



Competitive reactions and mechanisms in the simultaneous HDO of phenol and methyl heptanoate over sulphided NiMo/ γ -Al₂O₃

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ABSTRACT

Hydrodeoxygenation (HDO) of phenol and methyl heptanoate separately and as mixtures was carried out over a sulphided NiMo catalyst to compare the HDO of aromatic and aliphatic reactants. Some experiments were also carried out in the presence of a sulphur additive. The conversion of phenol was suppressed in the presence of methyl heptanoate, whereas the conversion of methyl heptanoate was practically unaffected by phenol. In addition, distributions of the hydrocarbon products were different for reactants in the mixture and the reactants tested separately. Sulphur additive changed the product distribution of the separate components more than that of the mixture. The findings indicate that reduction (including hydrogenation) reactions occur on coordinatively unsaturated sites (CUS) independently of the aromatic or aliphatic character of the component. Sulphur, too, adsorbs on CUS and competes with other reactants that have an affinity to CUS. Decarbonylation and acid-catalysed reactions are, instead, proposed to occur on sulphur-saturated sites.

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1. Introduction

Concern over the impact of fossil fuels on the environment is driving a quest for suitable, environmentally friendly alternatives for fuels. Biomass-based liquids are considered as one option, either as fuel components or as fuels in their own right. Wood-based bio-oils and vegetable-based fatty acid methyl esters (FAME) can be mixed with fossil fuels only in small amounts, however, because of their high oxygen content. In addition, their energy content is lower than that of fossil fuels. Hydrodeoxygenation (HDO) [1], in which oxygen is totally or partly removed under H₂ pressure, is a proven method for upgrading these mixtures to the required quality.

HDO can be carried out over sulphided NiMo and CoMo catalysts, which have been extensively studied in connection with hydrodesulphurisation (HDS) [2] and hydrodenitrogenation (HDN) [3]. Still, the H₂ activation mechanism and the active sites for hydrotreating over sulphided catalysts are not fully understood. First, H₂ may dissociate homolytically or heterolytically [4] and secondly, sulphided catalysts are known to have at least two types of active sites [5]. Breyse et al. [4] stated in their review dealing with H₂ activation that homolytic dissociation occurs mainly over a stoichiometric sulphide surface, whereas heterolytic dissociation

proceeds forming a hydride and a proton over pairs of coordinatively unsaturated sites (CUS) and sulphur ions. CUS associated with MoS₂ phase are generally accepted to be present over the sulphided catalyst, and heterolytic dissociation of H₂ is therefore the most commonly applied model. It should be added that heterolytic dissociation also describes the dissociation of H₂S.

Alumina support alone may have catalytic properties for hydrotreating reactions. Al atoms are Lewis acid sites where as the O atoms are basic sites. It is reported that H₂S may react with Al atoms but the oxygen sites are not adsorption sites for H₂S. In addition, hydroxyl groups may interact with adsorbing molecules [6]. The promoting effect of Ni or Co atoms is generally accepted to be due to an increase in the number of available vacancies. Promoter can donate electrons to Mo and lead to a weakening of the metal–sulphur bond. According to recent review by Prins [5], characterisation of supported metal sulphides is difficult, and quantitative determination of the active sites over promoted catalysts does not produce reliable results, because of the complexity of the catalyst surface.

In HDN studies, Bunch et al. [7] and Delmon [8] have proposed that hydrogenation sites are sulphur vacancies with Ni or Mo atoms and hydrogenolysis sites are Brønsted acid centres associated with Mo atoms. Detailed classification [9] suggests that the sites may have Lewis acid character referring to CUS sites, i.e., sulphur anion vacancies, and Brønsted acid character referring to SH[−] groups. Adsorption and dissociation of H₂S may change hydrogenation sites (CUS) to hydrogenolysis sites via formation of SH[−] groups [7,8]. However, it has been reported [10] that hydrogenation may occur

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over Ni- and Co-promoted Mo catalysts with and without sulphur vacancies.

Density functional theory (DFT) studies have provided new insights into the structure of sulphided catalysts and the active sites for hydrogenation. Besenbacher et al. [11] summarise the latest DFT studies as follows: unpromoted and promoted MoS₂ catalysts have specific metallic edge sites that give rise to bright brims in scanning tunneling microscopy (STM). These edge sites could play a role in hydrogenation reactions and also in hetero-atom removal. The DFT studies indicate the weak inhibiting effect of H₂S on hydrogenation reactions, since it is reported that H₂S is unable to bind to the fully coordinated brim site.

Previously, we studied the HDO of phenol and methyl heptanoate over sulphided NiMo/γ-Al₂O₃ and CoMo/γ-Al₂O₃ catalysts [12]. Phenol was used as an aromatic model component and methyl heptanoate as an aliphatic model component for biomass-based fuels and the reactants were tested separately. Phenol was found to be less reactive than methyl heptanoate in the experiments carried out in a flow reactor at 250 °C under 1.5 MPa pressure. In some tests, H₂S was added to the gas feed to maintain the activity of the sulphided catalyst. The effect of the sulphiding agent on the HDO of phenol was opposite to its effect on methyl heptanoate: the HDO conversion of phenol decreased as a function of increasing H₂S concentration in the feed, whereas the HDO conversion of methyl heptanoate increased. From this, the HDO of the aromatic alcohol and the aliphatic ester was concluded to occur on dissimilar active sites.

Earlier studies on the HDO of mixtures [10,13,14] have been carried out with aromatic components. Clearly, however, there are differences in the behaviour of aromatic and aliphatic components over sulphided catalysts and in this study we focus on the HDO of mixtures of aromatic and aliphatic oxygen-containing model components, i.e., phenol and methyl heptanoate. The aim is to understand the reactions of aromatic and aliphatic structures over a sulphided NiMo catalyst and to derive mechanistic information that applies both to the reactants separately and in their mixtures with and without sulphur additive.

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 stirring rate was 1000 rpm.

2.2. Experiments

Commercial NiMo/γ-Al₂O₃ catalyst was crushed and sieved to a fraction of 0.59–0.75 mm, dried at 100 °C for 5 h and packed (0.5 g) into the catalyst basket. The catalyst was presulphided in situ before the activity tests. At the start of the pretreatment period, the reactor was heated up to 350 °C under N₂ flow (atmospheric pressure), and the catalyst was dried at this temperature for 2 h. After drying, the catalyst was sulphided at 350 °C under H₂S/H₂ (5 mol%, atmospheric pressure) flow for 2 h. Activity test temperature (200 or 250 °C) was achieved under N₂ flow during 30 min.

The liquid reactant solution was introduced to the preheated reactor, and the total pressure was set with H₂, typically to 7.5 MPa. The liquid added to the reactor occupied 1/3 of the reactor volume. Duration of the reaction tests varied between 1 and 5 h. The test procedure has been described in detail previously [15].

The main reactants were phenol (Fluka, ≥99%) and methyl heptanoate (Merck, >98%) diluted with *n*-dodecane (Merck, ≥99%). The reactions of the model components were studied both separately

and as mixtures. In all tests, *n*-decane (Merck, >98%) was added as an internal standard. All gases were obtained with 99.999% purity from AGA. The effect of sulphur additive was tested in both types of experiments. The partial pressure of H₂S was adjusted with gaseous H₂S (up to 2000 ppm) or via the decomposition of a liquid sulphur component, dimethyl disulphide (0.2–0.8 wt%), DMDS (Fluka, ≥98%).

Compositions of the reaction mixtures (*T*=250 °C and *P*=7.5 MPa) were as follows: mixture of phenol and methyl heptanoate (both 3 wt%) was tested with H₂S (650 and 2000 ppm), with DMDS (0.2, 0.4 and 0.8 wt%) and without any sulphur additives. In addition, phenol alone (3 wt%) and methyl heptanoate alone (3 wt%) were tested with DMDS (0.4 wt%) and without any sulphur additives. To determine the effect of co-reactant amount on the product distribution, lower (2 wt%) and higher (4 wt%) amounts of phenol and methyl heptanoate were also tested (keeping the amount of the other co-reactant at 3 wt% and in the absence of any sulphur additive).

Supplementary experiments were carried out with benzene (Fluka, >99.5%), cyclohexanol (Fluka, ≥99.0%) and cyclohexene (Aldrich, 99%) to clarify the reaction pathways. These reactants were studied both individually and as reactant mixtures together with phenol.

The effect of H₂ pressure was evaluated at 6.0, 7.5 and 9.0 MPa at 200 °C and with 0.4 wt% DMDS at 7.5 and 9.0 MPa at 250 °C. Temperature of 200 °C was used for three experiments to obtain a lower reaction rate and allow clarification of the initial reaction steps. In addition, the stirring rate was varied from 1000 to 1750 rpm to assess the diffusion limitations at 250 °C and 7.5 MPa.

Catalytic character of commercial γ-Al₂O₃ was explored with methyl heptanoate as a reactant. The loading of the support was 0.4 g. Pretreatment of the catalyst was similar to the one described above for NiMo/γ-Al₂O₃.

2.3. Analytical methods

Liquid samples were analysed off-line with an Agilent Technologies 7890A gas chromatograph equipped with a capillary column (HP-1, 60 m × 0.25 mm × 1 μm) and a flame ionisation detector. The products were quantified by internal standard method. Supplementary qualitative analyses were obtained with an Agilent Technologies 5975C mass spectrometer connected to the gas chromatograph.

2.4. Definitions

Calculations were carried out on the basis of the analysed liquid samples. Molar concentration of the product is the number of moles of product divided by the total number of moles, including unreacted reactant and products, and multiplied by 100%. The total amount of hydrocarbon is the sum of the products containing no hetero atoms. Hence, complete deoxygenation is achieved when the total amount of hydrocarbon is 100%.

In this work, terms phenol and methyl heptanoate refer to experiments where either of the reactants was used alone together with the solvent. Mixture, in turn, describes experiments where both phenol and methyl heptanoate, with the solvent, were used together. Some of the experiments were performed in the presence of a sulphur additive, either H₂S or DMDS.

3. Results

3.1. Reactivity in the HDO of phenol and methyl heptanoate

HDO reactions were studied at 250 °C over the sulphided NiMo catalyst. Using the reactant mixtures, we first tested two H₂ pres-

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