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Catalytic co-aromatization of ethanol and methane

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ABSTRACT

This study demonstrates the technical feasibility of simultaneously converting ethanol and methane into liquid hydrocarbons at mild reaction conditions (400 °C and 1 atm) over silver and/or zinc modified zeolite catalysts. After GC–MS analysis, it is worth noting that aromatics are the major compounds contained in the liquid product collected from the run when 1%Ag/ZSM-5, particularly after H_2 pretreatment, is charged. Compared to the performance exhibited from the run with pure HZSM-5 support engaged, Ag addition into the HZSM-5 framework favors aromatics formation, which might be closely associated with better Ag dispersion and more abundance of strong surface acidic sites where aromatization might take place while Zn loading exerts a detrimental effect on the production of aromatics but promotes the ether generation possibly through dehydration reaction. Referred to that from its N_2 counterpart, the increased aromatics formation of the collected liquid product when methane is present indicates that methane existence might facilitate ethanol aromatization. Moreover, combined with the increased carbon number in the formed aromatics from CH_4 run when H_2 run is referred and zero liquid formation from CH_4-alone test as well as more prominent endothermic feature of methane run and more importantly the notably increased ^{13}C signals in ^{13}C NMR spectra of the liquid product collected during ethanol conversion under $^{13}CH_4$ environment, all the observations suggest that methane might be activated nonoxidatively and converted into higher hydrocarbons, preferentially into aromatics if suitable catalyst is charged under the assistance of co-existing oxygenated hydrocarbon. The reported synergetic effect could potentially lead to the more economic utilization of abundant natural gas and cellulosic ethanol.

1. Introduction

Along with the economic growth and population increase, world energy demand has been increasing dramatically, especially over the last five decades (raised by 3.5 times since 1965 [1]). More importantly, more than 85% of the energy consumption still heavily relies on fossil fuels [2], the use of which poses many concerns including unsustainability and environmental pollution. Therefore, it is important to search for an energy carrier which is renewable and environmentally benign. Ethanol obtained from the fermentation of biomass seems desirable to serve as a green alternative due to its low toxicity, its ease of handling and its availability from many different renewable sources, ranging from cellulose to algae [3]. However, compared to its fossil fuel counterparts, the relative low volumetric energy density and high cost of ethanol still limit its wide implementation, thus leading to a strong need for its valorization.

Natural gas, including its recently largely discovered form (shale gas), is an abundant natural resource with ever increasing proved reserves (raised by more than 57% over the past 10 years) [1] and claimed as the cleanest energy carrier among fossil fuels because of its least particle matters generation and CO_2 emission (45% less than coal and 30% less than oil) when combusted. However, due to its chemical inertness and low volumetric energy density, natural gas is currently dominantly used for heating residential area and not valuable for transportation or chemical production applications. Therefore, natural gas is sold at much lower price (\$0.23/GGE: gasoline gallon equivalent) than gasoline (~\$2/GGE) even under the current ugly-looking oil economics. Intensive studies have been carried out over the past sixty years by many researchers regarding natural gas utilization and breakthrough has not yet been reported. Under such background, developing a technology which can effectively convert natural gas into valuable chemicals will definitely attract the attentions from both industry and academia.

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Ethanol conversion into higher hydrocarbons has been intensively studied by many researchers over the past several decades [4–6] as an emerging alternative for ethanol valorization in addition to hydrogen production through steam reforming [7–9], among which aromatics formation through ethanol aromatization has been widely investigated with high popularity over zeolite supported catalyst due to its importance in chemical industries [10–12]. On the other hand, the conversion of methane, the main component of natural gas, into high value added chemicals has also drawn more and more attentions, particularly in recent years due to the vast exploitation of shale gas [13–15].

The state-of-art progresses in various directions for methane activation and utilization have been thoroughly reviewed by Tang, et al. [16] and Horn, et al. [17], among which methane dehydroaromatization deserves the most research concentration. In addition to the reforming of methane in an oxidative way for hydrogen production which has been well established in industry, aromatics formation from methane following a nonoxidative route has the most commercial potential because the reactant's energy is well remained into the liquid product with an additional benefit of generating valuable hydrogen as byproduct. Nonetheless, the requirement of extreme reaction conditions (e.g., high reaction temperature of at least 700 °C) and more importantly severe coke formation resulting in fast catalyst deactivation has to be managed in an appropriate and economical way before this process receives enough industrial attentions, which is mainly because of the high energy barrier for methane activation (~440 kJ/mol required for breaking down the first C—H bond in methane molecule) and poor selectivity toward aromatics from a thermodynamic viewpoint [18].

Nevertheless, thanks should be given to the promising work pioneered by Choudhary, et al. [19] and evidenced by a series of following publications [20–23] which indicates that methane conversion will be significantly improved in the presence of higher hydrocarbon and even oxygenated hydrocarbon reactants, particularly unsaturated hydrocarbons at much lower temperature region (400–600 °C) and atmospheric pressure, leading to the formation of liquid product abundant in aromatics. Among the synergetic effects reported, it is worth noting that Choudhary, et al. studied the simultaneous conversion of methanol and methane for the liquid hydrocarbons formation, which sets the background of this work [23]. In this paper, compared to that of its N_2 counterpart, higher amount of $C_{\geq 10}$ aromatics is obviously observed when methane is present over Mo-Zn/ZSM-5 at 500 °C and 1 atm, which might be due to the methane participation into the methanol aromatization reaction and further evidenced by engaging ^{13}C isotopic labeling technique. Moreover, the promotion effect of methane on ethanol aromatization is also briefly mentioned in the same paper but over Ga/ZSM-5 at temperature as high as 625 °C, which drives the motivation of seeking a new catalyst system for triggering the same reaction but at much lower temperature.

According to thermodynamic calculations, as expected methane aromatization is highly unfavorable, especially at lower temperatures. For instance, the reaction $6CH_4\ (g) = C_6H_6\ (g) + 9H_2\ (g)$ has Gibbs free energy (Δ_rG) as high as 68.9 kcal/mol at 400 °C and 1 atm. Nevertheless, when ethanol is added as a co-reactant, Δ_rG of $2C_2H_6O\,(g) + 2CH_4\,(g) = C_6H_6\,(g) + 2H_2O\,(g) + 5H_2\,(g)$ is reduced significantly to −9.9 kcal/mol at the same reaction conditions, strongly suggesting the synergetic effect occurring between methane and ethanol and thermodynamic feasibility of their co-aromatization.

In this study, the technical feasibility of co-aromatization of ethanol and methane under mild conditions (400 °C and 1 atm) is experimentally demonstrated on Ag- and Zn-modified ZSM-5 zeolites. These catalysts were selected because they are reported to show promising performances toward biomass upgrading [24–26] and heavy oil upgrading [27] under methane environment in our previous studies. Significantly more aromatics formation was witnessed when 1%Ag/ZSM-5 was charged. This novel process will not only valorize ethanol produced from biomass fermentation and thus open a big market for its wider application, but also pave a more efficient, economical, and environmentally friendly way for methane utilization.

2. Experimental

2.1. Catalyst preparation

The ammonium ZSM-5 zeolite with Si/Al = 23 and specific surface area of 425 $m^2\ g^{-1}$ was purchased from Alfa Aesar and calcined at 600 °C for 5 h in air to attain the H-type ZSM-5 for further use. The 5%Zn-1%Ag/ZSM-5 was prepared by incipient wetness impregnation of H-ZSM-5 with $Zn(NO_3)_2{\cdot}6H_2O$ (99%, Alfa Aesar) and $AgNO_3$ (99.9+%, Alfa Aesar) solution, dried in the oven at 92 °C overnight, followed by being calcined at 600 °C for 3 h in ambient air. In a similar manner, 5%Zn/ZSM-5 and 1%Ag/ZSM-5 were also prepared for the experiments.

2.2. Sample characterization

The adsorption and desorption of nitrogen on each catalyst were measured using a Quadrasorb SI from Quantachrome Instruments. Samples were outgassed under a vacuum at 350 °C overnight and then brought to 77 K via immersion in a liquid nitrogen bath. Total surface area was calculated using multi-point Brunauer–Emmett–Teller (BET) analysis. Pore surface area and pore volume were calculated using Barrett–Joyner–Halenda (BJH) analysis. The t-plot method was used with the DeBoer model for the calculation of the statistical thickness to distinguish the contribution of micropores (<2 nm) to the total surface area.

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 15 min, ramp to 70 °C at 1.5 °C/min, rise to 150 °C at 3 °C/min and hold for 30 min, then ramp to 250 °C at 3 °C/min and hold for 2 min.

The water content of liquid sample produced from each run was determined using Karl Fischer (KF) titration (Metrohm 870 Titrino Plus) through averaging the results collected from at least three independent measurements.

The Transmission Electron Microscopy (TEM) spectra were acquired on a Philips Tecnai TF-20 TEM instrument operated at 200 kV. An X-ray analyzer for Energy-Dispersive X-ray (EDX) spectroscopy is incorporated into the instrument for elemental analysis under STEM mode for improving image contrast between C and Ag phases. The sample was first dispersed in ethanol and supported on honey carbon on a 200 mesh Cu grid before the TEM images were recorded.

The X-ray Diffraction (XRD) analysis of the catalysts were carried out on a Rigaku ULTIMA III X-ray diffractometer with Cu Kα irradiation at a voltage of 40 kV and current of 44 mA in the 2θ of 5–80°.

The ^{13}C NMR experiments were conducted at 9.4 T ($\nu_0(^{13}C) = 100.6$ MHz) on a BRUKER AVANCE III 400 spectrometer with a BBFO probe. ^{13}C NMR chemical shifts were referenced to $CDCl_3$ at 77.26 ppm. A spectral width of 26 kHz and a pulse delay of 2 s were used to acquire 17,000 scans per spectrum.

Acidity measurements were performed by NH_3 TPD using ~200 mg samples in an Altamira AMI-390 system. Ammonia was selected due to its simplicity, small molecular size, and ability to