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Catalytic aromatization of naphtha under methane environment: Effect of surface acidity and metal modification of HZSM-5

Jack Jarvis, Ashley Wong, Peng He, Qingyin Li, Hua Song*

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

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ABSTRACT

The reformation of naphtha to obtain valuable chemical intermediates such as BTX has attracted much attention. Here we report a novel catalytic process whereby a bimetallic heterogeneous catalyst in the form of Zn-Pt/HZSM-5 is applied to a flow reactor system to reform a complex naphtha feed under a methane environment. Different levels of acidity of the HZSM-5 support are tested with a superior performance witnessed using a SiO_2:Al_2O_3 ratio at 80. Further testing is conducted using Zn as a dehydrogenating component with improved performance witnessed when Zn is loaded to a certain degree. A metal promoter is then combined with Zn to compare the effect of different promoters with superior performance witnessed using Ga and Pt as promoters with Zn. BTX selectivity and BTX yield are reported as 86.44% and 34.22% respectively under the Zn-Pt/HZSM-5 catalyst. External site coverage improves performance for all bimetallic catalysts with the exception of Zn-Pt/HZSM-5, suggesting that Pt might not promote the migration of metal functions to the internal pores during synthesis. XRD spectra demonstrate that Pt addition results in a more intact crystal structure after reaction when compared to Zn alone·NH_3-TPD and DRIFT analyses show a reduced amount of strong acidic sites upon metal loading with an increase in the number of Lewis acid sites and reduced Brönsted sites. This change in acidity could be one of the reasons for an improved performance when Zn-Pt/HZSM-5 is employed. The effect of methane is also witnessed over Zn-Pt/HZSM-5 with improved selectivity, yield (BTX and liquid) and active metal dispersion when compared to a nitrogen environment, suggesting the possible incorporation of methane into the products, BTX in particular. Ultimately, the catalyst employed here opens an avenue for further research into the possible industrial application of naphtha aromatization to form valuable chemical products under methane environment.

1. Introduction

Naphtha fractions obtained from petroleum refinement contain an abundant mixture of hydrocarbons in the form of paraffins, naphthenes and aromatics in varying distributions [1], although usually in respective decreasing order of percent by weight. Unless converted, these fractions can be both detrimental to the environment and economically unviable for the industry, making them otherwise undesirable. During current reforming processes, lower carbon number components of naphtha feeds (≤ 6 carbon atoms) tend to crack further into lower chain hydrocarbons [2], making them unsuitable for increasing the octane number of gasoline feeds as per governmental regulations [3,4] as well obtaining desirable liquid yields. It is also important to reduce olefin content (although seen in small quantities in most naphtha mixtures) as these compounds can result in gum formation in combustion engines which can further result in less efficient combustion [5].

Naphtha reforming requires an element of hydrocracking to reduce the number of larger carbon number components and is also one of the reactions that requires hydrogen. One predominant method of acquiring hydrogen for hydrotreating is through the process of steam reforming natural gas (whose main component is methane) at high temperatures (700–900 °C) along with high amounts of CO_2 production [6]. We are therefore encouraged to find an effective and inexpensive method for obtaining hydrogen. A cheap, naturally occurring, and abundant alternative source to expensive hydrogen is methane, a notoriously difficult molecule to activate given its stable C—H bond strengths of 439 kJ mol^{-1}, a result of its symmetric geometry and electronic configuration [7,8]. Given this challenge, high temperatures are required, but this inhibits selectivity towards desired products. Therein lies the problem and a strong desire within the scientific community to activate methane at lower temperatures so that selectivity is maintained along with affordable economics. This has indeed been achieved through the use of bifunctional catalysts at low temperatures and the presence of co-reactants where an increase in

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

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liquid product is seen under a methane environment when compared to nitrogen [9].

Another important aspect of naphtha reforming is the ability to produce useful aromatic products such as benzene (currently the second largest volume petrochemical), toluene and xylenes (henceforth called BTX) [10–13]; not to mention hydrogen as a byproduct which is seeing increased interest due to its application in many hydro-consuming processes such as fuel cells and even its potential as a future energy carrier. Thus, the prospect of producing these highly valued products used in polymer and other petrochemical syntheses from otherwise undesirable feeds has been investigated thoroughly since its conception by Vladimir Haensel in the 1950's [14]. In fact, between 1949 and 2013 there were over 600 publications dedicated to the process of naphtha reforming with 50% of these being dedicated to catalyst formulation and performance analysis [15].

Thanks to the works of many researchers [16–18], the key reactions that take place during the formation of aromatics from paraffins and naphthene's have been elucidated as: dehydrocyclization, isomerization, dehydrogenation, hydrodealkylation and hydrocracking. With regards to catalyst formulations, H type HZSM-5 has proved to be a promising catalyst for cracking hydrocarbons within the desired naphtha-range through two mechanistic pathways. Protolytic cracking is the first and proceeds through the protonation of alkanes to provide carbenium ions which then collapse to give the final products [19]. This pathway occurs because of the Brönsted acid function of zeolites which is attained through aluminum substitution with silicon and a resulting proton for electronic neutrality as well as their Lewis acid function through extra-framework aluminum [20]. The second is through hydride transfer between a reactant and an adsorbed carbenium ion in which a smaller carbenium ion is then obtained through β-scission [20]. Ultimately, the HZSM-5 acid functions provide sites for isomerization as well as cracking, but further catalyst alterations are needed to provide the necessary tools for desirable reactions. Thus, a metal function can provide additional pathways that lead to the desired products. For example, noble metals are very successful at enabling hydrogenation and dehydrogenation reactions which are vital processes in the aromatization processes of naphtha feeds. However, coke formation is extensive when these metals are employed and so this issue needs to be addressed [21]. Zn and Ga metal addition to HZSM-5 has shown some of the best results for the aromatization of paraffins [21–26] as well as reduced coking, with evidence of reduced undesirable cracked products and more aromatics. In addition to this, a promoter can allow for more flexibility for attaining desired reaction pathways and as a result, higher selectivity's towards desirable products. The synergy of Zn with other metal promoters however, is not well established and so is investigated here with a range of promoters to compliment the limited work already conducted [27–29]. Catalyst modification can be taken a step further by investigation of the effect of specific functions; for example, Ding et al. [30] investigated the effect of external acid sites by silanation of Mo/HZSM-5 using 3-aminopropyl-triethoxylsilane (APTES). This synthetic method allowed for effective blocking of external acid sites with SiO_2, formed after calcination and removal of bulky organosilicon molecules. Whilst leaving the acid sites within the internal pores free to contribute to catalytic reactions.

Thus, this research aims to provide a clear presentation of the effects of support acidity, Zn loading and promoter on a naphtha feedstock during its aromatization when placed under a methane environment.

2. Experimental

2.1. Catalyst synthesis

MFI Zeolite support material in the cationic ammonium form with SiO_2/Al_2O_3 molar ratios of 23, 30, 50, 80 and 280 were obtained from Zeolyst International. All supports were converted to their hydrogen forms by calcining in air at 10 °C/min to 100 °C, holding for 8 h, ramping again at a rate of 10 °C/min to 300 °C, holding for 20 min and finally ramping at a rate of 10 °C/min until 550 °C was reached and holding for 3 h. These catalysts were then loaded with varying amounts of Zn; 1%, 3%, 5% and 7%, calculated on a mass basis. The loadings were conducted using the wetness impregnation method: The appropriate mass of crystalline Zn nitrate hexahydrate [$Zn(NO_3)_3{\cdot}6H_2O$], 99% purity, from Alfa Aesar was added to deionized water (15 cm^3) and thoroughly stirred, dried catalyst (5 g) was then added to the mixture with stirring maintained for 8 h at room temperature (RT) post addition of catalyst support. The catalysts were then calcined using the previously mentioned calcination parameters. Promoter metals (Ag, Ga, Ir, Pd, Pt and Ru) were added at the same time as the Zn salt and the aforementioned procedure undertaken. Promoter salts used were obtained from Sigma Aldrich: Silver nitrate ($\geq$99%), palladium(II) nitrate dihydrate (99.8%), tetraammineplatinum(II) nitrate (99.995%) and ruthenium(III) chloride hydrate (99.98%), and Alfa Aesar: Ga(III) nitrate hydrate (99.9%) and iridium(III) chloride (63.9% min).

When coating the promoted catalysts with silica, the technique used is that of Ding et al. [30] with some minor alterations: A solution of anhydrous ethanol (100 g) from Commercial Alcohols and (3-aminopropyl)triethyoxysilane (APTES) (1.5 g), (99%) from Sigma Aldrich was added to a 200 (cm^3) beaker and stirring applied. Promoter loaded catalyst (5 g) was then added and vigorous stirring maintained for 4 h. The gel-like mixture was subsequently stirred at 75 °C until the ethanol was mostly evaporated. The residuum (coated catalyst with small amounts of ethanol remaining) was then placed in an oven (80 °C) overnight to complete the evaporation. The resulting catalysts were then calcined as above when obtaining the H-type zeolites.

2.2. Experimental procedure

Reactions were carried out in a fixed bed microreactor with a 1.46 mm i.d. and a length of 54 cm. The fixed bed microreactor system-4100C was obtained from the Xi'an Sino-Green Hi-Tech Co., Ltd. Catalyst (1 g) was added to the reactor and packed with ceramic beads to achieve comparable catalyst volumes. The naphtha feedstock was pumped into the system at a rate of 0.055 cm^3/min to achieve a 3.3 $g{\cdot}h^{-1}$ WHSV for all reactions and joined by methane gas (100 Standard Cubic Centimeters per Minute, SCCM) or nitrogen gas (100 SCCM) depending on the desired reaction. The feedstocks then entered the pressurized (5 MPa) reactor at 400 °C to undergo conversion for 1 h. A condenser at −20 °C was then applied to the system to capture the resulting liquid products. The liquid products were analyzed by a Gas Chromatography-Mass Spectrometer provided by PerkinElmer (PerkinElmer GC Claus 680 and MS Clarus SQ 8 T) and equipped with a paraffin/olefin/naphthene/aromatic (PONA) column provided by Agilent (HP-PONA). The temperature program was as follows: Hold at 35 °C for 15 min, ramp up to 70 °C at a heating rate of 1.5 °C/min, and subsequently elevate to 150 °C at 3 °C/min and maintain for 30 min. The system was then ramped at a rate of 3 °C/min to 250 °C and held for 30 min. Gas products were fed to a 490 micro-GC from Agilent Technologies and analyzed. The system is made up of 4 channels and is equipped with thermal conductivity detectors capable of precisely analyzing hydrogen, oxygen, nitrogen, methane, and carbon monoxide in the first channel; carbon dioxide, acetylene, ethylene, and ethane in the second channel; and paraffins between propane and hexane as well as olefins between propylene and n-pentene in the third and fourth channels. The channels were equipped with a 10-m molecular sieve 5A column, 10-m PPU column, a 10-m alumina column and an 8-m CP-Sil 5 CB column respectively. argon is employed as the carrier gas for the first channel with helium for the remaining three.

2.3. Characterization techniques

A plethora of techniques need to be employed to characterize a small selection of the catalysts that were tested under the reaction