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Semi-industrial studies of Tungsten-based catalyst for hydroisomerization/hydrocracking of *n*-hexane and *n*-heptane

M. Hasan[a], A.M. Mohamed[b], H. Al-Kandari[c,*]

[a] *Chemistry Department, Kuwait University, P.O. Box 5969, Safat, 13060, Kuwait*
[b] *Chemistry Department, Kuwait University, P.O. Box 5969, Safat, 13060, Kuwait*
[c] *College of Health Sciences, PAAET, P.O. Box 1428, Faiha 72853, Kuwait*

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ABSTRACT

WO_3/TiO_2(WTi) composite was prepared via an environmentally friendly, fast and facile wet impregnation method using distilled water as the solvent. The catalyst composite was investigated by in-situ XPS-UPS and ex-situ BET and XRD characterization techniques before and after the activation under hydrogen flow. The activation of the composite resulted in the formation of metallic and acidic catalytic sites in the form of $WO_{3-x}(OH)_y$ on the surface of the WTi composite. The distribution of these sites depends on the activation temperature. XPS results show the formation of a different oxidation state of tungsten after its activation. The formation of WO_{3-x} with metallic properties was confirmed by an examination of the density of states in the valence band region. On the other hand, the Brønsted acidic sites were attributed to the −OH group observed in the XPS peak fitting of the O1 s peak at 531.4 eV. The catalytic activity was evaluated for the hydroisomerization/hydrocracking of *n*-hexane and *n*-heptane using 15 cm^3 WTi in a large-scale reactor at different experimental parameters. At a reaction temperature of 598 K, the catalytic activity was 97.1% in the case of *n*-heptane in favor of β-scission (C3-iC4, 78.4%), compared to 76.1% activity in favor of the isomerization products (84.6%) in the case of *n*-hexane after the composite activation at 673 K. The research octane number (RON) was improved from 24.8 for *n*-hexane to the 70–80 range for hexane isomers and from zero in the case of *n*-heptane to cracking products with a high octane number. Upon increasing the activation temperature to 773 K, the hydrogenolysis of *n*-heptane was the dominant catalytic reaction.

1. Introduction

Since tetraethyl lead and aromatic additives are restricted in gasoline production for environmental protection, branched alkanes have been used to improve the gasoline octane number [1]. The hydroisomerization of linear alkanes to corresponding branched isomers and hydrocracking to small fractions are essential processes in petroleum technologies for the production of gasoline with a high octane number. These processes depend on the catalyst structure, alkane molecular weight, reaction temperature, pressure, and other parameters that can affect the catalytic reaction pathway. Bifunctional (metal-acid) sites are required for the hydroisomerization process, whereas monofunctional sites are sufficient for the hydrocracking process under hydrogen flow.

There are two types of cracking processes: hydrogenolysis and β-scission. The former is a metal-catalyzed reaction, while the latter is an acid-catalyzed reaction (i.e., Brønsted acid) [2]. The possible catalytic reaction pathways of *n*-hexane and *n*-heptane in the presence of metallic (M) and acidic (A) sites are illustrated in Scheme 1. The catalytic reaction pathway depends on the M/A ratio and the strength of each site. Commercially, Pt supported on acidic chlorinated alumina or zeolite are the most commonly used catalysts in hydroisomerization reactions [2,3], and acidic zeolite is utilized in the hydrocracking reactions [4,5]. Despite the higher yields of branched products at low operating temperatures, these catalysts are very sensitive to poisons, such as sulfur compounds or water, which are usually present in oil derivatives and cause severe corrosion and pollution problems. To address these problems, it is essential to discover and optimize new low-cost, earth-abundant, highly stable and easy to handle solid multifunctional catalysts in order to perform hydroisomerization/hydrocracking reactions at low temperature.

Tungsten oxide based-catalysts have been widely used and investigated as a solid acid catalyst for many applications such as dehydration of alcohols, hydroisomerization of alkane and alkene, metathesis of 1-hexene, electrochemistry, and photocatalysis [6–13]. A unique property of WO_3 is its reducibility to WO_{3-x}, producing a considerable amount of oxygen vacancies and providing the tungsten oxide with

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* Corresponding author.
E-mail addresses: m.hasan@ku.edu.kw (M. Hasan), ahmed.mohamed@ku.edu.kw (A.M. Mohamed), ha1.alkandari@paaet.edu.kw (H. Al-Kandari).

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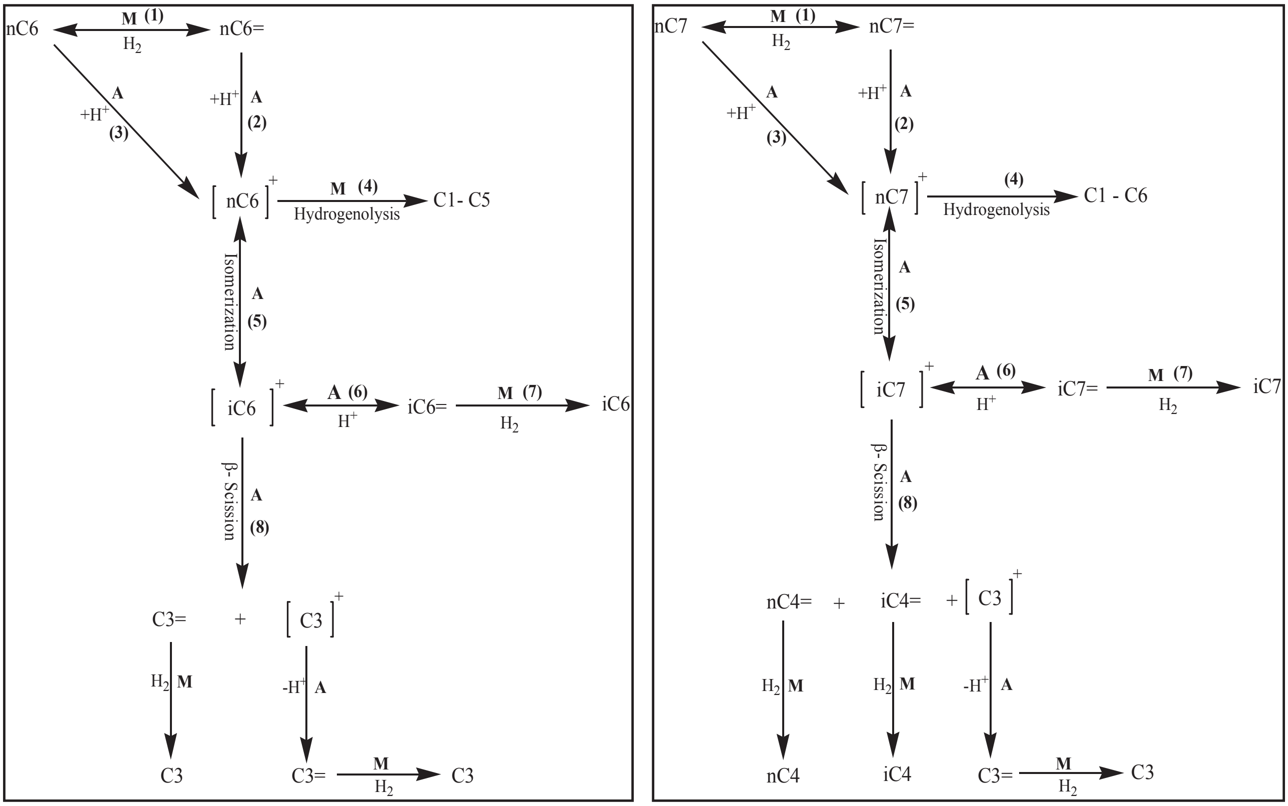

Scheme1. Possible catalytic reaction pathways of *n*-hexane (nC6) and *n*-heptane (nC7) over acidic (A) and metallic (M) sites.

some electrical conductivity and electron donor density [14]. Katrib et al. reported that the partial reduction of WO_3 under hydrogen flow resulted in the formation of WO_2 with metallic properties due to the presence of free electrons in the 5d and 6 s orbitals at the Fermi level, as observed in the XPS valence band region using the density of states. Dissociated hydrogen gas on the surface of WO_2 generates Brønsted acid sites, and thus bifunctional sites were generated. It was also mentioned that the formation of a bifunctional active phase on WO_3 required a high reduction temperature of 773 K [15–17].

To the best of our knowledge, most of the studies on W-based catalysts were carried out using small amounts of catalyst (0.1–1 g) in small-scale reactors using a metal with strong acid support such as Al_2O_3, SiO_2, and ZrO_2 [18–21]. In this study, WTi catalyst was of interest because WO_3 and TiO_2 are earth-abundant and inexpensive compared to Pt-based catalysts. Moreover, the low acidic property of the TiO_2 pellet was attractive due to its stability under high temperature its ability to support the catalyst with mechanical strength for easy handling. A large-scale reactor loaded with 15 cm^3 of catalyst was used under different experimental conditions to optimize the performance of the catalyst in order to simulate hydroisomerization/hydrocracking reactions under industrial conditions.

2. Experiment

2.1. Catalyst preparation

The composite was prepared via the wet impregnation method using distilled water (DW) as the solvent. The calculated amount (3.34 g) of ammonium metatungstate hydrate $(NH_4)_6H_2W_{12}O_{40}{\cdot}xH_2O$ (99.9%), supplied by Strem Chemicals and equivalent to 5 monolayers of tungsten trioxide (WO_3), was dissolved in 50 mL of DW. Then, the solution was poured into a 10 g P-25 TiO_2 pellet (obtained from Degussa in a cylindrical shape with the average dimensions of 4.3 × 1.7 mm with the pore volume of 0.5 cm^3/g and the BET surface area of 50 ± 5 m^2/g). This mixture was heated to 343 K under vacuum and rotated at 250 rpm in a Rotavapor to remove the excess water. The composite was dried in an oven at 383 K for 6 h. Finally, the composite was introduced into a tube furnace for calcination under a flow of air with a temperature ramping of 10 K/min to reach 773 K and was maintained at 773 K for 12 h. The composite was designated WTi, where W = WO_3 and Ti = TiO_2.

2.2. Characterization techniques

The BET surface area was evaluated using a surface area analyzer (*Gemini-V, Micrometrics, USA*) at the boiling point of liquid nitrogen (196 K). Small amounts of composites (100–300 mg) were degassed in a VacuPrep061 sample degassing system at a temperature of 110 °C for 3 h prior to starting the experiments. Surface areas were calculated using the Brunauer–Emmet–Teller model for the isotherms. For all composites, nitrogen gas of 99.999% purity was used as the adsorbate. The composite was activated first at the atmospheric pressure in a quartz microreactor at 623 K, 673 K, 723 K and 773 K each for 14 h under the hydrogen flow of 200 mL/min was then transferred to BET for measurements.

XPS-UPS spectra were recorded on a *Thermo Scientific ESCALAB 250Xi* spectrometer (UK), using Al Kα radiation (1486.6 eV) for XPS and a He(I) resonance of 58.4 nm radiation of 21.217 eV for UPS. The spectra acquisition and handling were carried out using an online *Avantage 4.5* data system (UK). The investigated sample was fixed on the sample holder as prepared in an ambient atmosphere and then mounted and stored in the preparation chamber until a vacuum below 1.0×10^{-7} bar was reached. Then, the sample was transferred to an analysis chamber at 1.0×10^{-9} bar and was exposed to X-ray radiation (XPS) or UV radiation (UPS) for a certain number of scans. After the data acquisition, the sample was transferred into a high-pressure gas cell built-in a preparation chamber with a maximum temperature and pressure of 773 K and 5 bar, respectively. For WTi activation, a flow of