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Atomic insights into hydrodesulfurization

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Chapter 1

Introduction

A catalyst is a substance that provides an alternative pathway with a lower activation energy for a chemical reaction to occur. This allows for the reaction to proceed faster at a given reaction condition, thereby saving energy and resources. In some cases, the reaction also proceeds with higher selectivity, so that unwanted byproducts are minimized or eliminated. A catalyst merely participates in a chemical reaction but is not consumed by it.¹ When a catalyst acts in the same phase as the reactants, it is called a homogeneous catalyst while when the catalyst is in a different phase as compared to the reactants, it is called a heterogeneous catalyst.¹ Chemical substances that enhance the activity, selectivity, or stability of a catalyst are called promoters. Catalysis has been traditionally used by humans for manufacturing products such as beer, yoghurt, cheese, soaps, ether and oil of vitriol since the ancient times, likely without knowing its true impact. In today's society, well-established and indispensable chemical engineering industries such as clean fuel production², bulk chemicals^{3,4}, pharmaceuticals^{4,5}, plastics and polymers^{6,7}, food processing⁸, and biotechnology⁹ have catalysis at their backbone. In fact, catalysis is fundamental to the very origins of life as we know it because without it, many fundamental biochemical reactions necessary to sustain life would not be possible.¹⁰

While the term 'catalysis' was first used in the work of Jöns Jakob Berzelius in 1835¹¹, the discovery of catalysis predates to 1794 in the published work of Scottish chemist Elizabeth Fulhame.^{12,13} Perhaps, the first large-scale commercial product that involved catalysis was the Döbereiner lamp in the 19th century where a platinum sponge catalyst was used.¹⁴ In the late 19th century, Wilhelm Ostwald investigated acid and base catalyzed reactions and the associated reaction rates for which he was awarded the 1909 Nobel Prize in chemistry. The ground work behind a large number of modern catalytic processes involving oxidation and hydro/dehydrogenation was performed by the Russian chemist Vladimir Ipatieff in the early 20th century.¹⁵ Ipatieff's work particularly focused on metals and metal oxide catalysts under high-pressure such as iron, copper and γ -alumina, which are extensively used in the petrochemical and refining industry today. Discovery and industrial applications of a large number of catalytic processes in the early 1900s such as the Haber-Bosch process for ammonia production and the Ostwald process for nitric acid were largely driven by the politics before and during the two world wars and led to a rapid industrialization of society.¹⁶

The industrialization of human society has, however, led to a world-wide dependence on fossil fuels, which continues to increase even to this day as the developing countries start to grow economically and industrialize rapidly. The fossil fuel dependence is further supplemented by the growing population. As of today, 2.5 billion tons of crude oil are processed on a daily basis to meet the existing demand.¹⁷ The trade of crude oil has become so important that the world economy is significantly influenced by it.¹⁸

As a result, clean gasoline and ultra-low sulfur diesel (ULSD) consumption is expected to grow by 1% and 2% annually, respectively.¹⁹ Over the last century, it has become very clear that the sulfurous impurities present in crude oil are released into the atmosphere as SO_x gases when the fractionated products are consumed, particularly through combustion. Given the risks posed by these gases on the environment and human health²⁰, a catalytic process called hydrodesulfurization (HDS) has been widely used to selectively remove these S-containing components from the crude oil fractions at the oil refineries with the help of hydrogen and a heterogeneous catalyst.

Typical crude oil contains a wide range of S-containing molecules such as aliphatic thiols, disulfides, thioethers, cyclic sulfur compounds and aromatic sulfur compounds.²¹ Over the last 100 years, HDS has been carried out using heterogeneous catalysts containing Co- and Ni-promoted MoS₂ slabs supported on alumina. These catalysts have a broad-spectrum HDS activity and have efficiently met the residual sulfur standards of up to ~100 ppm as they are very efficient in removing the non-aromatic sulfur compounds from refined crude oil fractions.²² However, the regulations on SO_x emissions worldwide have become significantly more stringent in the last decade. In the developed countries, the emission standards for sulfur have dropped to less than 10 ppm while in many developing countries especially in Asia, between 2015 to 2018, the on-road emission regulations have decreased from 350 ppm of residual sulfur to 10-50 ppm.²³ By 2025, it is expected that nearly all of the developing countries will adopt a sulfur emission standard of less than 10 ppm at least.²³ This rapid drive towards cleaner fuels has led to an increasing demand for hydrotreating of fuels worldwide. In a very recent kinetic study, it was shown that the left-over sulfur compounds after desulfurizing diesel using industrial catalysts to 100 ppm of residual sulfur are primarily the refractory substituted dibenzothiophenes.²² The existing Co(Ni)-promoted MoS₂ catalysts have a very poor activity towards desulfurizing these refractory sulfur compounds mainly due to steric hindrance effects. However, to meet the future sulfur thresholds of <10 ppm, the residual aromatic sulfides like thiophene derivatives and substituted dibenzothiophenes also must be removed. Despite these issues, until today, the existing catalysts have not been replaced significantly on the industrial scale in spite of several improvements in their synthesis strategies.^{19,24-27} In order to meet the catalytic demands of an ever decreasing emission threshold, it has become necessary to engineer a more efficient catalyst for HDS.

In order to develop a more-efficient HDS catalyst, fundamental understanding at the atomic level of the existing Co(Ni)-promoted MoS₂ catalysts is necessary. The precise working mechanism as well as the atomic structure of the active phase of the conventional HDS catalyst has been under considerable scientific discussion despite the process being well-established. This is an issue that is not isolated to HDS, but can also be encountered in many other heterogeneous catalytic processes.^{28,29} This is mainly because atomic-scale insights into the structure of the catalyst while the reactions occur were not available to scientists until about two decades ago as the characterization techniques that provide information on the structure and chemistry of the active phase were still under development.²⁸⁻³⁰ Early catalysis research in general considered a reactor with catalyst in it as a black-box and all the scientific

interpretations of the data were based on the analysis of the catalyst before and after the reaction, usually at conditions which were very different from the ones in which the reactions were carried out. This led to a large number of hypotheses and speculations, and as a result, contradictory models were suggested.^{28,29}

Early surface-science approaches to catalysis did not help with solving some of these issues. While many of these studies gave detailed insights into the atomic structure of the catalyst, these studies were carried out under clean ultra-high vacuum (UHV) conditions, usually on single-crystal surfaces while industrial catalysis is carried out at high-pressure and high temperature, and on a more complex material. A 5 to 9 orders of magnitude difference in the pressure between surface-science experiments and industrial catalysis is typical.^{28,29,31-34} The term ‘pressure gap’ has been used to refer to this large discrepancy in the pressure. Furthermore, an industrial catalyst is structurally very complex. A typical catalyst contains the active phase, the promoters, the co-promoters, and several other additives to optimize the activity and selectivity. The reductionist approach of a single-crystal model catalyst that is used in fundamental studies does not capture all the complex structural aspects of an industrial catalyst. The term ‘materials gap’ has been used to refer to this structural discrepancy between model catalysts used in fundamental studies and the industrial catalysts.³¹⁻³⁴ As the surface-science techniques evolved, in situ studies on catalysis were carried out under controlled environments.³⁵ These studies focused on the adsorption/desorption processes of the reactants and products and quasi in situ approaches where the reaction was quenched before characterization. Recently, spectroscopy and microscopy techniques such as infrared spectroscopy³⁶, Raman spectroscopy³⁷, X-ray diffraction³⁸, X-ray absorption spectroscopy³⁹, X-ray photoelectron spectroscopy (XPS)⁴⁰, Mössbauer spectroscopy^{41,42}, nuclear magnetic resonance⁴³, high-resolution electron microscopy⁴⁴, and scanning probe microscopy techniques such as a scanning tunneling microscope (STM)⁴⁵ have been developed and upgraded to perform such in situ characterization of catalysts. Many of these techniques have been combined with prior information from surface-science studies of single crystals and model catalysts to develop a comprehensive understanding of the catalytic process.

While these studies can give very important insights into the behavior of the active phase of an HDS catalyst, in order to link the observations to industrial catalysts, operando studies carried out at high-pressure are necessary.^{28,29,31-35} As mentioned above, many of these fundamental studies are carried out under controlled conditions wherein a large pressure gap still exists with the industrial HDS conditions. The structure of the catalyst has a very strong dependence on the gas environment it is exposed to and dynamically changes according to the reaction conditions. These changes are typically related to adsorbate-induced reconstruction of the active phase and could completely change the morphology of the working catalyst.⁴⁶ Therefore, the operando atomic structural characterization of the catalyst during the reaction is very important. Simultaneous recording of any activity data, if possible, provides additional information to link the atomic structure to the observed activity.^{28,29,31-35} Such structure-

activity relationships allow for the smart design of a HDS catalyst that is necessary to meet the near-future demands of clean fuels.

Scanning probe microscopy techniques in particular are very useful in this regard as their principle of operation allows them to work under a wide range of pressures and temperatures, and in media which are relevant for industrial catalysis. Several high-pressure scanning tunneling microscopes in particular have been developed in the last decades in order to try and bridge the pressure gap in catalysis.^{34,47-49} The ReactorSTM especially has been very successful in this regard as it can operate under the conventional UHV conditions as well as industrially relevant high-pressure conditions allowing for a model catalyst to be studied at a very broad range of reaction conditions without the loss of atomic resolution.⁴⁸ The ReactorSTM has been used in the recent past to provide operando structural insights into very important catalytic processes such as CO oxidation⁵⁰, automobile three-way catalysis⁵⁰, Fischer-Tropsch synthesis⁵¹, and importantly, hydrodesulfurization.⁵²

In this thesis, four chapters are presented with an objective of providing atomic-level insights into model catalysts that are relevant for HDS and to bridge the gap between prior surface-science studies of HDS model catalysts and the industrial catalysts.

In the Chapter 3, atomic-level structural characterization of 2D CoS₂, a novel MoS₂-like 2D transition metal dichalcogenide (TMDC) is presented. CoS₂ is formed as a byproduct of typical recipes for synthesizing HDS model catalysts and is one of the phases that have been observed in operando studies on industrial HDS catalysts where Co is used as a promoter.⁵³ Prior surface-science experiments show that Co can form MoS₂-like S-Co-S layered sheets on supports like Au(111) while density functional theory (DFT) calculations show that free-standing S-Co-S sheets are highly unstable.⁵⁴⁻⁵⁶ In our study, this disagreement is resolved by using a combination of experiments and DFT calculations. The results show that S-Co-S layered 2D CoS₂ sheets are stabilized by the interactions with the Au(111) support. The methods presented in this chapter can be applied to resolve the atomic structure of any supported 2D material.

In the Chapter 4, an alternative approach to synthesizing an HDS model catalyst via the simultaneous sulfidation of Co and Mo oxide nanoparticles on Au(111) is presented. The sulfidation of a mixed oxide precursor is the industrial method-of-choice for HDS catalyst preparation. A combination of STM and XPS is used to track the changes in chemistry and morphology at various stages of the model catalyst synthesis. The results presented in this chapter show that Co-promoted MoS₂ model catalyst for HDS can be prepared by this strategy. However, the yield of the Co-promoted MoS₂ is low because of the kinetically hindered sulfidation of the Mo oxide phase.

In the Chapter 5, we take a detour from model catalysts involving a weakly-interacting metal supports like Au(111) to one involving a strongly-interacting oxide support, namely, MoS₂ slabs supported on TiO₂(110). TiO₂ is also one of the supports that are used in the industry and by choosing this support,

an important step is made towards bridging the materials gap with the industrial catalyst. Previously reported research work to synthesize MoS₂ slabs on TiO₂(110) has predominantly made use of many high-temperature synthesis methods. The synthesis temperatures used in these studies are much higher than those used in the synthesis of an industrial HDS catalyst. In this chapter, a low-temperature synthesis strategy and the structural characterization of MoS₂ nanoclusters supported on TiO₂(110) are presented. A combination of STM and XPS is used to investigate the morphology and the chemistry of the Mo sulfide phases formed. The results presented in this chapter show that both flat-lying MoS₂ slabs and MoS_x stripe phases are formed. The formation of these phases is driven by the strong interaction of the support with both Mo and S. Such phases have never been observed to form in the high-temperature synthesis methods.

In the chapter 6, we present the first direct observation of a Co-promoted MoS₂ model catalyst supported on Au(111) studied in situ using the ReactorSTM under industrially relevant conditions of high-pressure and high temperature. A mixture of H₂ and CH₃SH are used to simulate the industrial HDS environment, with CH₃SH as the test gaseous aliphatic thiol contaminant. The results presented in this chapter show that the edges of the Co-promoted MoS₂ nanoclusters are very sensitive to the gasses they are exposed to. Under HDS conditions, a highly dynamic behavior of the Co-substituted edges of the Co-promoted MoS₂ slabs is observed. The behavior of the Mo-terminated edges is however, observed to match well with that of Mo-terminated edges of an unpromoted MoS₂ catalyst. Furthermore, a large number of irregularly-shaped CoMoS slabs with high index terminations are also observed to form during the desulfurization of methylthiol. Evidence from ex situ XPS analysis suggests that a migration of Co atoms from the CoMoS phase to the CoS₂ phase occurs when the CoMoS slabs are exposed to HDS reaction gasses. The findings of this study give us very important insights into the complex behavior of an HDS catalyst in action and further exemplifies the need to study catalysis at industrial reaction conditions.

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