Surface Science 605 (2011) 513–519

Contents lists available at ScienceDirect

Surface Science

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

Chemisorption on cobalt surfaces: The effect of subsurface rhenium atoms from quantum chemical cluster model calculations

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ARTICLE INFO

Article history:
Received 6 September 2010
Accepted 7 December 2010
Available online 17 December 2010

Keywords:
Ab initio quantum chemical methods and calculations
Catalysis
Chemisorption
Surface chemical reaction
Cobalt
Rhenium

ABSTRACT

We have calculated chemisorption energies for different sorbates on cluster models for a number of sites on pure and subsurface rhenium-doped cobalt surfaces. Bonding energies follow the trend water<CO<propyl<methyl<hydrogen<hydroxyl, and are in good agreement with experimental results where available. The results indicate that for single-bond radicals (hydrogen, alkyl, hydroxyl), rhenium inclusion stabilizes the chemisorbed species. Further, the stabilization leads to a greater number of sites being energetically close to the most stable ones, possibly enhancing surface mobility of chemisorbed species. Hydrogen is less stabilized by rhenium substitution compared to propyl, indicating a possible mechanism for the greater yield of long-chained hydrocarbons afforded by rhenium-doped catalysts. For carbon monoxide, the results are less conclusive as rhenium substitution does not influence chemisorption energies so strongly.

1. Introduction

Metal clusters have proven to be useful models for surface and bulk phenomena both in theoretical [1] and experimental [2–4] investigations. In particular smaller metal clusters are well suited for quantum mechanical studies, as indicated by the amount of existing literature on the subject [5]. It is worth noting that the quantum chemical literature on cluster studies mostly deals with copper [6] and nickel [7], and that relatively little has been published on cobalt [8,9].

Some of the most important heterogeneous catalysts are based on transition metals. They may consist of a single metal or an alloy. In the latter case, one speaks of a bimetallic or promoted catalyst. Statoil [10] has developed a bimetallic catalyst for Fischer–Tropsch (F–T) synthesis, in which cobalt promoted with rhenium, presumably an alloy, is supported on a stabilized γ-alumina. The F–T process was first described more than 80 years ago [11] and implemented on a full industrial scale more than 70 years ago [12]. F–T synthesis has seen renewed interest lately, at least partially due to high crude oil prices. Nevertheless, the process is still not fully understood; the role of rhenium or other dopants being one of the points still under debate.

Elsewhere we have reported the interaction between rhenium and cobalt through quantum chemical cluster model calculations [13,14] and Low Energy Ionic Scattering Spectroscopy (LEISS) [14]. Our results, which corroborate earlier computational semiempirical results published by Ruban et al. [15], strongly indicate that rhenium preferentially occupies subsurface sites. An interesting question is, then, how subsurface rhenium influences the reactivity of the cobalt surface. In the present contribution, we describe quantum chemical cluster model studies of chemisorption of a number of species known to be involved in elementary steps of F–T synthesis. The focus of this investigation is not the specific clusters as such, but rather to uncover trends in chemisorption energies for different sorption sites as subsurface rhenium atoms are introduced.

Hydrogen, one of the reactants, has been shown to chemisorb dissociatively on cobalt surfaces forming atoms; methyl is a postulated intermediate in the reaction; propyl represents the growing chain and is a direct precursor for propene, a by-product; CO is a reactant and H_2O is a primary product. Chemisorption energies for these species on pure cobalt and bimetallic cobalt/rhenium clusters have been computed to elucidate the effect of rhenium doping upon chemisorption energies.

2. Computational details

All calculations were carried out using the PW91 [16] density functional as implemented in the Amsterdam Density Functional package (ADF) [17–19]. The inner core orbitals (up to and including 3p for Co and 4f for Re), were kept frozen, while the valence orbitals were described by the TZP Slater-type basis sets built into the ADF package. Relativistic effects were taken into account using the ZORA method [20], and spin-orbit coupling has thus not been included in

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doi:10.1016/j.susc.2010.12.008

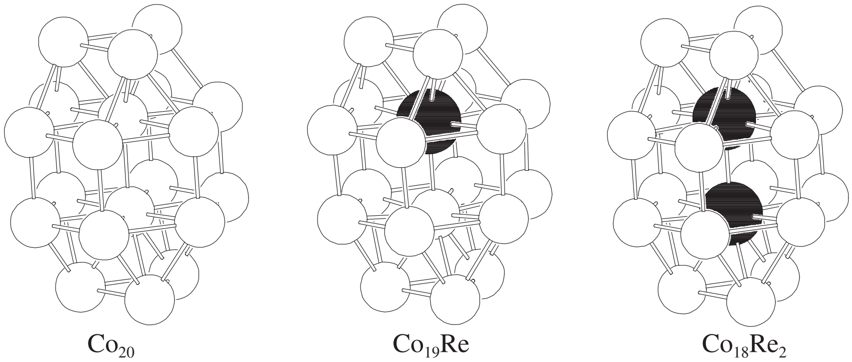

Fig. 1. 20-atom cluster models. Cobalt atoms are white, rhenium black.

the description of the electronic structures. Reported partial atomic charges are computed using the Hirshfeld formalism [21].

20-atom clusters have been used to model the pure and rhenium-doped cobalt surfaces; see Fig. 1. Ground-state spin multiplicities of the clusters were taken as reference states. For calculating chemisorption energies of sorbates that may be called “one-electron ligands” in organometallic parlance, the total spin polarization vas reduced by 2 compared to the sum of spin polarizations for the two separated systems (cluster and sorbate, the latter in these cases being a doublet radical). In the calculations involving closed-shell sorbates, spin polarization was kept at the ground-state value for the corresponding bare cluster. Literature results [22] suggest that sorption of small ligands on metal surfaces may be described as local phenomena. For clusters described by all-electron GGA DFT calculations, absolute binding energies for organic fragments are usually converged to within some 30 kJ/mol for clusters of even smaller size than the one used here. The primary focus in the present work is differences (trends) in chemisorption energies, and these will be more reliable than the absolute values due to cancellation of error.

3. Results and discussion

3.1. The clusters

Three 20-atom clusters, Co_{20}, $Co_{19}Re$, and $Co_{18}Re_2$, shown in Fig. 1, have been used to model different surface sites. Between them, they offer models for different sites of varying coordination and proximity of subsurface rhenium. The metal moieties of the FT catalyst are highly irregular, showing entwined oxide and metal regions and possibly even mixed phases (cobalt aluminates) [23]. While the metal agglomerates of the working catalyst contain much more than 20 atoms, it has been shown that single chemisorption events may be regarded as quite local phenomenae. Chemisorption energies and geometries of chemisorbed species on metal surfaces have been successfully determined using computational methods and quite small cluster models [7]. Reboredo and Galli [24] found that chemisorption energies for CO on cobalt clusters vary monotonically and predictably with cluster size down to 13 atoms. We conclude that the 20-atom clusters used should be entirely adequate for describing the trends that are the subject of the present contribution.

The cluster geometries were constructed based on our previous findings for smaller cobalt/rhenium clusters [25]. For reasons of computational feasibility, it proved necessary to use clusters that maintain a modicum of symmetry (*i.e.* at least C_s-symmetry) even after adsorption. The chosen clusters have D_{3h}-, C_{3v}- and D_{3h}-symmetry, respectively, yielding C_{3v}- and C_s-symmetry upon adsorption. Prior to the sorption calculations, each cluster was fully optimized with regards to both spin polarization and geometry within the given symmetry. The selected cluster geometries likely constitute low-energy structures, though they are not necessarily global minima for their stoichiometries. For example for Co_{20}, a twisted configuration having D_3-symmetry was found to be approximately 100 kJ/mol lower in energy than the D_{3h}-structure. However, the former structure was deemed unsuitable for the current investigation, due to the fact that the calculations of adsorbed species would have to be run without any symmetry. Our subject here is anyway not the clusters *per se*, but rather the qualitative changes in surface chemistry induced by rhenium doping.

The total partial Hirshfeld charge on rhenium is the same for $Co_{19}Re$ and $Co_{18}Re_2$: 0.2 e^-/atom in the former case and 0.1 e^-/atom in the latter. This should be compared to the partial charges on the two central atoms in the pure cobalt cluster which are essentially zero ($-0.03\ e^-$). The relatively small change correlates well with the fact that the two elements have quite similar electronegativities.

The spin polarization (defined as the difference between the numbers of electrons of majority and minority spin, $N\uparrow - N\downarrow$) of the most stable electronic state decreases by 6 units upon substitution of one cobalt atom with rhenium, and additionally 2 when the second substitution takes place. This downcoupling of spins is in line with results from earlier cluster studies [8,13,14]. Additionally, the substitution of cobalt by rhenium stabilizes the cluster by about 150 kJ/mol per rhenium atom.[4] The fact that the stabilization is almost identical for the first and second Re-atom indicates that the 20-atom clusters are large enough to model the energetics of incorporation of up to two rhenium atoms. This as opposed to the 14-atom clusters previously investigated [13].

Rhenium has a larger metallic radius than cobalt, and the replacement of cobalt with rhenium at the two central positions in the cluster unsurprisingly expands the cluster. Looking at the distance between the two interior positions, Co_{20} yields a Co–Co distance of 2.38 Å, whereas the Re–Re distance in $Co_{18}Re_2$ is 2.49 Å, although the trend is broken by $Co_{19}Re$ having a central Co–Re distance of 2.36 Å. The effect on the three cobalt atoms making up our chosen adsorption site is that the Co–Co distance is increased slightly from 2.39 Å in the pure cobalt cluster, to 2.40 Å/2.41 Å and 2.45 Å in $Co_{19}Re$ and $Co_{18}Re_2$, respectively. Experimentally, the closest bulk interatomic distances in the pure metals are 2.5 and 2.75 Å for cobalt and rhenium, respectively.

As the different sorbates are investigated, the clusters are kept frozen at their optimized geometries. Relaxing the cluster geometries upon chemisorption would lead to greater changes compared to the real catalyst, where the metal aggregates are much larger and supported by the oxide. Hence, we hold that relaxation of the clusters would waste computational resources without improving the predictive power of the calculations. One referee has raised the question of sorbate-induced segregation, *i.e.* the possibility that sorption could lead to rhenium being pulled out to the surface. Such a situation could

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[4] Substitution energies calculated relatively to the relevant clusters and single metal atoms in vacuum.