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Support effects in HDS catalysts: DFT analysis of thiolysis and hydrolysis energies of metal–support linkages

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ABSTRACT

We have carried out a theoretical investigation of the active phase–support interaction for HDS catalysts using density functional theory to calculate the thiolysis and hydrolysis reaction energies for the metal–support linkages. These metal–support linkages are represented by simplified cluster models with –SH or –OH terminations to represent the sulfide (active) and oxide (support) phases, respectively. The calculated rank order of the supports representing Type-I (strong interaction) tendency ($SiO_2 < \text{carbon} < Al_2O_3 < TiO_2 < ZrO_2 < Y_2O_3$) is in agreement with the experimentally observed behavior. Based on the calculated energetics the temperature-induced Type-II nature of the MoS_2–Al_2O_3 interaction is predicted by a higher equilibrium constant of the thiolysis reaction at higher temperature. Thus, the thiolysis energy provides a qualitative scale of the Type-I/Type-II nature of the support and is, therefore, a useful descriptor of catalytic behavior.

1. Introduction

In order to meet the future regulations for allowed sulfur content in gasoline and diesel fuels, an order of magnitude improvement in the efficiency of the hydrodesulfurization (HDS) processes is desired. Reaching that goal will include optimization of process conditions as well as discovery of new HDS catalysts. HDS catalysts are typically mixed metal sulfide materials impregnated on some amphoteric or acidic oxide support. The nature of support used in the catalyst plays a significant role in determining its activity as reviewed recently by Dhar et al. [1]. In addition to alumina (Al_2O_3), various other metal-oxides such as SiO_2, TiO_2 [2,3], ZrO_2 [4,5] and MgO [6] have been experimentally investigated. Novel catalytic supports such as zeolites [7], mesoporous materials [8–10] and clays [11] have also been proposed in the literature. It was found [2,3] that supports such as TiO_2 and ZrO_2 lead to catalysts with higher intrinsic activity. The choice of the support has important implications for catalyst properties, such as aging and deactivation, regeneration, reducibility, and ease of sulfidation, as well as the recovery of the spent catalysts. For example, use of carbon as the support provides a strategic advantage in terms of the recovery of the precious metal. However, the limited surface area and weak mechanical properties have prevented the commercialization of many of these supports.

In order to overcome the shortcomings of the individual single metal-oxide systems, binary mixtures of these have been recently pursued in the literature. The TiO_2–Al_2O_3 system, taking advantage of the higher activity of the titania and higher surface area of the alumina, is the important one with considerable scientific and commercial presence [12–16]. Such supports are prepared by coprecipitation, impregnation, chemical vapor deposition and grafting [13,17]. Other combinations of the mixed metal-oxide supports, such as SiO_2–Al_2O_3, B_2O_3–Al_2O_3, and ZrO_2–Al_2O_3, have also been tried and reviewed recently by Dhar et al. [1]. The dispersion, acidity (both Brønsted and Lewis), and redox properties of the support are highly dependent on the preparation method of the mixed metal oxides.

In this paper, we study the effect of different metal-oxides as supports for HDS catalysts using theoretical methods. We have focused on the supports for two primary reasons: (1) changing support properties is the easiest and most economic way to manipulate microscopic properties for commercial scale synthesis of the catalyst and (2) active phase–support interactions are not completely understood for HDS catalysts. In particular, our emphasis is on the interaction of transition metal sulfides (active phase) with the oxide supports and quantifying the nature of such interactions.

1.1. Type-I and Type-II supports

Metal–support interactions have long been known to play an important role in HDS catalysts. FTIR has shown [18–21] that

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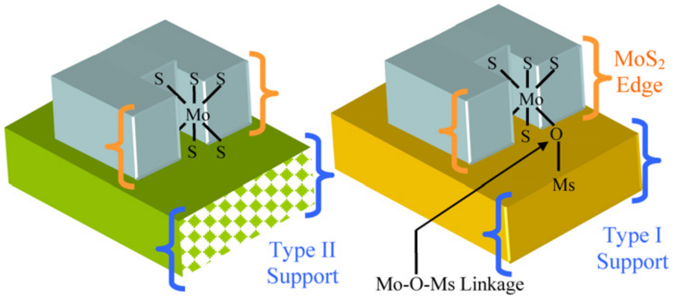

a) Type II Structure

b) Type I Structure
with Mo-O-Ms Linkages

Fig. 1. Schematic representation of the (a) Type-II and (b) Type-I structures showing the metal sulfide and support interaction.

oxide-supports tend to form chemical linkages with the Mo atoms of the MoS_2 phase. After deposition of the active metals from solutions, these catalysts are calcined at 400 to 600 °C when most of the metal–support linkages are formed. The tendency for the formation of such linkages differs from one support to another and it is also dependant on the sulfidation conditions. The catalysts with higher tendency of formation of such linkages are known as "Type-I catalysts." The absence of such linkages leads to "Type-II catalysts." Effect of such linkages on the morphology of the MoS_2 particles has been observed directly by Hensen et al. [22]. It is well established that use of alumina (Al_2O_3) as a support leads to the smaller MoS_2 particles since the metal–support interaction (i.e. chemical linkage between MoS_2 and Al_2O_3, see Fig. 1) inhibits the free lateral growth of the MoS_2 crystallite. Such inhibition is in-fact advantageous as it leads to smaller crystallites and consequently higher dispersion [22]. Further, as a consequence of these interactions, the mobility of the MoS_2 particles on the support surface is hindered, thereby preventing the sintering during calcination or sulfidation treatment. DFT investigation by Hinnemann et al. [23] has shown the spatial and quantitative nature of such metal–support interaction. These authors report that MoS_2 tends to form linkages to the support through oxygen atoms only on the periphery (edge) of the MoS_2 basal planes. Formation of such linkages from the bulk atoms (non-peripheral) atoms is energetically not favorable.

In addition to its formation of chemical linkages, the support also has an electronic effect on the transition metal–sulfide crystallite. DFT results by Hinnemann et al. [23] show that the molybdenum–sulfur binding energy at the MoS_2 edge increases upon formation of Mo–O linkages to the support. This was rationalized based on the increased polarity of the Mo–S bond in the vicinity of the Mo–O linkages. It was further observed that H_2 binding energy to such S atoms goes down with increasing S binding energy. Since S vacancies are considered as active HDS sites, the intrinsic activity of Type-I structures is expected to be lower. Questions that remain about these linkages are: (a) Why do some supports give rise to Type-I structures while others do not? and (b) Why does the formation of the Type-I or Type-II structures depend on the synthesis conditions?

The binding orientation of the MoS_2 particles has been studied extensively using transmission electron microscopy (TEM) and is important for determining the total MoS_2 edge area available for HDS reactions. MoS_2 particles are [24] bonded by basal planes on the (111) surface of Al_2O_3, while on the (100) surface, edge bonded particles dominate. On TiO_2 surfaces, the epitaxial similarity between the (110) surface of MoS_2 and the (001) surface of TiO_2 leads to formation of the edge bonded MoS_2 particles. It has also been shown that the concentration and the nature of the surface hydroxyl groups is sensitive to the epitaxial arrangement and surrounding conditions (p_{H_2O}, p_{H_2}, and T). For example, using ab initio calculations, Toulhoat and coworkers [25] found that a γ-Al_2O_3 (110) surface is highly hydroxylated as opposed to a (100) surface, which shows only Lewis acidity at temperatures above 600 K. Other model support studies include work by de Jong et al. [26] focusing on MoS_2 on SiO_2/Si(100) epitaxial growth. Their investigation included XPS (X-ray Photoelectron Spectroscopy), AFM (Atomic Force Microscopy), RBS (Rutherford Backscattering) and SIMS (Secondary Ion Mass Spectrometry) to show the sulfidation mechanism of Mo oxides on SiO_2 films. According to this mechanism the sulfidation of MoO_3 to MoS_2 proceeds through Mo(IV) oxysulfide. Other model support studies include Ni–W–S and Co–W–S on SiO_2/Si(100) to study the effects of chelating agents by Kishan et al. [27,28]. For such model supports, differential charging of the catalyst (common for the regular support) is prevented during XPS measurements. Resulting narrow XPS lines are easier to interpret in terms of the change in the oxidation state of the active metals. It was shown [27] that addition of the chelating agents prolongs the sulfidation of the Ni-containing phase. It was proposed that the chelating agents, such as CyDTA, complex with the Ni. The decomposition of the chelating agent was found to be coincident with the sulfidation of the Ni phase. Similar study of the CoWS system indicated that use of the chelating agents promotes the synergy of the two sulfide phases. These results indirectly suggest that the chelating agents can selectively modify the metal–support interaction by complexing with one of the transition metals.

Recently there have been several excellent reviews of the current level of the experimental and theoretical understanding of hydrotreating catalysts. A review by Besenbacher et al. [29] has covered recent aspects of the combined STM and DFT understanding of the MoS_2 particle shape and its dependence on the catalyst composition. A couple of recent papers [30,31] by Raybaud and coworkers have focused on a predictive approach to improve the HDS catalysts. Using recent advances in theoretical understanding [30], the group has focused on the metal–sulfur bond energy as the base descriptor for fine tuning the catalyst performance and proposed an improved NiMoWS catalyst [31].

Arrouvel et al. [25,32,33] carried out very detailed investigations of Mo_6S_n ($n = 10$ to 24) cluster binding on γ-Al_2O_3 and anatase (TiO_2) using DFT. These authors [25] quantify two types of metal–support interactions for determining the orientation and stoichiometry of the MoS_2 particle on these supports. The "chemical ligand effect," which is equivalent to chemical bonding, dominates the binding of smaller MoS_2 particles on the supports. As MoS_2 particle gets larger the "physical ligand effect," which is equivalent to a physisorption interaction, tends to dominate over the chemical ligand effect due to the larger number of S atoms involved in the van der Waals interaction with the support. It is expected that with increasing particle size the chemical ligand effect which is equivalent to number of the chemical bonds between the active phase grows only with particle radius, r, while the physical ligand effect grows with r^2. Arrouvel et al. [25] confirm that the chemical ligand effect is mainly governed by the epitaxial relationship between the support and the MoS_2 phase. The physical ligand effect depends on the tendency of the support surface to remain hydroxylated for the given temperature and partial pressures (T, p_{H_2S}, p_{H_2} and p_{H_2O}). It was found [25] that for Al_2O_3, the physical ligand effect remains dominant for small MoS_2 particles (diameter > 10 Å) and the preferred binding mode is parallel to Al_2O_3 surfaces (110 and 100). Under this binding mode, the sulfur coverages (S/Mo ratio) are higher than the expected coverages for the isolated MoS_2 particles as higher S-coverage leads to better van der Waals stabilization. In case of the anatase, MoS_2 particles as large as 45 Å tend to be edge-bonded due to epitaxial compatibility. The higher S-vacancies associated with such particles have been proposed [25] as a reason for the higher activ-