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Investigation on the light alkanes aromatization over Zn and Ga modified HZSM-5 catalysts in the presence of methane

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ABSTRACT

The catalytic co-aromatization of methane and paraffin-rich raffinate oil was investigated along with hexane, heptane and octane as its model compounds over zinc and gallium modified ZSM-5 zeolite catalysts. The benzene, toluene and xylene (BTX) components derived from light alkane aromatization were highly promoted with the assistance of methane. The co-existence of Zn and Ga metal species has a positive effect on the formation of BTX components, whereas the individual metal loaded catalyst resulted in the production of heavy aromatics, suggesting that zinc and gallium have a synergistic effect on the formation of BTX under the methane environment. When concerned with gaseous analysis, the introduced methane might interact with smaller intermediates and then transform into larger hydrocarbons. From the DRIFT observation, it was witnessed that the interaction between light alkane and methane occurred on the surface of the charged Zn-Ga/ZSM-5 catalyst. According to the comprehensive catalyst characterizations, the excellent catalytic performance may be closely associated with greatly dispersed metal species on the zeolite support, improved microporous characteristic, moderate Brönsted and increased Lewis acidic sites during the paraffin-rich liquid feedstock aromatization under methane environment. This research provides a promising pathway for the highly effective and profitable utilization of petrochemical resources and natural gas.

1. Introduction

Aromatic compounds have been considered as important intermediates in the production of chemical commodity products. The heavy aromatics with carbon number equal to or more than 9 are seldom utilized and commonly burned off as fuels, whereas the so-called BTX family, referred to benzene, toluene and xylenes, are of great interest in petrochemical industry due to their application on the formation of high value-added chemicals as the fundamental building blocks [1,2]. Catalytic aromatization of light alkanes has been considered as an effective pathway for BTX aromatic production, and has in fact been the subject of interest for the past few decades [3,4]. Raffinate oil is the remaining distillate from solvent extraction of catalytic reformates, and is rich in long-chain alkanes, alkenes and cycloalkanes. Therefore, due to its compositions, raffinate oil can be employed as a raw feedstock to acquire BTX products through an effective aromatization process, which can satisfy the growing demand for light aromatics. As C_6-C_8 alkanes are the dominant compositions in raffinate oil, these model compounds are chosen to investigate the aromatization performance over suitable catalysts.

Methane presents an inherent resistance to various applications due to its strong C—H bond energy, resulting in the blocked application for valuable chemical formation [5,6]. Despite this, methane's abundance in nature and low cost make it an attractive form of feedstock for chemical industry. Many attempts have been made to develop promising processes for the conversion of methane into larger hydrocarbons. One is referred to the oxidative coupling methane reaction, where methane can be directly transformed into ethane and ethylene in the presence of oxidants and a suitable catalyst [7]. However, few catalysts can provide the required conversion and product selectivity to meet the minimum criteria for industrial applications. The non-oxidative coupling of methane is capable of achieving higher hydrocarbon conversion [8]. However, thermodynamic limitations reduce the methane activity extremely, and thus the conversion of inert methane tends to require serious conditions.

One notable approach is acquired based on the contributions made

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from the Choudhary research group [9]. It was noticed that the introduction of alkanes as co-reactants made it more feasible for the transformation of methane [10–11]. Moreover, co-aromatization from methane and small hydrocarbons can be observed at moderate conditions, which allows cost saving and greatly lowers equipment specification. As well as this, the incorporation of methane for alkane aromatization exhibited a synergistic effect on the formation of aromatic compounds [12].

Co-aromatization of methane in the presence of ethane, propane and pentane was reported from previous work [13–15]. Clearly, the catalysts used played a vital role for the aromatization process. Recently, numerous research efforts have been directed at co-conversion of alkanes and methane facilitated by bifunctional zeolite catalysts. ZSM-5 with special channel structure and intrinsic acidity exhibited excellent catalytic performance for the conversion of light hydrocarbons [16–18]. It has been reported that a metal with dehydrogenation functions loaded on the ZSM-5 catalyst highly improves the feedstock conversion and aromatic yield. According to previous literatures, Zn and Ga loaded on the ZSM-5 catalyst can enhance the catalytic activity for aromatization process and increase the selectivity to aromatics [19,20]. Tshabalala and his co-workers reported the aromatization of hexane among different active metals, and zinc and gallium additives were expected to exhibit a high aromatization activity due to their high dehydrogenation ability [21]. Choudhary et al. concluded that the aromatization activity of hydrocarbon (propene and butane) was highly attributed to the presence of Ga species [22]. Hodala et al. found that the Zn and Ga-modified ZSM-5 catalyst promoted the dissociation chemisorption of light alkanes, and then accelerated the dehydrogenation and aromatization reactions [23].

So far, only a few investigations have been concerned with the co-conversion of methane and raffinate oil and its representative model compounds (C_6-C_8) for the aromatic production over Zn- and Ga-modified ZSM-5. However, based on previous work put towards biomass and heavy oil, these catalysts show excellent results on the feedstock upgrading under methane conditions, which demonstrated the technical feasibility of co-aromatization of light alkanes and methane [24–29]. In addition, the comparisons of co-aromatization performance from methane and different feedstocks have not been studied before. The influence of individual Zn and Ga metal species on the catalytic activity was critical for a comprehensive investigation. In this work, the co-aromatization of methane and raffinate oil and light hydrocarbons including hexane, heptane and octane was carried out at 400 °C and 30 bar over Zn- and Ga-modified ZSM-5 catalyst. The role of Zn and Ga in the co-aromatization process was also explored under the methane condition.

2. Experimental

2.1. Synthesis of the catalysts

The zeolite-based material in the NH_4 form with Si/Al ratio of 23 and 80 was purchased from *zeolyst*. Then the NH_4-from zeolite was transformed into its H-form through calcination at 600 °C for 5 h. The 5%Zn-1%Ga/ZSM-5, 1%Ag-1%Ga/ZSM-5, and 5%Zn-1%Ru/ZSM-5 was prepared using the wetness impregnation method. The metal nitrates used were $Zn(NO_3)_2 \cdot 6H_2O$ (99%, Alfa Aesar), $AgNO_3$ (99.9%, Alfa Aesar), $RuCl_3$ xH_2O (99%, Alfa Aesar), and $Ga(NO_3)_3 \cdot xH_2O$ (99.9%, Alfa Aesar). The metal-modified samples were firstly dried in the oven at 88 °C overnight, and then calcined at 600 °C for 3 h in air.

2.2. Catalytic performance evaluation

In the case of raffinate oil provided by Shandong Chambroad Petrochemicals Co., Ltd, the reaction performance of these catalysts was evaluated in a 34-mL fixed-bed continuous micro-reactor. The flow rate of liquid feedstock in 0.1 mL/min was introduced using Optos Metering Pump (Eldex Laboratories Inc., Napa, CA). The mass flow rate of methane (99.97% purity Praxair) with 100 sccm was controlled using the mass flow controller (Beijing Sevenstar Electroincs Co., Ltd). The system pressure of 50 bar was controlled using the Back Pressure Regulator (Gentec Corporation, Shanhai, China). The two grams of tested catalyst and a certain amount of ceramic balls were filled into the reactor, and the reaction temperature was set to 400 °C and held for 1 h. The liquid product was collected in a cold trap at −15 °C powered by a cooled chiller using ethylene glycol and DI water mixture (50:50 vol.%) as coolant, and weighted after the reaction was completed.

As to model compound experiments, 0.5 g catalyst was put into the 100-mL batch reactor. Subsequently, 1 g model compound (hexane, heptane and octane, Sigma Aldrich, 99%) was placed in a glass vial, and then put on the evenly distributed catalyst layer. 10 bar pressures of desired gas were used to replace the air inside and performed in triplicate, followed by pressurizing to 30 bar with the gas required in the reaction. The reactor was heated to 400 °C and then maintained at this temperature for 1 h. Once the reaction was completed, the reaction was immediately quenched using water bath. The gas was collected by a gas cylinder for further analysis. The resulted liquid was extracted by CS_2, and through filtration the remaining solid residue was recovered. The collected liquid was characterized by GC–MS to quantify the liquid product composition.

2.3. Catalyst characterization

X-ray powder diffraction (XRD) patterns were recorded using a Rigaku Multiflex diffractometer with Cu Kα radiation (0.15418 nm). Scans were conducted at a 2θ of 5–75°. The introduced voltage and current were 20 kV and 40 mA, respectively.

The Diffuse Reflectance Infrared Fourier Transform (DRIFT) characterization of samples was carried out through a Thermo Scientific Nicolet iS50 equipped with MCT detector. In a typical run, the tested catalyst was heated to 500 °C with 30 standard cubic centimeters per minute (sccm) pure N_2, and then maintained for 15 min. Subsequently, industrial N_2 at 35 standard cubic feet per hour (SCFH) was applied to purge the air inside. After pretreatment, the sample was cooled down to 25 °C to collect the background spectrum. In addition, the background spectrum at the desired temperatures were obtained by heating up the equipment. In each experiment, initially the reaction system was purged with 30 sccm N_2 and held for 5 min, and then the N_2 or CH_4 gas flow was sent through a bubbler containing the liquid samples and maintained for 10 min. After the feedstock was adsorbed on the catalyst surface, the gas flow was transferred to a pure N_2 atmosphere by controlling the three-way valve for 15 min. In the end, the DRIFT spectrum was collected under Kubelka-Munk mode. The spectrum with 512 scans and 4 cm^{-1} resolution was recorded under the atmospheric pressure.

The Brunauer-Emmett-Teller (BET) specific surface areas of these fresh metal-loaded catalysts were measured via N_2 adsorption-desorption using a Quadrasorb SI Quantachrom apparatus. Before the measurements, all tested samples were put through a degassing procedure at 350 °C overnight. Subsequently, these catalysts were immersed in a liquid nitrogen bath at 77 K. The multipoint BET method was utilized to calculate the total specific surface area, and pore surface area and pore volume were determined by Barrett-Joyner-Halenda (BJH) method. The contribution of microspores (< 2 nm) to the total surface area was also calculated using t-plot method employed with DeBoer model.

The determination of Lewis/Brönsted acid sites was conducted using DRIFT with pyridine as the adsorbed probe. The spectra collection followed the detailed experimental procedures discussed above. The spectra obtained from pyridine adsorption were subtracted from the corresponding background spectra to acquire the peaks referring to acidic sites.

The NH_3-Tempeature Programmed Desorption (NH_3-TPD) measurement was carried out on an Altamira AMI-390 system.