



Olefin Upgrading over Ir/ZSM-5 catalysts under methane environment



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ABSTRACT

Upgrading olefin in the synthetic oil to alkane is highly desired due to its high volatility and thermal instability as well as low energy density. Unlike conventional hydrotreating, methane (CH₄) was used in this study as the novel hydrogen donor for olefin saturation. The significant increase of H/C atomic ratio of product oil from 1.69 ± 0.02 (over pure ZSM-5) to 2.04 ± 0.02 (over Ir/ZSM-5 (10.0)) and the alkane content up to 83.8 ± 2.1% in the upgraded oil indicated that methane could exhibit comparable catalytic performance to what hydrogen (H₂) did for olefin (1-Decene) upgrading over the developed bifunctional catalysts with low Ir loadings. The HRTEM and XPS data revealed that the highly dispersed metallic Ir particles with average size of 1.32 nm was coexisting with IrO₂ species. The synergic effects of Ir/IrO₂ obviously promoted the activation of methane, which supplied sufficient hydrogen for the saturation and stabilization of olefin. The results from BET indicated that the pore size and volume of the ZSM-5 support were increased upon Ir introduction, which provided more active sites for cracking olefin (1-decene). NH₃-TPD results suggested that the presence of highly dispersed Ir increased the amount of surface acidity, which enhanced the formation and stabilization of carbenium ion intermediates. As a result, the produced alkanes were mainly composed of cyclopentane-derived compounds, like propylcyclopentane, 3-methylbutyl-cyclopentane and 1,2,4-trimethyl-cyclopentane, which has great application potential as immersion fluid and additive in the field of optics and petroleum.

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1. Introduction

Olefins including light and long-chain unsaturated compounds are abundant byproducts of catalytic cracking [1] and Fisher-Tropsch synthesis [2] but are underutilized as energy carriers because of their high volatility and low energy density [3]. In addition, the presence of olefin could not only cause the formation of polymeric deposit due to its thermal instability during long-term storage and long distance transportation but also lead to gasoline insufficient combustion, generating negative environmental impact. Therefore, upgrading olefin to alkane is critical not only for the enhancement of product stability but also for the protection of our environment. Generally, hydrotreating is widely employed to saturate olefins for the improvement of gasoline quality [4,5]. However, the involvement of hydrogen (H₂) obviously increases the cost of this upgrading step since H₂ is not naturally available. Current steam reforming of natural gas (mainly composed of CH₄) accounts for almost 50% of the world feedstock for hydrogen (H₂) production but is operated in a high temperature range of 973–1173 K

[6,7], which not only increases the operation cost but also leads to huge emission of CO₂. Hence, if methane could be directly used as the novel hydrogen donor and act as an alternative to expensive hydrogen gas for olefin upgrading, not only the operation costs but also greenhouse gas emission could be significantly reduced.

Although direct activation of CH₄ is uneasy due to its symmetrically geometric and stable electronic structure [8,9], the previous research reveals that the methane could be efficiently activated over bifunctional catalysts [10–14] (M/zeolites, M: metal species) in the presence of alkene and higher alkane at near atmospheric pressure and mild temperature (400–600 °C). For instance, the presence of n-butene could efficiently facilitate CH₄ conversion up to 45.0% at 600 °C and 1 atm, which produces not only high value products of aromatics and H₂ but also exhibits high selectivity toward aromatics (up to 92.0%) formation [10]. From the aspect of thermodynamics, the reaction barrier could be significantly reduced to zero or even negative when methane reacts with alkenes or higher alkanes under appropriate conditions; for example, the positive Gibbs free energy change (ΔGr) value of direct formation of benzene from methane could become −4.1 kcal/mol at 500 °C and −10.6 kcal/mol at 600 °C when the ratio of n-butene/methane was 1.0 [10]. Moreover, Har [4] and Song et al. [15–18] reported that methane could act as comparable or even better hydrogen donors

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than H₂ for upgrading heavy oil and crude bio-oil during biomass pyrolysis. Hence, CH₄ could be employed as a novel hydrogen donor for olefin upgrading from both theoretical and practical viewpoints.

On the surface acidic centers of bifunctional catalysts, olefin could be cracked down through α -C-C scission and β -C-C scission to smaller molecules [19–22], which contain unsaturated hydrocarbons featured by the presence of C=C and C \equiv C bonds in their molecular structures. Surface acidic centers could easily catalyze the unsaturated bonds to form the carbenium ions [20,23], which are highly reactive fragments for further agglomeration, isomerization, cyclization, hydrogen redistribution and so on [24–26].

Therefore, it would be a feasible and efficient method to saturate olefin by CH₄ over well-developed bi-functional catalysts based on the aforementioned reaction between methane and co-existing unsaturated hydrocarbons. In the meantime, the reaction between activated CH₄ and highly reactive fragments formed after olefin cracking would efficiently increase the H/C atomic ratio and alkane contents of product oil, which could not only make the product oil more stable but also efficiently inhibit the formation of coke during its further processing and application. In addition, the formed CH_x moiety from methane activation might be incorporated into the upgraded oil product, leading to the enhancement of oil yield. Shortly, taking methane as a novel hydrogen donor would not only effectively reduce the greenhouse emission and operation costs for olefin upgrading but also supply a novel way for CH₄ utilization, which could make olefin upgrading more economically attractive and environmentally friendly.

Ir-based catalysts are widely used and studied in the fields of environment and fundamental researches [27–30]. Both of Ir and IrO₂ species exhibit excellent capability of C–H bonds activation of CH₄ [3,31–35]. IrO₂ could exhibit very high reactivity for methane activation because the electron density transfer from the d_z² orbital of coordinately unsaturated Ir (Ir_{cu}) atom to C–H bond could weaken the C–H bond of CH₄ through the interaction between the σ bond of C–H of CH₄ and the Ir_{cu} atoms [33]. The activation energy for methane dissociative chemisorption on Ir (111) could be as low as 15 kJ/mol [35]. Furthermore, C–H bond activation is the only kinetically limiting step in CH₄ activation on supported Ir species, the reactivity of which increases with increasing dispersion of Ir species [32]. Therefore, the supply of hydrogen donors could be promoted with the increase of Ir dispersion, which would enhance the saturation of carbenium ions [20].

Hence, in this paper, highly dispersed Ir/ZSM-5 bifunctional catalysts are synthesized by the deposition precipitation method (DP). The prepared highly-dispersed Ir catalysts not only significantly lower the loadings of noble metal and promote methane activation but also appropriately tune the surface acidity of ZSM-5, which could supply sufficient hydrogen donors and efficiently modulate the catalytic cracking for olefin upgrading.

2. Experimental

2.1. Synthesis of the catalysts

Unlike the conventional Ir catalysts mainly prepared by impregnation methods, which have Ir particles poorly dispersed on and weakly interacted with support, the Iridium catalysts developed in this research were prepared using the following procedures [18,36–39], which could strengthen the interactions between Ir metal particles and the zeolite supports. An IrCl₃ (Sigma, 99.8%) aqueous solution with concentration of 1.0 mmol/L was dropwisely introduced into a 200 mL aqueous solution suspended with HZSM-5 powder manufactured by Zeolyst® (2.0 g, activated at 600 °C in air for 5 h) under stirring. The pH of the resulting solution was adjusted to set values using aqueous solutions of HCl and NaOH.

The SiO₂/Al₂O₃ (Si/Al) ratio of ZSM-5 used in our experiment was 80:1 unless otherwise stated. The resultant slurry was further aged at room temperature for 2 h and was then washed with distilled water for several times. The achieved solid material was dried at 80 °C for 12 h and calcined in air at 400 °C for 2 h.

It is widely recognized that the dispersion of a noble metal on a support is prominently influenced by the affinity of its precursor to the support and strong affinity could facilitate its good dispersion [40]. Therefore, different pH values (pH = 7.0, 8.0, 9.0 and 10.0) were chosen to prepare the well-dispersed Ir mounted onto ZSM-5 support according to the aforementioned synthesis recipe. And the corresponding catalysts were named as Ir/ZSM-5 (x), where x was pH value. The Ir actual loadings of these samples were 0.11 wt.%, 0.19 wt.%, 0.18 wt.% and 0.26 wt.%, respectively, when the preparation pH values were chosen at 7.0, 8.0, 9.0 and 10.0. The reported loading of Ir here was measured by ICP-AES (Varian 710). In order to investigate the effects of surface acidity on the catalytic performance, Ir/ZSM-5 catalysts with Si/Al ratio of 50:1 and 280:1 were also prepared following the same procedure as that of Ir/ZSM-5 (80:1, 10.0) and the corresponding loadings of Ir were 0.30 wt.% and 0.21 wt.% for Ir/ZSM-5 (50:1) and Ir/ZSM-5 (280:1), respectively.

2.2. Catalytic performance evaluation

1-Decene (C₁₀H₂₀, Alfa, 96%) was used as the model compound of olefin to evaluate the catalytic performance of catalysts prepared for olefin upgrading. The activity of catalysts was evaluated in a batch reactor (300 mL, Parr Instrument Co.). 8.5 g 1-decene was mixed with 0.085 g Ir/ZSM-5 catalyst and charged into the batch reactor. 30 bar CH₄ was introduced to the reactor after purging with methane for 3 times to remove air residue. The reactants were heated to 400 °C for 40 min (different reaction time and temperature was used when otherwise mentioned). The H/C molar ratio, alkane content and heating value of the resulted product oil were measured to characterize the catalytic performance as detailed in the followings.

The CHNS elementary analysis of the liquid product was carried out using an Elemental Analyzer (Perkin Elmer 2400 Series) in order to determine the weight percentage of C and H in the liquid samples. The atomic ratio of H to C was calculated from the corresponding weigh percentages with accuracy of ± 0.01 .

The heating value of the liquid product was determined by an oxygen bomb calorimeter (Parr 6100 Compensated Jacket Calorimeter). The measurement was carried out at room temperature.

The composition of the product oil was determined by the pre-calibrated Gas Chromatography-Mass Spectrometer (GC-MS: PerkinElmer GC Claus 680 and MS Clarus SQ 8T) equipped with a Paraffins-Olefins-Naphthenes-Aromatics (PONA) column (Agilent HP-PONA). The oven temperature of the GC was programmed to hold at 35 °C for 0.5 min, ramp to 200 °C at 5 °C/min, and hold for 0.5 min.

2.3. Catalyst characterization

The XRD patterns were obtained with Rigaku D/max 2550 VB/PC diffractometer using a Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$). The X-ray tube was operated at 40 kV and 100 mA. The intensity data was collected at room temperature in a 2 θ range from 10° to 70° with a scan rate of 6°/min.

The N₂ adsorption-desorption isotherm analysis was measured through nitrogen adsorption at liquid nitrogen temperature by using a surface area and porosity analyzer (Quantachrome NOVA 4000e apparatus). Before measurement, the samples were degassed at 180 °C for 6 h in vacuum.

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