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In-situ IR study for elucidating the adsorption cracking mechanism of toluene over calcined olivine catalyst

Youhua Zhang ^{a,b,*}^a College of Chemistry Engineering, Guangdong University of Petrochemical Technology, No.139 Guandu Second Road, Maoming, Guangdong 525000, China^b Department of Energy Chemical Engineering, School of Mining Technology, Liaoning Technical University, No.188 South Street of Longwan, Huludao, Liaoning 125105, China

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ABSTRACT

In order to improve the energy conversion efficiency of hydrogen production from biomass gasification and reduce environmental pollution, it is necessary to study the mechanism of tar catalytic cracking. In present work, in-situ infrared spectroscopy has been used to study the adsorption cracking of toluene on calcined olivine catalyst from room temperature to 500 °C. The experimental results indicate that there is no chemical adsorption of toluene on calcined olivine catalyst from room temperature to 200 °C. When the temperature is higher than about 300 °C, the toluene is chemically adsorbed on α -Fe₂O₃, which is the surface active site of the calcined olivine catalyst. The chemical adsorption occurs between the benzene ring and Fe³⁺, and it promotes the breakage of methyl from the benzene ring. With the increasing of reaction temperature, the delocalization large π bond in the benzene ring is destroyed by Fe³⁺, which makes the benzene ring easier to break into smaller products or intermediate products.

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Introduction

Hydrogen production technologies have attracted growing research attentions all over the world in recent years, due to the significantly increasing in hydrogen demand as an alternative energy source as well as a feedstock for the production of chemicals and food-oil industries [1]. Today, hydrogen is mainly produced from natural gas via steam methane reforming as well as coal gasification [2]. However, the production of hydrogen from these energy sources will aggravate

the depletion of fossil fuels and increase the emission of carbon dioxide to the atmosphere. The increase in the energetic demands of the world and the growing problems caused by the emissions of greenhouse effect gases force us to search for an alternative feedstock for hydrogen production. Biomass, as a renewable and carbon neutral resource, has attracted considerable attentions. Biomass gasification has been regarded as a key thermochemical route for hydrogen production [3,4]. Tar is one of the main obstacles of biomass gasification technology, which is mainly composed of

* Corresponding author. College of Chemistry Engineering, Guangdong University of Petrochemical Technology, No.139 Guandu Second Road, Maoming, Guangdong 525000, China

E-mail address: 280512356@qq.com.

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aromatic hydrocarbon [5]. These impurities could deactivate the downstream catalytic reforming catalyst, particularly Ni-based catalysts (by coking), so they must be removed by gas cleaning inside or downstream of the gasifier. Olivine and calcined dolomite have been widely tested and used as primary catalysts to reduce the content of tar in the product gas [6,7]. Olivine shows a slightly lower activity in tar reforming, but stronger abrasion resistance than dolomite. Therefore, more and more attentions have been paid to olivine catalysts in recent years.

Matthias Kuba et al. [8] investigated the mechanism of layer formation on olivine bed particles. The mechanism they proposed suggests that the interaction between wood biomass ash and olivine bed particles is based on a solid–solid substitution reaction, where Ca^{2+} is incorporated into the crystal structure. As a consequence, $\text{Fe}^{2+/3+}$ and Mg^{2+} ions are expelled as oxides. This substitution results in the formation of cracks in the particle layer due to a volume expansion in the crystal structure once Ca^{2+} is incorporated. Cui Quan et al. [9] studied the effects of iron loading over Fe/olivine catalyst on gas composition and carbon conversion. Results indicate that the Fe/olivine catalyst exhibits a good activity in steam reforming of bio-oil, and that the couple of $\text{Fe}^{2+/3+}/\text{Fe}^{2+}$ is sufficiently efficient for breaking of C–C, C–O, and C–H bonds. Lopamudra Devi et al. [10] and Jose Corella et al. [11] reported that the catalytic decomposition of biomass tars over dolomite and olivine. Lopamudra Devi's observation is that the conversion of all tar classes increase as the temperature was raised from 800 to 900 °C for both olivine and dolomite. At the temperature of 900 °C, the water-soluble heterocyclic compounds are completely converted, heavy PAHs was reduced by 48% with pure sand. Addition of 17 wt.% olivine to the sand leads to a 71% decrease of PAHs at 900 °C, whereas addition of 17 wt.% (pre-calcined) dolomite converted 90%. The results of Jose Corella show that dolomite is 1.40 times more active than olivine in biomass gasification. Continuous steam gasification of biomass is carried out in a fluidized bed reactor with the utilization of 10 wt% Fe/olivine catalyst by Sergio Rapagnà et al. [12]. What they have found is that when 10 wt% Fe/olivine is utilized in the gasifier, the gas yield increases on average by 40% and the hydrogen yield by 88%, and the 10 wt% Fe/olivine catalyst is fairly stable. Lopamudra Devi et al. [7] studied olivine catalyst characterization. It is observed that the calcination of olivine improves the performance of the catalyst due to severe segregation of iron at the surface of the olivine after calcination. Hans O.A. Fredriksson et al. [13] investigated catalyst dynamics of olivine as tar removal catalyst. The results of the study show that a large fraction of the Fe in the investigated material is present as free Fe-phases, which are sensitive to changes in the gas environment. After exposure to oxidizing gases, the free Fe phases are: Fe_2O_3 and Fe_3O_4 or MgFe_2O_4 . Upon exposure to reducing gases, the iron oxides are converted into Fe-0 and Fe_3C and formation of graphitic carbon is observed. Lopamudra Devi et al. [14] reported that the pretreatment of olivine to improve its activity. The experimental results show that the catalytic activity of olivine is greatly improved by 10 h of heating at 900 °C in the presence of air.

Although good progress has been made in many aspects of catalytic cracking tar over olivine catalyst, the reaction

mechanism including adsorbed state of toluene or reaction intermediate, has not been clarified yet. To elucidate the reaction mechanism of steam reforming of toluene, direct observation of adsorbed species on the catalyst by in-situ infrared spectroscopy is applied as an effective method [15–17]. In this study, we investigated the adsorption of toluene (model compound of biomass derived tar) and its pyrolysis step on olivine catalyst using an in-situ FT-IR method by temperature programmed adsorption.

Material and methods

Catalyst details

Olivine from Yichang City, Hubei Province, China was used in all experiments. A 4 h, 900 °C calcination of the material was performed before samples were sized to 75–180 μm range by mechanical treatments.

Catalyst characterizations

The calcined olivine catalysts used in the experiments were characterized using X-Ray Fluorescence (XRF), BET-surface, X-ray Diffraction (XRD) and Temperature Programmed Reduction (TPR) techniques as follows. XRF investigation was carried out on the Bruker RSR 3400X X ray fluorescence analyzer. The BET-surface was determined by means of N_2 chemisorption on Micromeritics ASAP-2020 equipment. A powder XRD measurements were conducted on a D/MAX 2550 VB/PC instrument using Cu K α radiation in the scanning angle range of 20–80° at 100 mA and 40 kV. TPR was performed with a sample amount of around 150 mg. The temperature is increased at a rate of 10 °C/min from 80 to 900 °C.

Experimental instrument

The infrared spectrometer is Tensor type 27 produced by German Bruker company. Its resolution is 16 cm^{-1} , in-situ tracking scanning number is 80, and wave number accuracy is better than 0.05 cm^{-1} . In situ infrared reaction chamber is produced by Tianjin Xianquan Instrument Co. Ltd. Its window material is CaF_2 , and operating temperature is from room temperature to 500 °C.

Experimental procedures

The calcined olivine powder, as described in 2.1, is pressed into a self supporting thin disk with a diameter of 13 mm and a thickness of about 0.1 mm by a powder compressing machine (The pressure is 3 Mp, and pressure holding time is 30 s), which is placed in the in-situ infrared reaction chamber. The vacuum pump in the in situ infrared reaction system was opened to vacuum for 45 min (The standard vacuum of the system is 5×10^{-5} mbar. The time required to reach the standard vacuum is ~40 min). In order to eliminate the influence of water vapor and other impurities on the infrared spectrum of olivine catalyst, the reaction chamber was heated from room temperature (~30 °C) to 500 °C at the rate of 10 °C/min and kept for 30 min at 500 °C. The samples were then

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