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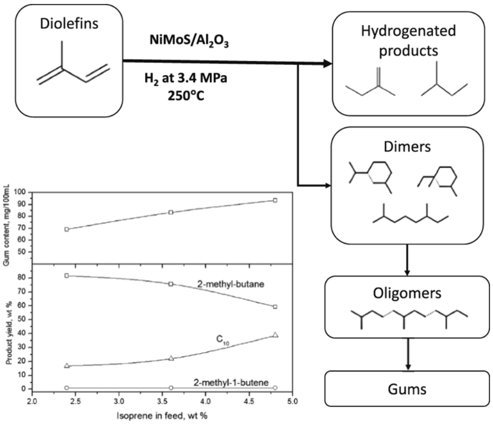
Full Length Article

Impact of molecular structure on the hydrogenation and oligomerization of diolefins over a Ni-Mo-S/γ-Al_2O_3 catalyst

Ali Alzaid[a], Jason Wiens[b], John Adjaye[b], Kevin J. Smith[a,*]

[a] *Department of Chemical and Biological Engineering, University of British Columbia, 2360 East Mall, Vancouver, BC V6T 1Z3, Canada*
[b] *Syncrude Canada Ltd., Edmonton Research Centre, 9421 – 17th Avenue, Edmonton, Alberta T6N 1H4, Canada*

GRAPHICAL ABSTRACT



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ABSTRACT

The hydrogenation of a series of linear and cyclic diolefins diluted in decalin, at conditions (≤250 °C, 3.4 MPa H_2 and LHSV of 1–2 h^{-1}) chosen to mimic the hydrogenation of a Canadian oil sands naphtha (~20 wt% olefins and 4–5 wt% diolefins) over a NiMoS/Al_2O_3 catalyst, is reported. The yield of dimers was minimal on fresh NiMoS/Al_2O_3 catalyst but increased significantly on spent NiMoS/Al_2O_3 catalyst recovered from a commercial hydrotreater. Dimer yield was also strongly dependent on the diolefin molecular structure. High dimer yields were obtained from molecules with conjugated double bonds, provided the double bond was not sterically hindered. Addition of 1-octene did not impact the dimer yield and 4-methylstyrene had the highest oligomer yield compared to all other diolefins examined. The results are consistent with the formation of resonance stabilized allylic carbocations being key to dimer formation. Increased concentration of the diolefin in the feed resulted in increased dimer yield and gum content of the product oil, providing a direct link between the presence of conjugated diolefins, their dimerization and gum formation that is the likely cause of catalyst activity loss and fouling of the catalyst bed.

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[*] Corresponding author.
E-mail address: kjs@mail.ubc.ca (K.J. Smith).

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1. Introduction

The Canadian oil sands constitutes about 10.5% of the world's oil reserves with an estimated 173.2 billion barrels of oil [1]. The bitumen recovered from the Canadian oil sands is upgraded to a synthetic crude oil, either by carbon rejection (such as fluid coking) or H_2 addition processes (such as LC-Fining), to increase the hydrogen/carbon (H/C) molar ratio of the recovered liquid. Following distillation, the resulting naphtha and gas oils undergo further hydrotreating steps to remove metals, sulfur and other contaminants, yielding a synthetic sweet crude oil [2].

The naphtha cut from a typical fluid coker processing oil sands bitumen has high concentrations of olefins (20 wt%, Br number = 57–65.8 g/100 g) and diolefins (4.4 wt%, diene value = 8.3–9.7 g I_2/100 g) [3]. Note that the diolefin content (wt%) was inferred from the measured diene value using the UOP Method 326 equation: conjugated dienes, wt% = $[C^*D]/253.8$, where C is the diolefin average molecular weight and D is the diene value (see Supporting Information). Although the molecular structure of the olefins and diolefins present in the naphtha are not well defined, they are known to oligomerize at typical hydrotreating reaction conditions, producing gums and carbonaceous deposits [2,3] that result in rapid catalyst deactivation, increased reactor fouling, and eventual reactor shutdown. Consequently, the naphtha undergoes a low temperature (< 275 °C) hydrogenation to saturate the olefins and diolefins prior to hydrotreating [2,3]. However, catalyst deactivation and reactor fouling may still occur at the relatively mild temperature of the hydrogenation, and it is believed that both are related to loss in catalyst hydrogenation activity such that olefin or diolefin oligomerization become significant [3].

The hydrogenation of olefins and diolefins has been investigated on noble metals (Ru, Pd, Pt, Ir and Cu) and metal sulfides (Ni, Mo, Co, W) [4–9], with most studies focused on low molecular weight alkadienes such as isoprene and butadiene. Co-Mo-S/Al_2O_3 and Ni-Mo-S/Al_2O_3 catalysts are widely used in industrial hydrogenation processes because of their relatively low cost and strong resistance to poisoning by sulfur and other contaminants present in hydrotreating feedstocks [10,11]. Due to the tightening regulations on sulfur content in gasoline, many recent studies have focused on naphtha hydrotreating reactions over MoS_2 catalysts operated at temperatures > 250 °C and H_2 pressure > 3.4 MPa [12–16].

The molecular structure of the olefin/diolefin (conjugated/non-conjugated, cyclic/branched/linear) plays an important role in determining the hydrogenation and isomerization activity on MoS_2 catalysts. For example, Okuhara et al. [8] reported that isoprene hydrogenation over MoS_2 at room temperature and 4.3 kPa H_2 was more selective toward 2-methyl-1-butene (77.0%) than 3-methyl-1-butene (20.6%), indicating selective adsorption of the double bond located at the 3 position carbon. Hubaut et al. [17] reported similar results on a $MoS_2/\gamma\text{-}Al_2O_3$ catalyst operated at 50 °C, 101.3 kPa H_2 pressure, 38 mol/mol H_2/feed ratio in a packed bed reactor. They reported the hydrogenation of isoprene and 1,3-pentadiene (conjugated diolefins) to be 2–3 times faster than that of 1,4-pentadiene (non-conjugated diolefin), 1,3-cyclohexadiene (cyclic-diolefin) and 2-methyl-2-butene (mono-ethylenic olefin). The differences in reactivity reflect a low reactivity of the non-conjugated diolefin and steric hindrance in the cyclic diolefin. These data clearly indicate the importance of the diolefin molecular structure in determining the reactivity and product distribution of diolefin reactions.

Given the high olefinic content of naphtha derived from Canadian oil sands (approximately 20 wt% olefin and Br number = 57–65.8 g/100 g), the competition between conjugated olefin/diolefin and mono-olefin hydrogenation reactions is important. Nijhuis et al. [18] reported that the rate of hydrogenation of styrene was 3.5x's faster than that of 1-octene at 50 °C and 1.6 MPa H_2 on Pd/Al_2O_3. The hydrogenation rates of cyclopentadiene (5 wt%) and styrene (5 wt%) were reported to be 6.6 and 3.9 times higher than that of 1-hexene (3 wt%) at 60 °C and 2 MPa H_2 also on Pd/Al_2O_3 [19]. The differences were explained by the strong electrophilic character of the conjugated diolefins [17]. The carbocation formed from conjugated diolefins during electrophilic addition is stabilized by resonance and therefore it is easier to form than the mono-olefin carbocation intermediate. The higher reactivity of conjugated diolefins was also attributed to the stronger adsorption on the catalyst compared to mono-olefins [19].

However, the hydrogenation of olefins and diolefins at conditions relevant to the hydrogenation of naphtha derived from Canadian oil sands has not been reported. Furthermore, there is limited information on the dimerization of olefins and diolefins at these conditions and hence the link between the oligomerization of these components, gum formation, catalyst deactivation and reactor fouling has not been directly established. Since the oil derived from the Canadian oil sands is highly aromatic, the molecular structure of conjugated olefins present in the aromatic molecules of these feedstocks, may also impact the rate of oligomerization and hence catalyst fouling. In the present study, the effect of the diolefin structure, comparing linear versus cyclic conjugation, and sterically hindered diolefins, on oligomerization and hydrogenation reactions is reported. In addition, the effect of diolefin concentration and the addition of olefin in the form of 1-octene to several diolefins on hydrogenation/oligomerization activity is also examined. The results aid in understanding how dimerization occurs for each model diolefin and how the structure, diolefin concentration, and olefin addition affect the dimerization reactions responsible for catalyst deactivation, reactor fouling and reduced hydrotreater catalyst lifespan.

2. Experimental

A spent, commercial Ni-Mo-S/$\gamma\text{-}Al_2O_3$ catalyst, taken from a commercial hydrotreater, was used throughout the study. The catalyst had been soxhlet extracted after removal from the reactor and was used without further pretreatment. In one experiment, a fresh, unused sample of the same catalyst was sulfided and used for hydrogenation of 2,5-dimethyl-2,4-hexadiene.

The Brunnauer-Emmett-Teller (BET) surface area, pore volume and pore size of the spent catalysts were determined from N_2 adsorption/desorption isotherms measured at 77 K using a Micromeritics ASAP 2020 analyzer. The catalyst sample was first degassed at 1.33 kPa/s and heated at a ramp rate of 10 °C/min until 0.04 kPa and 250 °C, holding the temperature for 240 min. The sample was then cooled and analyzed using N_2 adsorption at 77 K.

A Perkin-Elmer 2400 Series II CHNS/O analyzer was used for elemental CHNS analysis of the catalyst and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was used to determine the Al, Mo, P and Ni contents of the catalyst, in accordance with the US EPA 6010C method. This analysis was performed by Canadian Microanalytical Service Ltd. in Delta, BC.

The hydrogenation reactions were carried out in a micro-scale trickle-bed reactor (length 50 cm; hot zone 30 cm) with an internal diameter of 1.18 cm, operated in gas and liquid downflow mode. A schematic diagram of the reactor system is shown in Fig. 1. The catalyst was loaded into the reactor with glass beads and SiC diluent in order to control heat and mass transfer effects. The packing at the bottom of the reactor consisted of 3 mm glass beads (height 15.3 cm) followed by three layers of SiC with mesh sizes #16, #46 and #80 and bed height 3.5, 1.4 and 1.4 cm, respectively. The 2 g of catalyst was then loaded on-top of the SiC in two layers, each layer consisting of SiC (mesh size #80, height 2.3 cm) and 1 g of catalyst (approximately 1.1 cm height). Above this bed more SiC was added with mesh sizes # 80, #46 and #16 and bed heights each of 1.1 cm. Finally, the top of the bed was loaded with 3 mm glass beads (height 18.2 cm). This catalyst loading was recommended by several studies for similar micro-scale reactors and 2–3 mm trilobe commercial catalyst to eliminate poor catalyst wetting, wall effects and backmixing and to produce results in agreement with