

Hydrogenation of naphthalene on NiMo- and Ni/Al₂O₃ catalysts: Pre-treatment and deactivation

Ana Cristina Alves Monteiro-Gezork*, Astrid Effendi, John Mike Winterbottom

Department of Chemical Engineering, School of Engineering, The University of Birmingham, Birmingham B15 2TT, United Kingdom

Available online 5 July 2007

Abstract

Nickel (Ni) and nickel molybdate (NiMo) supported on alumina (Al₂O₃) catalysts, both in a presulphided and prereduced forms, were investigated for the hydrogenation (HYD) of naphthalene. The deactivation of the catalysts with time on stream and sulphur (S) content in feed was studied and a detailed characterization of the catalysts was performed. The catalytic activity of the presulphided NiMo/Al₂O₃ catalyst was found to be 2.5 times higher than the prereduced form, at the same HYD conditions. Testing the commercial prereduced Ni catalyst, it was observed that, although the catalyst aged quite quickly, it gave a higher turnover frequency at a temperature that was significantly lower than the one needed for the presulphided NiMo/Al₂O₃ catalyst. The presulphided Ni/Al₂O₃ catalyst showed a low activity towards naphthalene HYD, for the same experimental conditions applied to the prereduced form. The presulphided form of this catalyst was not the active site for this HYD. The Ni catalyst should be used in a sulphur free environment in order to fully make use its hydrodearomatisation (HDA) properties, whereas the NiMo/Al₂O₃ catalyst exhibited a higher HYD activity in the presulphided form.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Naphthalene hydrogenation; Hydrodearomatisation; Hydrotreating; Catalyst pretreatment; Catalyst deactivation; NiMo/Al₂O₃; Ni/Al₂O₃

1. Introduction

HYD of aromatics is an essential process stage in the oil refining, which produces environmentally friendly fuels. A high aromatic content is associated with poor fuel quality, giving a low cetane number in diesel fuel and a high smoke point in jet fuel [1–3] making it important to reduce the aromatics content in liquid fuels [4]. During the hydrotreating process, the HYD of the aromatic rings prior to sulphur removal is considered essential to alleviate the steric hindrance of substituted dibenzothiophenes, which are regarded as most unreactive towards hydrodesulphurisation (HDS), and therefore facilitate HDS reaction [5,6]. Moreover, nitrogen removal from polycyclic aromatics does not take place until ring saturation has occurred. There is also evidence that particulate emissions in diesel exhaust gases correlate with the aromatic content of the fuel [3]. Because of the health hazards associated with these emissions [7], tighter environmental regulations have been

introduced to limit the aromatic content of the fuel. The importance of HDA is therefore increasing together with tightening legislation of fuel quality and exhaust emissions, leading to new catalyst and process development.

Aromatic HYD in industrial feedstocks may be carried out over supported metal or metal sulphided catalysts. For hydrotreating of feedstocks that contain appreciable concentrations of sulphur and nitrogen, sulphided NiMo, NiW (nickel tungsten) or CoMo (cobalt molybdenum) on gamma alumina (γ -Al₂O₃) catalysts are generally used, whereas supported Ni or noble metal catalysts have been used for sulphur- and nitrogen-free feedstocks, i.e., relatively clean pretreated feedstocks. As a result, poisoning by asphaltenes, metals or fouling is minimized or does not occur. Consequently, chemical poisoning by coke and sulphur are the most relevant deactivation mechanisms for hydrotreating catalysts.

In hydrotreating, the deactivation of catalysts is fast when the catalyst is first brought on line and subsequent deactivation is slower. A review by Absi-Halabi and Stanislaus [8] shows that an initial deactivation is usually caused by coke deposition, which appears to reach a pseudo steady-state (in terms of activity) rather rapidly. Continued deactivation over a longer period of time is then caused by metal deposits and the final

* Corresponding author. Present address: Stühlinger Straße 17, 79106 Freiburg, Germany.

E-mail address: acm848@yahoo.com (A.C.A. Monteiro-Gezork).

Nomenclature

| | |
|-----------------|---|
| DMDS | dimethyldisulphide |
| HDA | hydrodearomatisation |
| HDS | hydrodesulphurisation |
| HYD | hydrogenation |
| $r_{w,N}^{obs}$ | observed naphthalene reaction rate per mass of active phase of catalyst ($\text{mol}_N \text{ kg}_{\text{NiMo}}^{-1} \text{ s}^{-1}$, $\text{mol}_N \text{ kg}_{\text{Ni}}^{-1} \text{ s}^{-1}$) |
| Rc | correlation coefficient |
| S | sulphur |
| T | temperature |
| TPO | temperature programmed oxidation |
| TPR | temperature programmed reduction |
| TPS | temperature programmed sulphidation |
| XRD | X-ray diffraction |
| \mathcal{P} | poisoning factor |

Subscripts and superscripts

| | |
|-----|---------------|
| cat | catalyst |
| L | liquid (bulk) |
| N | naphthalene |
| obs | observed |

total loss in activity is attributed to pore constriction and ultimate pore blocking. Initial catalyst deactivation is a major issue in the refining industry [9] and the replacement of the deactivated catalyst is an economically demanding and time consuming procedure.

It is usually assumed that hydrogen sulphide (or sulphur content), H_2S , has an inhibiting effect on the HYD activity of hydrotreating catalysts [10,11]. However, many studies can be found in the literature on the effect of H_2S partial pressure in hydrotreating reactions and the conclusions differ widely. These studies have shown that the effect of H_2S partial pressure is complex with reports of promotional [12–14], inhibiting [13,15–17] or absence of effect [13,18] depending on the reaction, the reactant and the experimental conditions considered.

In the present work, commercial NiMo and Ni supported on trilobe Al_2O_3 catalysts have been investigated for the HYD of naphthalene in both prereduced and presulphided forms. In view of the interest in getting a better knowledge of the HYD properties of these catalysts, the resistance of the catalysts to high sulphur content of feed was tested and the deactivation of the catalysts due to coke deposition was also addressed. In order to elucidate the catalyst deactivation, a temperature programmed oxidation (TPO) of fresh and spent presulphided and prereduced NiMo and Ni/ Al_2O_3 catalysts, was performed. This technique also allowed the qualitative and quantitative determination of sulphur present in the catalyst. The NiMo catalyst, both in the presulphided and prereduced forms, was also characterized by means of a temperature programmed reduction (TPR) and sulphidation (TPS) analysis. TPR and TPS analysis of the Ni/ Al_2O_3 have been carried out by Hoffer et al. [19]. Moreover, an X-ray diffraction (XRD) analysis of the

catalysts, in both presulphided and prereduced forms, was also carried out. The objective of the characterization carried out in the present study was to obtain a general insight into the chemical nature of the active phase and crystallinity of the catalysts, after the two pretreatments, in order to explain their activity towards naphthalene HYD.

2. Experimental

2.1. Apparatus

The kinetic study was carried out in a Carberry reactor, a three-phase spinning catalyst basket autoclave reactor, operated as a dead-end mode. The reactor was automated and controlled to ensure reliable and reproducible experiments. For the monitor and control of the operation parameters, LabVIEW software was installed. A more detailed description of the apparatus can be found elsewhere [20].

2.2. Catalysts and materials

Commercial Al_2O_3 trilobe support based catalysts namely NiMo/ Al_2O_3 (26 wt.% MoO_3 , 5 wt.% NiO, 4 wt.% P_2O_5 , Grace Davison) and Ni/ Al_2O_3 (15 wt.% Ni, HTC 400 RP, Johnson and Matthey) with a particle size of $2.5 \times 10^{-3} \text{ m}_{\text{cat}}$ were used. As a feed, naphthalene (99%, Aldrich) was dissolved in *n*-hexadecane (99%, Avocado) to the required concentration and *n*-octadecane (99%, Aldrich) was used as an internal standard. With the presulphided Ni based catalysts, dimethyldisulphide, DMDS, (99%, Acros) was added to the reaction mixture, providing a source of sulphur that was essential to stabilize the catalyst maintaining it in the sulphided form. Liquid products were analysed using a gas chromatograph (Ai Cambridge GC, model GC94M) equipped with a capillary column (CP-Wax 52CB FS $25 \times 0.25(1.2)$, Chrompack). The nitrogen (oxygen free), argon (Ar), air, hydrogen (H_2) and helium (>99.995%) cylinder gases were supplied by BOC Gases.

2.3. Pretreatment of the catalysts and activation

2.3.1. Sulphidation of the NiMo and Ni/ Al_2O_3 catalysts

The NiMo and Ni/ Al_2O_3 catalysts were presulphided in the same way in the Carberry reactor. Initially, the catalysts were dried *in situ* at 573.15 K in a 250 ml min^{-1} nitrogen stream for 2 h to remove traces of moisture. A stirring rate of 8.3 s^{-1} was used. The reactor was cooled to room temperature. Then DMDS in *n*-hexadecane (10% of the weight of the catalyst, BP-private communication) was charged into the reactor. The temperature was increased to 493.15 K and held for 1 h at this temperature with a hydrogen pressure of $20 \times 10^5 \text{ Pa}$. Subsequently, the temperature was increased slowly to 573.15 K at 20 K h^{-1} and held isothermally for 1 h. The catalyst was cooled down in hydrogen. The reactor was depressurised, the excess of DMDS was drained and finally the reactor was flushed for a considerable period of time with nitrogen.

Download English Version:

<https://daneshyari.com/en/article/58380>

Download Persian Version:

<https://daneshyari.com/article/58380>

[Daneshyari.com](https://daneshyari.com)