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Insight to sulfur species in the hydrodeoxygenation of aliphatic esters over sulfided NiMo/γ-Al_2O_3 catalyst

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ABSTRACT

The hydrodeoxygenation (HDO) network of aliphatic esters was investigated over reduced and sulfided NiMo/γ-Al_2O_3 catalysts in a batch reactor at 250 °C and 7.5 MPa. Methyl and ethyl heptanoate and their main HDO reaction intermediates were used as reactants. The participation of surface OH^- and SH^- groups in the various reaction steps and the stability of the surface sulfur are discussed. Although the surfaces of the reduced and sulfided catalysts under H_2 have identical properties, the reactivity of the oxygen-containing compounds is greater over the sulfided catalyst. This is due to the stronger nucleophilic strength of the SH^- groups compared to the OH^- groups. Methyl and ethyl heptanoate react via various reaction pathways, of which alkaline hydrolysis is demonstrated to be of special importance. Sulfur-containing intermediates are formed in the HDO reactions with surface SH^- groups. Accordingly, sulfur level on the catalyst surface is diminished.

1. Introduction

Diminishing fossil fuel reserves and environmental challenges associated with the greenhouse effect are driving an intensive search for new biomass-based energy sources. Biomass can either be combusted as such or converted to energy-rich gaseous and liquid products [1–3]. Thermochemical conversion of wood by pyrolysis yields a complex mixture of aromatic and aliphatic compounds. The liquid part of the product is known as bio-oil. Mechanical extraction is typically used to produce vegetable oils from the seeds of various biomass crops. Vegetable oils of rapeseed can also be upgraded to obtain rapeseed methyl ester (RME), known as biodiesel. Unfortunately, wood-based bio-oils, vegetable oils, and RME contain even as much as 35–40 wt% oxygen-containing compounds, which are responsible for several unwanted properties, e.g. low energy density, immiscibility with hydrocarbon fuels, and chemical instability. Upgrading by hydrodeoxygenation is essential to remove at least part of the oxygen atoms. As positive effects, hydrotreated oils do not produce harmful SO_x emissions, and NO_x emissions are lower than those of fossil fuels. Hydrotreated oils are also accepted as CO_2 neutral. The work reported in this paper is a contribution to resolving the complex chemistry of hydrodeoxygenation of bio-oils.

Hydrodeoxygenation (HDO) reactions are most commonly carried out over sulfided NiMo/Al_2O_3 or CoMo/Al_2O_3 catalysts. It is generally assumed that the active sites of the catalysts are coordinatively unsaturated sites (CUS) such as sulfur anion vacancies. The probable location of the active sites is at the edges of the MoS_2 or Ni–Mo–S or Co–Mo–S structures [4]. In addition, protonic sulfhydryl groups (SH^-) are proposed to be involved in the supply of hydrogen and in providing Brønsted acidity [5].

Delmon [6] has categorized the active sites for hydrogenation and hydrogenolysis as follows: hydrogenation sites consist of threefold coordinatively unsaturated Mo atoms and hydrogenolysis sites of coordinatively unsaturated Mo atoms with neighboring SH^- or H^+ groups. In addition, acid sites have a function based on Lewis acidity (sites on the support) and Brønsted acidity (the sulfided phase, as SH^- groups). Bunch and Ozkan [7] have modified this model by proposing that hydrogenolysis sites are formed by the adsorption and dissociation of H_2S molecules. Further, they proposed that the hydrogenolysis sites are Brønsted acid centers associated with Mo atoms. The hydrogenation sites, in turn, could be sulfur vacancies associated with Ni or Mo atoms. The theory describing the differences between hydrogenation and hydrogenolysis sites is under debate, however [4].

In earlier studies [8,9] exploring the reaction pathways of HDO of methyl heptanoate over sulfided catalysts, we observed the formation of alkanethiols even in the absence of H_2S addition. Alkanethiols were concluded to form from primary alcohol by the S_N2 nucleophilic substitution mechanism. Other research groups [10,11] have also reported the formation of sulfur-containing

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compound, but their studies have mainly been performed under partial pressure of H_2S. In work exploring the simultaneous hydrodenitrogenation (HDN) of alkylamines and hydrodesulfurisation (HDS) of alkanethiols over sulfided Mo-based catalysts, Zhao and Prins [10] deduced that, in the HDN of alkylamines, alkenes and alkanes are formed indirectly by elimination and hydrogenolysis of alkanethiol intermediates. As a new insight, they pointed out that thiols react (hydrogenolysis) on vacancies on the catalyst surface that can be regarded as Lewis acid sites. HDO of *n*-propanol and *n*-butanol with H_2S was investigated by Mashkina and Khairulina [11] over catalysts with Lewis acid sites such as Al_2O_3 or W/Al_2O_3. The catalysts were sulfided before the reaction tests. The selectivity of alkanethiol formation was 20–50%. They concluded that alcohols react to alkanethiols and alkenes by distinct routes. In addition, catalysts that contain both Lewis acid sites and basic sites were noted to be active for the formation of alkanethiols in the presence of H_2S.

$NiMo/Al_2O_3$ and $CoMo/Al_2O_3$ catalysts are typically reduced and sulfided before use in the HDO process. The surface structure of the catalyst is strongly influenced by the catalyst pretreatment conditions [12,13]. Early on it was suggested [14] that both OH^- and SH^- groups on the catalyst surface could provide active hydrogen atoms for heteroatom removal. More recently, participation of OH^- groups in the HDO reaction of benzofuran was reported by Bunch and Ozkan [7]. In their work, a reduced catalyst exhibited a similar hydrogenolysis function to a sulfided catalyst. As a consequence, they proposed that the action of the SH^- groups could be supported by the OH^- groups, and that the two species could be simultaneously active on the surface of the sulfided catalyst.

In the present study, we investigated further the reaction pathways involved in the HDO of aliphatic esters in order to understand the role of sulfur on the catalyst surface. The stability of the surface species and the role of surface OH^- groups in the reactions were of interest, too. For these purposes, experiments with methyl and ethyl heptanoate and with their main intermediates were carried out over reduced and sulfided $NiMo/\gamma\text{-}Al_2O_3$ catalysts. Supplementary experiments were carried out with the addition of sulfiding agent, H_2S, to the gas feed.

2. Experimental

2.1. Reactor

The HDO experiments were performed in a 50-ml batch reactor (Autoclave Engineers) equipped with a fixed catalyst basket and a magnetic stirrer. The catalyst loading was 0.5 g. The stirring rate was kept at 1000 rpm.

2.2. Catalyst and chemicals

A commercial $NiMo/\gamma\text{-}Al_2O_3$ catalyst was crushed and sieved to a fraction of 0.59–0.75 mm, dried at 100 °C for 5 h, and packed into the catalyst basket. The catalyst was pretreated in situ before the reaction studies by reduction or sulfidation. Reduction consisted of drying the catalyst for 3 h at 350 °C under N_2 flow and 2 h reduction at 350 °C under H_2 flow. In sulfidation the drying period of 3 h at 350 °C under N_2 flow was followed by 2 h sulfidation at 350 °C under H_2S/H_2 (5 mol%) flow. All the gases were obtained with 99.999% purity from AGA.

The main reactants were methyl heptanoate (Merck, >98%), 1-heptanoic acid (Merck, ≥99%), and 1-heptanol (Merck, ≥99%), and these reactants were diluted with *n*-dodecane (Merck, ≥99%) to 5 wt%, 2 wt%, and 2 wt% mixtures, respectively. *n*-Decane (Merck, >98%) was used as an internal standard during the reaction tests. Supplementary experiments were carried out using 1-heptene (Merck, ≥99%), 1-heptanal (Fluka, ≥95%), or ethyl heptanoate (Aldrich, 99%) as a reactant in 2 wt% mixtures diluted with *n*-dodecane.

2.3. Experiments

After catalyst reduction or sulfidation the reactor was cooled down to the temperature of the HDO reaction (250 °C) under N_2 flow to ensure that the gas phase was free of the pretreatment gases. Liquid feed was introduced to the preheated reactor (250 °C), and the pressure was set to 7.5 MPa with H_2 or N_2. The liquid feed occupied one-third of the total reactor volume. The reduced catalyst was always studied under H_2 atmosphere and the sulfided one under N_2 or H_2 atmosphere. The change in the liquid-to-gas ratio was minimized by limiting the number of liquid samples to five. The length of the experiments was between 5 min and 120 min. A series of experiments with H_2S/H_2 mixture (200 ppm or 400 ppm) as gas reactant were performed to study the formation and reactivity of sulfur-containing intermediates.

2.4. Analytical methods

Liquid samples were analyzed with an Agilent Technologies 7890A gas chromatograph equipped with a capillary column (HP-1, 60 m × 0.25 mm × 1 μm) and a flame ionization detector. The products were quantified by the internal standard method. Supplementary qualitative analysis was performed with an Agilent Technologies 5975C mass spectrometer connected to the gas chromatograph. In some of the experiments, the gas phase was quantitatively probed for H_2S with Dräger tubes. The catalyst samples were dried in a separate oven for 24 h at 100 °C before analysis of the sulfur and carbon contents of the catalysts with a LECO SC-444 series analyzer. The reactor system did not allow inert transfers.

Carbon balance was calculated on the basis of the acid part of methyl heptanoate as alcohol part forms gaseous compounds that were not analyzed. The amount of CO was estimated on the basis of C_6 formation. At low conversion levels the carbon balance was $90 \pm 2\%$ and decreased in the course of the experiment to $78 \pm 2\%$. The loss was considered to be mainly due to vapor–liquid equilibrium of the compounds. In addition, coke deposition was observed.

2.5. Definitions

In this paper, totally deoxygenated molecules consisting only of carbon and hydrogen atoms are referred to as hydrocarbon products. Thus, alkenes and alkanes are summed together. The molar concentration of the product is the number of moles of product divided by the total number of moles of reactant and products multiplied by 100%. These values are calculated from the analyzed liquid samples.

3. Results

3.1. Reactivity of methyl heptanoate

The products of deoxygenation of methyl heptanoate over the reduced and sulfided NiMo are listed in Table 1. The main products over the sulfided NiMo under H_2 atmosphere are the same as reported earlier [8]. In addition, the improved qualitative analysis allowed the detection of 2-heptanone and 2-heptanol. The HDO of ethyl heptanoate over the sulfided catalyst produced identical products but with ethanol and diethyl ether in place of methanol and dimethyl ether. Under H_2 atmosphere the reduced and the