

The role of reaction pathways and support interactions in the development of high activity hydrotreating catalysts

Henrik Topsøe^{a,*}, Berit Hinnemann^b, Jens K. Nørskov^b, Jeppe V. Lauritsen^c,
Flemming Besenbacher^c, Poul L. Hansen^a, Glen Hytoft^a,
Rasmus G. Egeberg^a, Kim G. Knudsen^a

^a Haldor Topsøe A/S, Nymøllevej 55, DK-2800 Lyngby, Denmark

^b Center for Atomic-scale Materials Physics, Department of Physics, Technical University of Denmark, DK-2800 Lyngby, Denmark

^c Department of Physics and Astronomy, Interdisciplinary Nanoscience Center (iNANO), University of Aarhus, DK-8000 Aarhus C, Denmark

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Abstract

Scanning tunneling microscopy (STM) investigations have recently provided the first atom-resolved images of reaction intermediates in the key steps of the hydrogenation (HYD) and direct desulfurization (DDS) pathways in hydrodesulfurization over MoS₂ nanoclusters. Surprisingly, special brim sites exhibiting a metallic character are observed to be involved in adsorption, hydrogenation and C–S bond cleavage. The insight is seen to provide a new framework for understanding the DDS and HYD pathways and the role of steric hindrance and poisons. Density functional theory (DFT) calculations have illustrated how support interactions may influence the activity of sulfided catalysts. The brim sites and the tendency to form vacancies are seen to differ in types I and II Co–Mo–S. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) studies show that the high activity Type II structures may be present as single sulfide sheets. Thus, stacking is not an essential feature of Type II catalysts. The article illustrates how the new scientific insight has aided the introduction of the new high activity BRIMTM type catalysts for FCC pre-treatment and production of ultra low sulfur diesel (ULSD).

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1. Introduction

The legislative requirements for ultra low sulfur transport fuels have resulted in new hydrodesulfurization (HDS) challenges for the refining industry [1–9]. In addition to the issues related to the legislative drive for removing sulfur, the refiners are also faced with a growing demand for diesel fuels. This demand may partly be met by producing less low value products such as heating oil. There is also a desire to convert heavy fractions by hydrocracking or ‘mild hydrocracking’ processes and one may introduce upgrading processes e.g. for light cycle oil.

In order to produce low sulfur transport fuels, the refiner may choose between different revamp or grassroots options and the most cost-effective solution will depend on the specific refinery situation with respect to configuration, feedstock blends and product-slate. The selection of catalyst types is an important decision. As sulfur conversion increases, we are left with the most refractory species, typically dialkylated dibenzothiophenes [1,3,4,6,10–12]. Under idealized conditions, the conversion of these sterically hindered molecules mainly proceeds via a pre-hydrogenation route (HYD) instead of the direct desulfurization route (DDS) which is dominating for molecules like DBT [1,3,4,6,10]. Since NiMo catalysts are generally more active for the indirect hydrogenation route and CoMo catalysts more active for the direct route, one could imagine that NiMo would be the preferred option for ultra deep

* Corresponding author.

E-mail address: het@topsoe.dk (H. Topsøe).

desulfurization. However, at low hydrogen pressures and high space velocities, CoMo catalysts are often seen to outperform NiMo catalysts [5]. One of the factors, which may also influence the choice of the catalyst, is the presence of nitrogen compounds in the feed which may inhibit the reactions [1,6,8,12,13–18]. Detailed studies of inhibition effects under real feed conditions [17] have revealed that it is especially specific basic nitrogen compounds that have an effect on the HDS and HDN activity. Although the nitrogen compounds inhibit both the direct and indirect desulfurization pathways, the effect is largest for the latter. Thus, selection of catalyst depends on both feedstock and operation conditions. It is furthermore important to consider the hydrogen availability [19] and the different deactivation rates of the DDS and HYD pathways.

The details of the HDS mechanism are poorly understood, since for a long time only limited direct information has been available regarding the nature of the sites involved in the different reaction pathways [1]. This situation has recently changed and we will presently discuss STM results and the DFT calculations which have provided direct images of key sites and reaction intermediates [20–24]. Of particular importance is the observation of a new class of fully sulfur-coordinated sites, the so-called brim sites, which may play a role in the HYD pathway. We will discuss how the presence of such sites may explain different catalytic and poisoning characteristics.

Recently, DFT studies [25] have been used to provide insight into support interactions and the origin of the activity differences between Type I and Type II MoS₂ and Co–Mo–S. It is seen that support interactions may cause large changes in the tendency to form vacancies and in the properties of the brim sites. Although support interactions may also influence the tendency to form stacked MoS₂ layers, HAADF-STEM studies [26] show that the active Type II structures may be present as single-layer.

The improved scientific understanding of key factors influencing the activity and selectivity of hydrotreating catalysts has had a significant impact on catalyst design and development. The present article discusses the development of the BRIMTM family of improved ULSD and FCC pre-treat catalysts.

2. Active sites and reaction pathways

The information regarding active sites and reaction pathways has in the past mainly been inferred from structure–activity correlations and kinetic studies [1,4,6]. The correlations have suggested that the active sites are located at the edges of the MoS₂ or Co–Mo–S nanoclusters. Furthermore, since the early studies of Lipsch and Schuit [27] and Kolboe [28], it has been widely accepted that the active sites are vacancies or coordinatively unsaturated sites created in a reaction with hydrogen [1]. It has been proposed that the vacancies will have an affinity for direct σ -type bond

formation with the sulfur atom of the reactant. Likewise, it has also been assumed that the vacancies will also bind H₂S and that this is the origin of the H₂S inhibition effects found in many studies [1]. Although the above simple picture can explain many observations, there exists little information on the nature of vacancies and their role. Furthermore, the simple picture does not explain that molecules, like dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT), are desulfurized by two pathways, a direct desulfurization pathway (DDS) and a hydrogenation pathway (HYD) [3,10]. Also, it has not been understood in detail why the relative role of the two pathways varies significantly with the type of reactant molecule and the presence of poisons.

It has been observed that DBT is mainly being desulfurized by the DDS pathway, whereas 4,6-DMDBT predominantly reacts via the HYD pathway depending on feedstock and operating conditions [1–6,8,11,29]. The dramatic decrease in the DDS pathway with alkyl substitutes is generally interpreted based on the above-mentioned vacancy type mechanism. The alkyl groups located close to the sulfur atom are expected to introduce a steric hindrance and make the σ -type (η_1) interaction with the vacancy difficult.

The HYD pathway is generally assumed to proceed via π -bonding of the reactant to the catalyst surface [11]. In this flat wise adsorption mode, the alkyl substitutes are expected to give rise to less steric hindrance. Separate adsorption experiments also show that 4,6-DMDBT adsorbs with similar adsorption strength as DBT [30]. Although there appears to be general agreement on the π -type bonding, there is a large disagreement in the literature regarding the nature of the sites involved in the hydrogenation reaction [1,4,6,8,11,31]. Many authors have proposed that the sites for hydrogenation are also vacancies at the edges, but that they are different from the vacancies involved in the DDS pathway. In order to accommodate the required flat π -bonding, more open multi-vacancy sites have been advocated. For example, it was suggested [31,32] that the hydrogenation occurs on the Mo edges with exposed naked Mo atoms since such atoms could be expected to be involved in π -bonding of large reactant molecules. Several other authors have considered reactions involving naked Mo edges [33–36]. However, the DFT studies by Byskov et al. [37] showed that the exposure of naked Mo atoms is not favored. This and later studies [38–40] have calculated the most favorable structures at the Mo edges for different sulfiding and reaction conditions. The studies also show that it is not favorable to have singly bonded sulfur monomers at the edge, since they tend to reconstruct into dimers with significant sulfur–sulfur binding. Other edge reconstructions may also be encountered, but, as mentioned above, it was found very unfavorable energetically to create multiple vacancies in the different structures. In light of these new results there is a need for re-addressing our thinking regarding the nature of the HYD pathway and the sites

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