



Full Length Article

Olefin upgrading under methane environment over Ag-Ga/ZSM-5 catalyst



Peng He, Yang Lou, Hua Song*

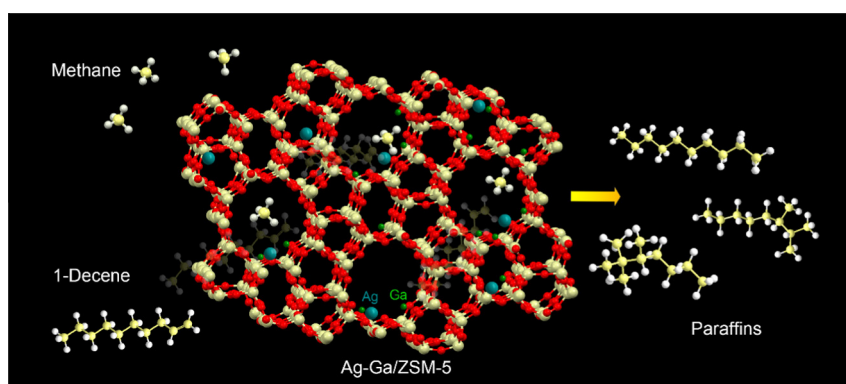
Department of Chemical and Petroleum Engineering, University of Calgary, 2500 University Dr NW, Calgary, Alberta T2N 1N4, Canada

HIGHLIGHTS

- A novel catalytic methanotreating process is developed to reduce olefin content.
- Olefin prefers to be converted to paraffin when methane is present over Ag-Ga/ZSM-5.
- Methane involvement into olefin upgrading reaction is evidenced via DRIFTS study.
- Methane presence favors metal dispersion and Ga migration to catalyst surface.

GRAPHICAL ABSTRACT

The model compound selected to represent cracked distillates from bitumen thermal cracking gets upgraded to saturated hydrocarbons under methane environment over Ag-Ga/ZSM-5 catalyst.



ARTICLE INFO

Article history:

Received 1 March 2016

Received in revised form 24 May 2016

Accepted 28 May 2016

Keywords:

Methane
Methanotreating
Olefin
Catalytic upgrading
Cracked distillates
DRIFT

ABSTRACT

The upgrading of the petroleum cracking distillates using cheap methane rather than naturally unavailable hydrogen is an economically attractive process. This work clearly demonstrates the feasibility of methanotreating by directly using methane over zeolite-supported catalyst to convert olefins. The introduction of methane decreases the fraction of olefins and increases the fraction of paraffins in the liquid products obtained from the reaction using 1-decene as the olefin model compound when Ag-Ga/ZSM-5 is charged. It also improves the quality of liquid product in terms of higher H/C atomic ratio, higher heating value and lower bromine number. The interaction between olefins and methane on the surface of the catalyst is evidenced by DRIFT spectroscopy. When propylene is used as the olefin model compound, the shift of the peaks due to the interaction between adsorbed propylene species and catalyst surface as well as the generation of new peaks after the introduction of methane are observed. When 1-decene is used as the model compound, the suppressed intensity of —C=C— signal and enhanced alkane C—H bending peak intensity when CH_4 is present indicate the conversion of olefins into paraffins. The improved particle dispersion of the charged catalyst upon the reaction under CH_4 environment is also noticed from the TEM images, which might be closely related to its better olefin upgrading performance. The outcomes from this study might create an alternative route for cracked distillates upgrading and provide a positive attempt for more valuable methane utilization.

© 2016 Elsevier Ltd. All rights reserved.

* Corresponding author.

E-mail address: sonh@ucalgary.ca (H. Song).

1. Introduction

As the reserves of conventional petroleum cannot meet the fast increasing energy demand of human societies, non-conventional petroleum is drawing attention. Among the non-conventional petroleum sources, heavy oil could contribute a larger portion of petroleum consumption in the future due to its large reserves. For example, the remaining proven reserves of heavy oil in Canada are 165 billion barrels by the end of 2015 [1]. In 2015, the heavy oil production in Canada were 2.5 million barrels per day [1]. Heavy oil was formed from conventional oil, degraded by bacteria upon the migration towards the surface region. Some light hydrocarbons were consumed during the biological reaction process. As a result, bitumen is deficient in hydrogen and has high carbon content. Another obstacle faced by the utilization of heavy oil is its high viscosity, impeding its transportation to existing refineries, especially through pipelines [2,3]. Thermal cracking is widely employed to lower the viscosity of bitumen by breaking down the long carbon chain and complicated polycyclic molecular structure of heavy oil at high temperatures. According to the statistics released by the US Energy Information Administration, the thermal cracking capacity of the refineries in US is 3.0 million barrels per day in January, 2015 [4]. However, such treatment results in higher content of olefins which will create implementation issues such as carbon deposition during storage and transportation, incomplete combustion and generate negative environmental impacts such as photochemical smog and toxic dienes [5,6]. Olefins contained in the produced oil are oxidatively and thermally unstable and may gradually form polymeric deposit during storage [5]. Carbonaceous gum formation on the fuel injector and in the engine's intake system will lead to gasoline insufficient combustion, resulting in increased hazardous emissions such as CO, hydrocarbon, and NO_x. Moreover, these olefinic hydrocarbons may also contribute to photochemical reactions in the atmosphere, resulting in the formation of photochemical smog in susceptible urban areas. Olefins in the atmosphere can contribute to ozone formation and toxic dienes [6]. Thus, the olefins produced in the thermal cracking processes must be eliminated before the product can be sent to downstream refineries.

Hydrotreating is commonly practiced in petroleum industry to convert the olefins into saturated species, while hydrodesulfurization, hydrodenitrogenation, hydrodeoxygenation and hydrodemetalization take place simultaneously in the presence of catalysts and substantial hydrogen supply [7]. According to the statistics released by US Energy Information Administration, the catalytic hydrotreating capacity in US is as large as 17.3 million barrels per day in January, 2015 [8]. However, hydrotreating process consumes expensive hydrogen, which is mainly obtained from the reforming of natural gas. The reforming of natural gas is a highly endothermic reaction and often requires high operating temperatures (>800 °C) and pressures (1.5–3.0 MPa) [9,10]. Besides the large amount of energy input, the reforming process also emits CO₂ when carbon is rejected from natural gas. If natural gas, including its recently largely discovered form (shale gas), can be directly used as the reducing agent under mild pressure, the capital and operation cost for the upgrading process would be reduced significantly. At the same time, the CO₂ emissions from steam reforming process will be avoided as carbon is incorporated into the upgraded oil rather than rejected as CO₂, thus effectively reducing the greenhouse gas contributions from petroleum industries. In 2015, the price of natural gas in US is averaged US \$2.77 per million British thermal units (MBTU), while that of West Texas Intermediate (WTI) light sweet crude oil is averaged US \$48.79 per barrel, which is equivalent to US \$8.79 per MBTU [1]. Therefore, the incorporation of methane, the principal component of natural

gas, into the synthetic oil molecules not only enhances the productivity of the product oil, but also converts the low cost methane into high value added commodities, making the process more profitable. Another disadvantage of the hydrotreating process is the high operating pressure, which is typically 70–140 atm and even higher than 200 atm [11,12], resulting in a high operating cost. If the upgrading under CH₄ atmosphere (methanotreating) could be achieved at a lowered pressure, the cost of this process would again be reduced since the pressure tolerance standard of the fabrication materials and connections of the reaction units is less strict as well as reduced energy consumption on gas compression.

In order to make the aforementioned methanotreating reactions taking place, a specially tailored catalyst system should be developed. Methane is the most inert hydrocarbon molecules due to the high C–H bond energy of 435 kJ/mol, which is the highest among all hydrocarbons, as well as the large energy gap between the highest occupied molecular orbital and lowest unoccupied molecular orbital (HOMO–LUMO) [13]. Correspondingly, the effective activation and direct conversion of methane into more commercially useful chemicals and liquid fuels represent a great challenge for the entire catalysis field. There are two main approaches for the activation and conversion of methane. The first one is to produce ethane and ethylene through the oxidative coupling of methane (OCM), which involves the presence of oxidants to make the reaction more thermodynamically favored. This approach, however, needs to improve the conversion and selectivity to meet the criteria of the industry application [13]. The other approach is to convert methane into higher hydrocarbons under non-oxidative environment. Many catalyst systems have been reported over the past three decades. Among them, zeolite supported molybdenum catalyst system demonstrates the most promising activity. Even though, less than 10% methane conversion is observed when the temperature is higher than 700 °C with major products in aromatics. The high reaction temperature and low conversion dent its commercial potential.

Choudhary et al. [14] showed that methane can be effectively converted into higher hydrocarbons and aromatics in the presence of alkenes and/or higher alkanes at low temperatures (400–600 °C) over H-gallosilicate ZSM-5 type zeolite under non-oxidizing condition at atmospheric pressure. A series of related research work also demonstrates that the conversion of methane will be significantly enhanced when methane was co-fed with hydrocarbons, such as ethane, propane, pentane, hexane, light gasoline, liquefied petroleum gas, and even oxygenated hydrocarbons like methanol [15–22]. Baba et al. [23] noticed that Ag/ZSM-5 could effectively activate methane at 400 °C, and this process was assisted by the presence of C₂H₄. Gabrienko et al. [24] utilized solid-state NMR (SSNMR) to study the catalytic methane activation mechanism over Ag/ZSM-5. The SSNMR study confirmed that the cleavage of the C–H bond in methane takes place through the “carbenium” pathway, indicating that the CH₃ species was positively charged, to form methoxy groups. These results shed light on the olefin elimination using methane as the hydrogen source, because various alkanes and alkenes are generated during the olefin upgrading, which can act as promoters for methane activation. Under this condition, with specially tailored catalyst system, the methane molecules can be cleaved into H_x and CH_x, and the following engagement of these species into the unsaturated bonds would contribute to the elimination of olefins.

This paper thus studies the feasibility of olefin reduction under methane environment over Ag-Ga/ZSM-5 catalyst using 1-decene as the model compound to simulate the cracked distillates formed from heavy oil thermal cracking.

Download English Version:

<https://daneshyari.com/en/article/6633509>

Download Persian Version:

<https://daneshyari.com/article/6633509>

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