FUTURE CHALLENGES OF HYDROTREATING CATALYST TECHNOLOGY

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Summary

In this presentation we will discuss the advent of tighter fuel specifications and in particular how the very low sulfur content allowed in transportation fuels has set a new agenda for the refining industry. Each refiner must decide how to most cost-effectively implement the needed technology upgrading, whilst also being able to shift the product slate composition as demand for different fuels grows. The decision on e.g. whether to revamp an existing HDT unit or build a grassroots unit requires a detailed analysis of the whole refinery and a deep understanding of the detailed kinetics of the hydroprocessing reactions.

In recent years, several scientific advances have provided new fundamental insight into HDS catalysis. Recent scanning tunneling microscopy (STM) experiments and density functional theory (DFT) calculations have shed light on the atomic-scale structure of Co-Mo-S catalysts, the origin of the high-activity Type II sites, and the detailed molecular reactions that take place. We will also discuss the discovery of a metallic edge state on the active catalyst nanoparticles that has spurred the development of a new series of high-activity catalysts based on the so-called BRIMSM technology.

Challenges in Catalyst Technology

The demand for low sulfur transportation fuels requires that refiners evaluate the many different options for reaching the target. Selection of catalyst types is one of the important decisions. As sulfur conversion increases, we are left with the most refractory species – alkylated dibenzoanthiophenes. Under idealized conditions, the conversion of these molecules that are sterically hindered mainly proceeds via a prehydrogenative route instead of direct desulfurization (1-5). Since NiMo catalysts are generally more active for the indirect hydrogenative route and CoMo catalysts more active for the direct route, one should think that NiMo is the preferred option for ultra deep desulfurization. However, at low hydrogen pressures and high space velocities CoMo catalyst are often seen to outperform NiMo catalysts (4). It has been observed that nitrogen compounds may inhibit the hydrogenative pathway (6-9), and by conducting detailed studies into the influence of such effects under real feed conditions (9) it was found that specific basic nitrogen compounds have a profound effect on HDS and HDN activity. This is presumably a result of competitive adsorption. These nitrogen compounds inhibit both direct and indirect desulfurization but the effect is largest for the latter. Thus, selection of catalyst depends on both feedstock and operation conditions. In addition, issues such as hydrogen availability and other product properties may play a role (10).

Besides the issues related to the legislative drive for removing sulfur the refiners are also faced with a growing demand for diesel fuels. Such a demand may partly be met by producing less low value products such as heating oil. This can be done by converting heavy fractions by hydrocracking or 'mild hydrocracking' processes or one may adopt upgrading processes e.g. for light cycle oil. The latter alternative requires new technology that not only removes refractory sulfur species in the presence of high amounts of nitrogen but also perform a certain degree of ring opening to reach a reasonable product cetane number.

The development of new catalysts no longer proceeds by trial-and-error but goes hand in hand with the insight gained from fundamental desulfurization studies. Some recent developments are highlighted below.

Support Interaction and Origin of Type I/II Sites

The role of support interactions in desulfurization catalysts has been an important topic for a number of years. Most studies have dealt with alumina-supported NiMo or CoMo sulfides that are predominantly used in the industry. By using alumina as a support, the dispersion of MoS2 edges is quite high due to the formation of small stable nanoclusters. A high edge dispersion is important since it increases the amount of Co (Ni) that can be accommodated at the edges forming the active Co(Ni)-Mo-S structure (1). However, the support interaction also has important implications for the intrinsic activity of the active sites. Several years ago we observed (11) that increasing the sulfiting temperature from 673 K to 873 K resulted in modified Co-Mo-S structures (Type II Co-Mo-S) with substantially higher activity per active site than those formed at the lower temperature (Type I). The existence of these two different structures is related to the interaction between Mo and surface alumina OH groups during preparation leading to monolayer type structures that are difficult to sulfide. Other studies (12,13) also show some evidence for Mo-O-Al linkage in Type I structures and thus corroborate the idea that a weak support interaction is needed to create Type II sites. The linkages can be broken by high temperature sulfiting but this decreases the MoS2 edge dispersion and it is therefore preferable to find alternate procedures. This may occur by introduction of additives or chelating agents or by using weakly interacting supports (14-18).

The formation of multi-stack MoS2 structures has been observed in catalysts containing Type II sites. However, multi-stacking may only be a by-product of weaker support interactions and it is also possible to produce single slab Type II Co-Mo-S samples (1). Furthermore, as discussed below, only the top layer of multi-stacks will expose the special brim sites that seem to play a critical role in hydrogenation desulfurization.

Recently, the origin of intrinsic activity differences between Type I and Type II structures has been the subject of a DFT study (19). Here the direct connection between the presence of linkage to the alumina and HDS activity was addressed by calculating the difference in Mo-S bond strength when oxygen linkages are introduced. It was shown that Mo-O linkages are most probably located on the S edge and the presence of such oxygen linkages was seen to increase the energy required to form sulfur vacancies significantly. Since the sulfur vacancies are necessary for sulfur extraction reactions, this provides us with a consistent picture of the influence of support interaction on the Type I and Type II reactivity.

Figure 1. Consecutive STM images of thiolate species adsorbed on the brim sites of a MoS2 nanocrystal. The time lapse between the images recorded at room temperature is ca. 1 min showing a high mobility of the adsorbed molecules along the brim. Adapted from (20).
**BRIM™ Technology**

The existence of both direct and prehydrogenative desulfurization routes has been known for many years, yet very little information on the precise molecular reaction steps has been available. STM studies have provided interesting clues as to how these reactions proceed. MoS₂ nanoparticles with a triangular geometry posses special brim sites with metallic character. By combining these studies with DFT calculations, it was found (20) that thiophene can be hydrogenated and ring opened on the brim sites, whereas the butenethiolates diffuse to sulfur vacancies on the cluster edge, where the second sulfur-carbon bond is broken. Consecutive STM images (Figure 1) show how the hydrogenated species are highly mobile supporting the outlined two-step reaction pathway.

In parallel with these findings, Haldor Topsøe has developed a new preparation procedure that provides high activity hydrotreatment catalysts. This new BRIM™ technology not only optimizes the brim site hydrogenation functionality but also increases the direct desulfurization pathway. The first two commercial catalysts based on this technology are Topsøe’s TK-558 BRIM™ (CoMo) and TK-559 BRIM™ (NiMo) for FCC pretreatment service. They show superior activity (Figure 2) and have very recently been successfully adopted by many refiners.

**Figure 2.** Relative activities of Haldor Topsøe’s new BRIM™ technology catalysts for FCC pretreatment service. These catalysts rely on the highly active brim sites present on catalyst nanoparticles.

**Conclusions**

The challenges that the refining industry is facing now and in the years to come call for major developments within hydrotreatment catalyst technology. To assess how a specific refinery successfully adapts to the new legislation and market demands, a detailed knowledge of reaction kinetics and catalyst reactivity and selectivity is required. The progress in fundamental HDS studies on support interaction, catalyst morphology and reaction pathways is expected to continue to provide new opportunities for the development of improved commercial catalysts.

**References**

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