



Research article

Catalytic bitumen partial upgrading over Ag-Ga/ZSM-5 under methane environment



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ABSTRACT

Partial upgrading of viscous heavy oil, such as bitumen extracted from Canadian oil sands, to meet the specifications of pipeline transportation is highly desired. Conventionally, this is achieved by catalytic hydrotreating under a hydrogen pressure of 15–20 MPa, which consumes naturally unavailable hydrogen. Recently a novel methanotreating technology using methane, the principal component of natural gas, as the hydrogen donor has been explored over metal modified zeolites to catalyze the upgrading process. In the present work, the formula of the catalyst was optimized in terms of the species of metal cations, morphology of the support materials and acidity of the support. The catalytic performance was evaluated by comparing the viscosity and coke formation as well as compatibility of the product oil upon methanotreating. When a silver and gallium cation modified ZSM-5 with a silica to alumina ratio of 30:1 was used to catalyze the upgrading of heavy oil at 380 °C and 5 MPa, the viscosity of heavy oil was reduced to 278 mPa·s at 25 °C with an acceptable coke yield of 0.8 wt.% and without compromising the compatibility of the resulting oil product, which were desirable for pipeline transportation and downstream refining. This study demonstrates the feasibility of upgrading heavy oil with natural gas at fairly mild operation conditions instead of expensive hydrogen at rather stringent ones.

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1. Introduction

Unconventional petroleum resources including bitumen have been an important sector of the petroleum industry, contributing to the production of fuels and chemical feedstock. Bitumen is an abundant resource in Alberta, Canada. According to data released by the Alberta government, heavy oil production in Canada averaged 2.5 million barrels per day in 2015 [1]. Such bitumen has a dynamic viscosity of 2×10^5 – 2×10^6 mPa·s at atmospheric conditions [2] making it challenging to transport bitumen, especially through pipelines, which requires a dynamic viscosity of <330 mPa·s (at 7.5–17 °C) [2,3], to refineries in the United States. Hydrotreating is a commonly practiced process in the petrochemical industry to reduce the viscosity of oil, while hydrodesulfurization, hydrodenitrogenation, hydrodeoxygenation and hydrodemetallization take place simultaneously in the presence of catalysts and substantial hydrogen supply. The catalytic hydrotreating capacity in US is as large as 17.3 million barrels per day in January 2015 according to the data released by US Energy Information Administration. However, this process has to consume a large amount of hydrogen, which is not naturally available, at high pressures of 10–20 MPa. In industry, >50% of hydrogen is obtained through steam reforming of methane, the principal component of natural gas. The reforming of methane is a highly endothermic reaction and often

requires high operating temperatures (>800 °C) and pressures (1.5–3.0 MPa) [4,5]. The involvement of such a naturally unavailable hydrogen source will inevitably result in a significant cost for this upgrading process. If a partial upgrading technology can be developed to reduce the viscosity and improve the qualities of bitumen by directly utilizing methane as the H-donor to carry out the upgrading process, such cost could be significantly reduced. The incorporation of methane into the products also fulfills the task of converting cheap methane into high value added commodities. In 2015, the price of Henry Hub natural gas in US is averaged US \$2.77 per 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. The greatly underestimated value of methane makes the proposed process more profitable. Besides, the carbon from methane will be incorporated into the products, rather than ejected as CO₂ during the reforming process, thus reducing the greenhouse gas emission of petroleum industry.

Through this so-called methanotreating route, the usage of the steam reformer is avoided and the heat integration is improved. Therefore, the profitability of the methanotreatment process compared to its hydrotreatment counterpart will be enhanced. If methanotreatment could be achieved at a lower pressure, the cost of this process would again be reduced since the standard of the materials and connections of the reaction units is reduced. In order to make methanotreating industrially applicable, the reactions should take place under similar or even less severe reaction conditions. Compared with H₂, CH₄ has a much more stable molecular structure, resulting in its inert nature and

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Table 1Viscosity and coke yield of the product oil collected over HZSM-5 with variable SiO₂/Al₂O₃ molar ratios under methane environment at 5.0 MPa and 380 °C for 150 min.

	Bitumen	No catalyst	HZSM-5 (23:1)	HZSM-5 (30:1)	HZSM-5 (50:1)	HZSM-5 (80:1)	HZSM-5 (280:1)
Viscosity (mPa·s)	$8.5 \pm 0.2 \times 10^5$	$1.62 \pm 0.08 \times 10^3$	$1.52 \pm 0.08 \times 10^3$	$9.6 \pm 0.5 \times 10^2$	$1.40 \pm 0.07 \times 10^3$	$1.20 \pm 0.06 \times 10^3$	$1.46 \pm 0.07 \times 10^3$
Coke yield (%)	–	0.55	0.69	0.73	0.84	1.28	0.89

low reactivity. Its C—H bond energy of 435 kJ/mol is the highest among all naturally available hydrocarbons. In order to make the aforementioned methanotreating reactions take place, a specially tailored catalyst system must be developed to trigger the cleavage of the C—H bond. Once the first C—H bond is broken, reactive methyl radicals will be generated to carry out the methanotreating process. Therefore, a catalyst that is able to effectively lower the activation energy of methane and allow the C—H bond cleavage under less severe reaction conditions is crucial.

Over the past decades two approaches have been practiced to achieve methane activation and following conversion. One of them is through an oxidative route, i.e., the reaction is under an oxidative environment so that the oxidative coupling of methane (OCM) makes the conversion of methane towards ethylene thermodynamically favored. Despite the fact that hundreds of catalysts have been tested since the 1980s, the poor product yields (<25%) do not meet the industrial application criteria [6–10]. Another approach is the conversion of methane under a non-oxidative environment. Lots of catalyst systems have been studied to catalyze the conversion of pure methane [11–15], but their industrial application is impeded by the low conversion and high reaction temperature, which may be higher than 700 °C [16,17]. When higher hydrocarbons are co-fed with methane, however, the activation of methane and the following conversion are enhanced significantly. Choudhary et al. showed that methane can be efficiently converted into higher hydrocarbons as well as aromatics in the presence of alkenes and/or higher alkanes at mild conditions, i.e., low temperatures (400–600 °C) and atmospheric pressure, over Gallium modified ZSM-5 type zeolite catalyst [18]. Similar results have been widely reported using a variety of catalysts when methane was co-fed with hydrocarbons, such as ethane, propane, pentane, hexane, light gasoline, liquefied petroleum gas, and even oxygenated hydrocarbons like methanol [19–24]. These results shed light on the partial upgrading of bitumen using methane as the hydrogen source, since bitumen is rich in the hydrocarbons that assist the methane activation. The methane activation can be promoted by the hydrocarbons generated by the cracking of bitumen molecules during the upgrading process. This idea has been explored in our previous study, and it is noticed that silver and zinc cation-modified HZSM-5 can catalyze the upgrading of heavy oil, at 380 °C and 5 MPa, under methane environment to produce partially upgraded crude oil with improved quality for pipeline transportation and downstream refining [25].

Besides the activation of methane molecules, phenomena such as instability and incompatibility of the produced crude oil also draw great attention in the partial upgrading of heavy oil under methane environment, which are due to the formation of degradable products or other undesirable changes in the formed oil product, resulting in the formation of a precipitate or separate phases. Addressing this issue is critical for pipeline transportation because the oil must be able to remain in a uniform phase during its storage and transportation over an extended time period without deposit formation.

It is noticed in the open publications that among the catalysts employed for methane activation and conversion, most of them are based on ZSM-5 type zeolites, which might be due to its excellent aromatization activity [26,27]. When methane is used to upgrade heavy oil, ZSM-5 based catalysts have been proven effective. As reported in our earlier research, the synergistic effect between methane and bitumen has been witnessed during the methanotreating process when Ag-Zn/ZSM-5 with a SiO₂/Al₂O₃ molar ratio of 23:1 is charged, resulting in improved quality of oil in terms of lower viscosity, density, acidity, asphaltene content and molecular weight, and higher gasoline and diesel contents as well as acceptable coke formation [25]. The support

material, ZSM-5, is widely used in the petrochemical industry as a fluid catalytic cracking catalyst. The effect of the support material structure on the partial upgrading process under methane environment, however, remains unclear. Like in many scientific fields [28–33], the optimization of the parameters, which are related to the catalyst formula and structure in this work, is crucial to attain the desired performance. It is necessary to study whether ZSM-5, or other candidate support materials, would be more suitable for triggering heavy oil upgrading. The obtained knowledge would improve the understanding of the catalyst systems and optimized the catalysts. When zeolites are used as the support materials of the catalyst, one of the parameters that has profound effect on the catalytic activity is its surface acidity. Within the zeolite framework, the charge-balancing proton (H⁺) species are in the OH[−] group of the Si(OH)Al species, which could act as Brønsted centers in the catalytic processes [34]. The Brønsted sites of zeolites are responsible for the cracking of hydrocarbon molecules [35]. They are also considered the active sites for the isomerization and alkylation reactions [36,37]. The acidity of the zeolite is closely related to the concentration of the Brønsted sites, which can be tuned by changing the ratio of Al to Si within the framework, i.e., variable SiO₂ to Al₂O₃ molar ratios. In the previous study, HZSM-5 with a SiO₂ to Al₂O₃ molar ratio of 23 is used as the catalyst support and witnessed improved oil quality for pipeline transportation and downstream refining [25]. ZSM-5 could be a good support because of its outstanding methane activation performance under non-oxidative environment, particularly in the presence of higher hydrocarbons, which is widely reported in aforementioned literature as well as the author's ongoing research [38–40]. But the effect of the surface acidity of ZSM-5 on the catalytic performance was not revealed. Other parameters in catalyst formula optimization, such as the species of metal cations, morphology of the support materials and their acidity, also need to be investigated. Therefore, HZSM-5 with various SiO₂ to Al₂O₃ molar ratios along with another three support materials including Zeolite Y, Zeolite A and ZrO₂ are employed to prepare the catalyst samples. Among them, Zeolite Y and zeolite A, which are widely used in petroleum industry, are chosen as the candidate for their larger pore sizes of 11.24 and 11.05 Å, while that of ZSM-5 is 6.36 Å [41,42]. The larger pore size might benefit the conversion of the large bitumen feedstock molecules. The Sulfated ZrO₂ (S-ZrO₂) has been numerous reported in the literature [43–45] with high surface acidity which might facilitate heavy crude oil cracking. Therefore, these four types of support materials are chosen as the test samples to evaluate the effect of aforementioned factors on the catalytic performance.

These catalysts are used to catalyze the methanotreating of bitumen by employing low-temperature and low-pressure upgrading conditions, i.e., 380 °C and 5.0 MPa. The catalytic performance is evaluated by comparing the viscosity and coke yield as well as the compatibility of the product oil, which have profound effects on the transportation of heavy oil. The formula of the catalyst that boosts the flowability without

Table 2

Reference spot description for oil sample compatibility and stability measurement.

Reference spot no.	Characterizing features
1	Homogeneous spot (no inner ring)
2	Faint or poorly defined inner ring
3	Well-defined inner ring, only slightly darker than the background
4	Well-defined inner ring, thicker than the ring in reference spot Mo.3 and somewhat darker than the background
5	Very dark solid or nearly solid area in the center. The central area is much darker than the background

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