, J.F. Paul, E. Payen, D. Bougeard, S. Clémendot, F. Hutschka, J. Phys. Chem. B 104 (2000) 11220.
[50] X.-D. Wen, T. Zeng, Y.-W. Li, J. Wang, H. Jiao, J. Phys. Chem. B 109 (2005) 18491.
[51] S. Cristol, J.F. Paul, E. Payen, D. Bougeard, S. Clémendot, F. Hutschka, J. Phys. Chem. B 106 (2002) 5659.
[52] H. Schweiger, P. Raybaud, G. Kresse, H. Toulhoat, J. Catal. 207 (2002) 76.
[53] J.V. Lauritsen, M.V. Bollinger, E. Lægsgaard, K.W. Jacobsen, J.K. Nørskov, B.S. Clausen, H. Topsøe, F. Besenbacher, J. Catal. 221 (2004) 510.
[54] T. Shido, R. Prins, J. Phys. Chem. B 102 (1998) 8426.
[55] C. Calais, N. Matsubayashi, C. Geantet, Y. Yoshimura, H. Shimada, A. Nishijima, M. Lacroix, M. Breysse, J. Catal. 174 (1998) 130.
[56] N. Matsubayashi, H. Shimada, M. Imamura, Y. Yoshimura, A. Nishijima, C. Calais, C. Geantet, J. Synchrotron Radiat. 6 (1999) 428.
[57] A. Travert, C. Dujardin, F. Maugé, S. Cristol, J.F. Paul, E. Payen, D. Bougeard, Catal. Today 70 (2001) 255.
[58] T. Zeng, X.-D. Wen, G.-S. Wu, Y.-W. Li, H. Jiao, J. Phys. Chem. B 109 (2005) 2846.
[59] T. Zeng, X.-D. Wen, Y.-W. Li, H. Jiao, J. Phys. Chem. B 109 (2005) 13704.
[60] M.-A. Lelias, A. Travert, J. van Gestel, F. Maugé, J. Phys. Chem. B 110 (2006) 14001.
[61] R.R. Chianelli, A.F. Ruppert, M. Jose-Yacaman, A. Vazquez-Zavala, Catal. Today 23 (1995) 269.
[62] S. Kasztelan, H. Toulhoat, J. Grimblot, J.-P. Bonnelle, Appl. Catal. 13 (1984) 127.
[63] H. Topsøe, B.S. Clausen, N.Y. Topsøe, E. Pedersen, W. Niemann, A. Müller, H. Bögge, B.J. Lengeler, Chem. Soc., Faraday Trans. 1 83 (1987) 2157.
[64] J.V. Lauritsen, S. Helveg, E. Lægsgaard, I. Stensgaard, B.S. Clausen, H. Topsøe, F. Besenbacher, J. Catal. 197 (2001) 1.
[65] P. Faye, E. Payen, D. Bougeard, J. Catal. 183 (1999) 396.
[66] L.S. Byskov, J.K. Nørskov, B.S. Clausen, H. Topsøe, J. Catal. 187 (1999) 109.
[67] M. Sun, A.E. Nelson, J. Adjaye, J. Catal. 226 (2004) 32.
[68] A. Travert, H. Nakamura, R.A. van Santen, S. Cristol, J.-F. Paul, E. Payen, J. Am. Chem. Soc. 124 (2002) 7084.
[69] P. Raybaud, J. Hafner, G. Kresse, S. Kasztelan, H. Toulhoat, J. Catal. 190 (2000) 128.
[70] L.P. Nielsen, S.V. Christensen, H. Topsøe, B.S. Clausen, Catal. Lett. 67 (2000) 81.
[71] H. Schweiger, P. Raybaud, H. Toulhoat, J. Catal. 212 (2002) 33.
[72] A. Travert, C. Dujardin, F. Maugé, E. Veilly, S. Cristol, J.-F. Paul, E. Payen, J. Phys. Chem. B 110 (2006) 1261.
[73] H. Toulhoat, P. Raybaud, S. Kazstelan, G. Kresse, J. Hafner, Catal. Today 50 (1999) 629.
[74] R.R. Chianelli, G. Berhault, P. Raybaud, S. Kasztelan, J. Hafner, H. Toulhoat, Appl. Catal. A: Gen. 227 (2002) 83.
[75] F. Dumeignil, J.-F. Paul, E.W. Qian, A. Ishihara, E. Payen, T. Kabe, Res. Chem. Intermed. 29 (2003) 589.
[76] A. Ishihara, F. Dumeignil, D. Wang, X. Li, H. Arakawa, E.W. Qian, S. Inoue, A. Muto, T. Kabe, Appl. Catal. A: Gen. 292 (2005) 50.
[77] M. Sun, A.E. Nelson, J. Adjaye, J. Catal. 233 (2005) 411.
[78] M. Sun, A.E. Nelson, J. Adjaye, Catal. Today 105 (2005) 36.
[79] A. Sierraaltaa, O. Lisboaa, L. Rodriguez, J. Mol. Struct.: THEOCHEM 729 (2005) 91.
[80] M. Lacroix, H. Jobic, C. Dumonteil, P. Afanasiev, M. Breysse, S. Kasztelan, Stud. Surf. Sci. Catal. 101 (1996) 117.
[81] P. Sundberg, R.B. Moyes, J. Tomkinson, Bull. Soc. Chim. Belgium 100 (1991) 967.
[82] P.C.H. Mitchell, D.A. Green, E. Payen, A.C. Evans, Faraday Trans. 24 (1995) 4467.
[83] V.M. Kogan, Appl. Catal. A: Gen. 237 (2002) 161.
[84] X.-D. Wen, T. Zenga, B.-T. Teng, F.-Q. Zhang, Y.-W. Li, J. Wang, H. Jiao, J. Mol. Catal. A: Chem. 249 (2006) 191.
[85] Y.-W. Li, X.-Y. Pang, B. Delmon, J. Mol. Catal. A: Chem. 169 (2001) 259.
[86] M. Neurock, R.A. van Santen, J. Am. Chem. Soc. 116 (1994) 4427.
[87] T. Todorova, R. Prins, T. Weber, J. Catal. 236 (2005) 190.
[88] T. Todorova, R. Prins, T. Weber, J. Catal. 246 (2007) 109.
[89] J.-F. Paul, E. Payen, J. Phys. Chem. B 107 (2003) 4057.
[90] P. Raybaud, J. Hafner, G. Kresse, H. Toulhoat, Phys. Rev. Lett. 80 (1998) 1481.
[91] H. Orita, K. Uchida, N. Itoh, J. Mol. Catal. A: Chem. 193 (2003) 197.
[92] S. Cristol, J.-F. Paul, C. Schovsbo, E. Veilly, E. Payen, J. Catal. 239 (2006) 145.
[93] P. Raybaud, J. Hafner, G. Kresse, H. Toulhoat, Stud. Surf. Sci. Catal. 127 (1999) 309.
[94] H. Orita, K. Uchida, N. Itoh, Appl. Catal. A: Gen. 258 (2004) 115.
[95] X.-Q. Yao, Y.-W. Li, H. Jiao, J. Mol. Struct.: THEOCHEM 726 (2005) 81.
[96] J. Pérez-Jordà, A.D. Becke, Chem. Phys. Lett. 233 (1995) 134.
[97] A. Logadottir, P.G. Moses, B. Hinnemann, N.-Y. Topsøe, K.G. Knudsen, H. Topsøe, J.K. Nørskov, Catal. Today 111 (2006) 44.
[98] P.G. Moses, ICTAT 11, 11-14/06/2006 Schmöckwitz, Berlin (Germany).
[99] M. Sun, A.E. Nelson, J. Adjaye, Catal. Lett. 109 (2006) 133.
[100] H. Yang, C. Fairbridge, Z. Ring, Energy Fuels 17 (2003) 387.
[101] H. Yang, C. Fairbridge, J. Chen, Z. Ring, Catal. Lett. 97 (2004) 217.
[102] S. Cristol, J.-F. Paul, E. Payen, D. Bougeard, F. Hutschka, S. Clémendot, J. Catal. 224 (2004) 138.
[103] E. Veilly, PhD Thesis, Lille University, 2003.
[104] M. Sun, A.E. Nelson, J. Adjaye, Catal. Today 109 (2005) 49.
[105] M. Sun, A.E. Nelson, J. Adjaye, J. Catal. 231 (2005) 223.