Investigating the effect of Fe as a poison for catalytic HDO over sulfided NiMo alumina catalysts

Prakhar Arora[a], Houman Ojagh[a], Jungwon Woo[a], Eva Lind Grennfelt[b], Louise Olsson[a], Derek Creaser[a,*]

[a] Competence Centre for Catalysis, Chemical Engineering, Chalmers University of Technology, SE-412 96, Gothenburg, Sweden
[b] Preem, Gothenburg, Sweden

ARTICLE INFO

ABSTRACT

The effect of iron (Fe) as poison present in renewable feeds was studied during hydrodeoxygenation (HDO) over molybdenum based sulfided catalysts. The study was carried out at 6 MPa and 325 °C in batch reaction conditions. Different concentrations of Fe in the feed were tested over MoS_2/Al_2O_3 and $NiMoS/Al_2O_3$. A notable drop in activity for the conversion of oxygenates was observed for both catalyst systems with an increased concentration of Fe in the feed. However, the changes in selectivity of products was opposite for unpromoted and Ni-promoted catalysts. In the case of the NiMoS catalyst, at higher Fe concentration, the decarbonated product (C_{17} hydrocarbons) decreased while the direct hydrodeoxygenation product (C_{18} hydrocarbons) increased. On the contrary, for the base catalyst (MoS_2), there was a decrease in the yield of direct hydrodeoxygenation (C_{18} hydrocarbons) products and an increase in yield of decarbonated products (C_{17} hydrocarbons). These sulfided catalysts have different sites for these two different reaction routes and they interacted differently with Fe during the deactivation process. With surface deposition of Fe, the ability of these catalysts to create active sites i.e. via sulfur vacancies deteriorated. TEM-EDX results suggested that the effect of Ni as a promoter for the decarbonation route was nullified and a resultant FeMo phase explains the drop in activity and change in selectivity.

1. Introduction

The world's total energy consumption due to the transportation sector stood at 104 quadrillion Btu in 2012, which has been predicted to steadily climb to 155 quadrillion Btu by 2040 [1]. From different sources, liquid fuels like: Petroleum, natural gas-to-liquids, biofuels, and coal-to-liquids; are the preeminent fuel for the fleet of vehicles anywhere in the world. Liquid transportation fuels accounted for a share of 96% of total energy use by the transportation sector in 2012 which is expected to decline only modestly to 88% in 2040 [1].

To meet this huge demand, and in the face of ever rising CO_2 levels and fewer new discoveries of conventional oil, there is a dire need to develop alternate sources of oil for transportation fuels. A new type of renewable liquid fuel, hydroprocessed esters and fatty acids (HEFA) are gaining considerable attention. They are molecularly identical to the fuels derived from fossil resources. These are hydrocarbons produced by hydrotreating feeds like slaughterhouse wastes, vegetable or animal waste oils and forestry residues like tall oil. HEFA biofuels are the most common biofuels produced with a capacity of more than a billion gallons in 2014 [1]. NEXBTL™, Ecofining™, Vegan™ & Hydroflex are some

of the commercial processes to produce renewable HEFA fuels in refineries including Neste, ENI, Total & Preem across the world [2–9]. These processes have advantages such as feed flexibility and reduced CO_2 emissions. Also, existing refineries could be modified with minimal investment to produce HEFA biofuels. However, the core of these processes is catalytic hydrodeoxygenation (HDO), which is the removal of oxygen from bio-feeds over a catalyst in the presence of hydrogen to produce predominately water as a side product [10].

In most of the above commercial processes, bi-metallic catalysts such as sulfided CoMo & NiMo are employed during the HDO of oils from bio-origins. Triglycerides, methyl esters and fatty acids are examples of the major components of oils from bioresources, irrespective of their sources. Their chemistry is quite similar because of the carboxyl group they have in common. Also, the fatty acids are in the feedstocks or are the intermediates during the conversion of all of these starting components to hydrocarbons [11]. In this study, we have employed oleic acid (OA) as the realistic model compound since it is the major component of renewable feedstocks like oil from Jatropha (42%), microalgal oil (23%) and tall oil (15%) [12–14] etc. There is a wide range of literature available on the conversion of carboxylic acids and its

---

related feeds using such hydrotreating catalysts [4,14–19]. There was then notable early work by the Murzin group that screened a broad range of catalysts in which it was determined that Pd over C was most active for deoxygenation of stearic acid [20]. Researchers are also working on other catalyst systems like noble metals (Pt, Pd, Ru and Rh) supported on a gamut of interesting supports like ZrO_2, TiO_2, etc [21,22] or in the form of metal-nitrides [23] and phosphides [24] which have yielded promising results. However, their use has so far been limited to laboratory scale evaluations due to factors like cost, availability and poisoning due to for example low quantities of sulfur present in oils from bio-origins. Since the mechanisms for HDS (hydrodesulfurization) and HDO are quite similar, MoS_2 based catalysts are inherently effective for removing oxygen to give hydrocarbons. Such, catalysts become deactivated due to the effect of water, coking and poisoning. Also, these catalyst systems are well-studied as they have been used in refining for fossil feeds for many years now [25]. Still, it is critical to study their deactivation in HDO processes due to the differences in reaction routes, the large amount of water produced as a side-product and the different impurities present in feeds of bio-origin. There are excellent reviews on deactivation of hydrotreating catalysts [26] and hydrodeoxygenation processes [10,27] which cover certain aspects of the aforementioned issues. There are several studies covering different aspects of deoxygenation of esters and fatty acids and related model compounds on promoted Mo based catalysts. Kinetics and the reaction mechanism for HDO of compounds with carboxyl groups has also been studied [4,11,28–30]. The role of promoters like Ni and Co has been studied in detail which gives further insights into the mechanisms and their influence on selectivities [31,32]. And, there are a few articles giving insight into the effect of water [33–35]. Moreover, the effect of different sulfiding agents [36] or partial pressure of H_2S [34,37,38] has been studied in depth. Since the metal-sulfide is the active phase of such catalyst systems, the loss of sulfidity is also a probable cause of deactivation. However, there is only a limited number of contributions studying the effect of impurities during upgrading of oils from bio-origins via catalytic HDO.

Alkali metals like Na, Ca, Mg and non-metals like Phosphorus and Chlorine are present in oils from waste streams and may cause deactivation of the catalyst [35,39]. Kubicka and Horáček concluded that there were synergistic effects between phospholipids and alkali metals causing deactivation of the catalyst, while DMDS (dimethyl disulfide) restrained this deactivation [39]. Also, in a similar study, a close relationship between the amount of sulfiding agent used and the activity of NiMo catalysts was established [40]. Mortensen et al. studied the catalyst stability toward H_2S, H_2O, potassium and organically bound chlorine. However, for a different catalyst system (Ni-MoS_2/ZrO_2) and a feed of phenol and 1-octanol, they observed that poisoning was due to blockage of vacant sites by K along the MoS_2 edges. In two patent studies it was suggested that Fe or its compounds present in renewable feedstocks may play a role in deactivation [41,42]. These renewable feedstocks have high total acid number (TAN) values and are corrosive. As a result, during storage and transportation in iron vessels, acids and their derivative compounds can react to yield Fe containing complexes [27]. However, there are to our knowledge no studies available in the scientific literature that have studied the iron poisoning over Ni/Mo containing catalysts during hydrodeoxygenation, which is the objective of the current work.

We have looked into the poisoning effect of Fe on a NiMoS catalyst during HDO of OA in a batch-reactor setup. Four different iron-oleate complex concentrations in the feed were investigated, in addition to a baseline experiment. We have used higher concentration of Fe in feed to emulate the effect of large quantities of feed treated in a refinery-scale reactor during continuous operations for several months. To build on the initial insights, another set of experiments were carried out, keeping the process conditions the same but with the unpromoted MoS_2 catalyst. During these HDO experiments, it was observed that both catalyst systems deactivated as a function of the poison concentration in the

feed. While there was an apparent change in selectivity for products, it was opposite for the Ni-promoted and unpromoted catalyst. Therefore, catalysts (NiMoS) recovered after the HDO experiments were extensively characterized using elemental analysis for carbon and sulfur, Brunauer-Emmett-Teller (BET), Inductively coupled plasma sector field mass spectrometry (ICP-SFMS), Temperature-programmed reduction (TPR) and Transmission electron microscopy (TEM), to elucidate the mechanistic causes of the deactivation and changes in selectivity that could be attributed to Fe.

2. Experimental

2.1. Materials

The γ-Al_2O_3 (PURALOX®, Sasol GmbH) in size range 150–200 μm with a specific surface area of 199 m^2/g, and a pore volume of 0.48 ml/ g was employed as support for NiMo and unpromoted Mo catalysts. These two sets of catalysts were prepared by conventional impregnation of the alumina powder using aqueous solutions of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (Sigma Aldrich) and $Ni(NO_3)_2 \cdot 6H_2O$ (Sigma Aldrich). Initially, 15 wt% Mo was impregnated from a solution of Mo precursor in water on alumina and then dried to remove water. An aliquot was removed at this stage and used as unpromoted catalyst after being calcined. Calcination was done by heating to 450 °C (ramp rate of 10 °C/min) in air for 2 h. The Ni-precursor equivalent to 5 wt% was dissolved in water and impregnated on the dry Mo-based catalysts. Again, the excess water was removed by overnight drying. Finally, the catalyst sample was calcined at 450 °C for 2 h. The detailed procedure can be found here [40]. The catalysts were marked as Mo/Al_2O_3 and NiMo/Al_2O_3.

Oleic acid (Fluka, 90%) was employed as a feedstock in all experiments and used as received. Based on GC analysis, this technical grade oleic acid consisted of the two isomers of oleic acid (86%). The rest was 9-Hexadecenoic acid (palmitoleic acid) about 5%, hexadecanoic acid (palmitic acid) about 4%, tetradecanoic acid (myristic acid) about 3%, while stearic acid and eicosenoic acid were less than 1%. We shall classify these acids other than oleic acid as "Other acid impurities".

The iron oleate complex which was employed as poison (containing Fe) in the experiments was synthesized following a procedure as described elsewhere [43].

2.2. Catalytic activity measurements

All catalytic reactions in this study were performed in a 300 ml batch reactor (Parr Instruments) equipped with an internal stirrer and an arrangement to collect liquid samples during the experiment. In each of the experiments, 1 g of catalyst and oleic acid (15 wt%) solution in dodecane (Sigma Aldrich), with a total volume of 150 ml were charged. Experiments for both catalysts with different concentrations of iron oleate (poison) were carried out as depicted in Table 1. Both catalysts: Mo/Al_2O_3 and NiMo/Al_2O_3 were sulfided using DMDS (Sigma Aldrich) before each of the experiments following a procedure reported earlier [44]. Dodecane was used as solvent to minimize possible temperature excursions due to reaction exotherms during HDO. 0.1 ml of DMDS was

Table 1
Concentrations of poison in weight ppm studied for each catalyst and experiment abbreviations.

Poison in feed (ppmw)	Catalyst	
	NiMo/Al_2O_3	Mo/Al_2O_3
0	NiMo_0 Fe	Mo_0 Fe
20	NiMo_20 Fe	–
100	NiMo_100 Fe	Mo_100 Fe
500	NiMo_500 Fe	Mo_500 Fe
2000	NiMo_2000 Fe	–