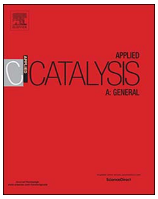
Applied Catalysis A, General 543 (2017) 51–60

Contents lists available at ScienceDirect

Applied Catalysis A, General

journal homepage: www.elsevier.com/locate/apcata



Research Paper

# Promotion on light olefins production through modulating the reaction pathways for *n*-pentane catalytic cracking over ZSM-5 based catalysts

Xu Hou, Yuan Qiu, Enxian Yuan, Fuqiang Li, Zaizheng Li, Shuang Ji, Zhenning Yang, Guozhu Liu, Xiangwen Zhang*

*Key Laboratory of Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Collaborative Innovation Center of Chemical Science and Engineering, Tianjin University, Tianjin 300072, PR China*

## ARTICLE INFO

*Keywords:*
*n*-Pentane
Light olefins
Protolytic cracking
Hydride transfer
Dehydrogenation cracking
Redox cracking

## ABSTRACT

Insights into reaction mechanism were vital to direct naphtha catalytic cracking process to produce light olefins. In order to reveal influences of reaction pathways modulation on light olefins production, Zr-ZSM-5, Ag-ZSM-5, and the regenerated HZSM-5 (ZSM-5(R2)) were prepared and employed in *n*-pentane catalytic cracking. It was found that light olefins yield obtained over Zr-ZSM-5, Ag-ZSM-5, and ZSM-5(R2) at 500 °C was 58%, 81%, and 113% higher than that over the parent HZSM-5 (12.0%), respectively. Promotion on light olefins production caused by Zr-incorporation can be attributed to the enhancement of hydride transfer reactions increasing the utilization of Brønsted acid sites and the catalytic activity accompanied with the proximate stability compared to the parent HZSM-5. Different from Zr-ZSM-5, Ag-ZSM-5 and ZSM-5(R2) respectively introduced dehydrogenation cracking and redox cracking to *n*-pentane catalytic cracking, which selectively promoted the formation of light olefins and significantly enhanced *n*-pentane protolytic cracking. However, both Ag-ZSM-5 and ZSM-5(R2) went through a rapid deactivation at 550 °C, which was probably due the selective enhancement of alkenes accelerating the side reactions to coke formation.

## 1. Introduction

Light olefins play a leading role in the petrochemical industry, and its derivatives are directly related to the development of plastics, rubber, textile, packaging materials, chemical machinery manufacturing, transportation, automobile manufacturing, building materials, etc., which make a huge difference on the social life [1,2]. The rigid demand for light olefins continues to grow promoting the progress of the world petrochemical market. Production of light olefins has become a key symbol to measure the economic development. Traditionally, naphtha thermal cracking process is the main source for light olefins; however, it suffers from the high energy consumption and $CO_2$ emission, the low light olefins yield and propylene/ethylene ratio, etc. Compared with thermal cracking, naphtha catalytic cracking process can make up the mentioned defects via the introduction of a high-efficiency catalyst [3–9]. Due to the unique structure and acidity, zeolites, especially ZSM-5, are promising to create a prospect for naphtha catalytic cracking process [10–15]. In the past decades, several generations of scientists have devoted themselves to the related studies hoping to complete the theoretical system, achieve the well-design catalyst, and promote the progress in the chemical industry [16–23].

Analysis and modulation of reaction pathways can provide guidelines for catalyst and process design to optimize light olefins technology. Huang et al. [24] found that in $C_3$—$C_7$ olefins transformation over high-silicon HZSM-5, the main reaction pathways gradually changed from monomolecular cracking to bimolecular cracking, and further to trimolecular cracking with molecular chain length decreasing from $C_7^{=}$ to $C_3^{=}$. Lin et al. [25,26] found that tailoring reaction temperature and acid strength significantly influenced the reaction pathways in 1-butene/1-pentene transformation over HZSM-5 that high temperature and strong acidity benefited monomolecular cracking, while low temperature and weak acid sites preferred dimerization cracking. Epelde et al. [27] found that K-incorporation (1 wt%) tailored HZSM-5 acid properties, and increased the selectivity to propylene in 1-butene transformation. Li et al. [28] found that Fe-incorporation recovered partial B acid sites of P/HZSM-5 catalyst, and created some L acid sites, which significantly increased feedstock conversion and the selectivity to ethylene, while decreased the selectivity to propylene in the coupling cracking of butene and pentene. Miyaji et al. [29] found that in pentene catalytic cracking, when the specific spatial volume of zeolite was close to the volume of pentyl cations, it benefited monomolecular cracking and selectively promoted the formation of ethylene

---

* Corresponding author.
*E-mail address:* zhangxiangwen@tju.edu.cn (X. Zhang).

http://dx.doi.org/10.1016/j.apcata.2017.06.013
Received 6 April 2017; Received in revised form 29 May 2017; Accepted 9 June 2017

and propylene; while, a wider spatial volume enhanced dimerization cracking, and led to the formation of butenes and hexanes. Bortnovsky et al. [30] found that compared to ferrierite, mordenite, ZSM-12, beta, etc., ZSM-5 and ZSM-11 exhibited a high and stable selectivity to light olefins in pentene catalytic cracking, and it can be attributed to their 10-MRP intersecting channels, which benefited the formation of oligomeric intermediates and simultaneously suppressed the formation of coke-like species.

The reaction network for alkanes catalytic cracking was different from that of alkenes, especially the bimolecular cracking route. In alkanes catalytic cracking, bimolecular cracking involved hydride transfer between reactant molecules and carbenium ions, and β-scission of the generated carbenium ions [21,31]. Lukyanov et al. [32] found that hydride transfer reactions played an important role in *n*-hexane cracking over HZSM-5 below 400 °C. Wielers et al. [33] defined the "cracking mechanism ratio (CMR)" to express the relative contributions of monomolecular and bimolecular cracking mechanisms in *n*-hexane catalytic cracking, and found that zeolites pore structure remarkably tailored the relative contributions of the two cracking mechanisms, e.g. decreasing zeolite pore dimensions suppressed bimolecular cracking. Corma et al. [34] proposed the "paraffin/olefin ratio (P/O)" to evaluate the contribution of hydride transfer in *n*-heptane catalytic cracking, and found that decreasing zeolite pore dimensions suppressed hydride transfer reactions. Wang et al. [35] found that reducing acid sites within the supercages of MCM-22 suppressed hydride transfer reactions and coke formation, and thus, promoted the selectivity to propylene and achieved a proximate stability comparable to HZSM-5. Williams et al. [36] found that compared to H-Y, the high activity of H-USY can be attributed to the enhancement of hydride transfer reaction; while, it also introduced the oligomeric cracking mechanism into the reaction network, accelerating coke formation and catalyst deactivation. It was found that Zr-incorporation over HZSM-5 can enhance hydride transfer reactions in *n*-pentane catalytic cracking [37], and promote light olefins yield in naphtha catalytic cracking [38]. Wang et al. [39] modified HZSM-5 with rare earth (RE = La, Ce, Pr, Nd, Sm, Eu or Gd) impregnation, and found that it greatly promoted the selectivity to light olefins, especially to propylene in butane catalytic cracking. Ce-incorporation gave the highest yield of total light olefins, and Nd-incorporation gave the highest yield of propylene at 600 °C. Lu et al. [40] found that a tiny Fe-loading over HZSM-5 greatly improved both the catalytic activity and the selectivity to light olefins, which was probably attributed to the acidic modification of catalyst or enhancement of dehydrogenation route caused by Fe-incorporation. Hu et al. [41] found that the introduction of $V_2O_5/Al_2O_3$ into the equilibrium ZSM-5 catalyst offered another reaction pathway for *n*-heptane conversion, and significantly improved the initial reaction rate and the selectivity to light olefins. Qiu et al. [42] pointed out that Ag sites generated by Ag-incorporation over HZSM-5 can initiate dehydrogenation cracking for *n*-dodecane conversion promoting C—H bond breaking. Thus, Ag-ZSM-5 catalysts greatly enhanced the dehydrogenation rate and the selectivity to light olefins in alkanes catalytic cracking [37,43].

It has been emphasized that in naphtha catalytic cracking, a certain portion of feedstock was inevitably converted into coke species, blocking zeolite pore openings and resulting in catalyst deactivation [44–46]. Usually, the spent catalysts have to go through the high-temperature treatment in air/oxygen flow promoting coke combustion and recovering catalytic activity [47]. Nakasaka et al. [48] pointed out that coke combustion led to the steep jump of temperature that remarkably affected the structure and acidity of zeolites. Al-majnouni et al. [49] found that the high-temperature treatment generated redox sites over HZSM-5, which can activate propane by the redox mechanism, and promoted C—H bonds breaking. Yun et al. [50] found that the high-temperature treated SSZ-13 selectively enhanced propane dehydrogenation, and proposed the redox cracking mechanism to explain the role of redox sites in propane conversion. It can be deduced that redox cracking initiated by the redox sites promoted the selectivity to hydrogen and alkenes in alkanes conversion [51].

Generally, modification of zeolites, e.g. element incorporation, high-temperature treatment, etc., can modulate the reaction pathways for alkanes catalytic cracking, and the probable roles can be described as followings: (1) Zr-incorporation over HZSM-5 enhanced the hydride transfer reactions between carbenium ions and reactant molecules, (2) Ag sites generated by Ag-incorporation initiated dehydrogenation cracking and promoted C—H bond breaking, (3) redox sites generated by the high-temperature treatment initiated redox cracking and promoted C—H bond breaking. In this paper, influences of reaction pathways modulation on alkanes catalytic cracking to produce light olefins were investigated using *n*-pentane as a model reactant. Zr-ZSM-5, Ag-ZSM-5, and the high temperature regenerated HZSM-5 were prepared and employed in *n*-pentane catalytic cracking. A particular attention has been paid to the measurement of catalytic activity and stability, as well as the product distribution, especially light olefins; meanwhile, element balance analysis and deactivation rate were also defined and calculated according to the experiment results. Finally, a straightforward scheme was proposed to express the potential relationship among catalysts, reaction pathways, and catalytic performance.

## 2. Experimental section

### 2.1. Reactant and catalysts

Reactants: *n*-Pentane (> 99 wt%), $Zr(NO_3)_4$ (> 98 wt%), and $AgNO_3$ (> 98 wt%) were purchased from Huadong Reagent Company (Tianjin, China), and used without further purification.

Parent HZSM-5: The commercial HZSM-5 with a $Si/Al_2$ ratio of 25 and an average particle size of 1 μm was purchased from Nankai University Catalyst Plant (Tianjin, China). It has been calcinated in the dry air at 550 °C for 6 h, and denoted as P-Z5.

Zr-ZSM-5 and Ag-ZSM-5: The metal-incorporated ZSM-5 catalysts were obtained by impregnating P-Z5 with $Zr(NO_3)_4$ and $AgNO_3$ aqueous solutions (0.1 mol $L^{-1}$), respectively. As a typical run, the parent HZSM-5 (2 g) powder was suspended in $Zr(NO_3)_4$ and $AgNO_3$ aqueous solutions (40 mL, 0.1 mol $L^{-1}$), respectively. Stirring speed was 600 rpm and maintained at room temperature for 0.5 h. And then, the samples were collected, dried at 120 °C for 4 h, and calcinated in the dry air at 550 °C for 4 h. The obtained metal-incorporated ZSM-5 catalysts were denoted as Zr-Z5 and Ag-Z5, respectively.

ZSM-5(R2): After the test run, the spent HZSM-5 went through the regeneration treatment that was carried out at 550 °C under air flow for 4 h promoting coke combustion. ZSM-5(R2) referred to the parent HZSM-5 that has experienced the test/regeneration process twice, and was denoted as Z5(R2).

### 2.2. Characterization

XRF (X-ray Fluorescence) spectrum was recorded by on a Bruker S4/Pioneer to determine the real percentage of Zr and Ag loading on ZSM-5 zeolites. XRD (X-ray diffraction) patterns were recorded with a Rigaku instrument in the range of 5–50° with a scan rate of 5° $min^{-1}$. TEM (Transmission Electron Microscopy) images were obtained on a Tecnai $G^2$F-20 transmission electron microscope with a field-emission gun operating at 200 kV. $NH_3$-TPD (Ammonia Temperature Programmed Desorption) profiles were measured on a Micromeritics 2910 (TPD/TPR) instrument. Sample (ca. 100 mg) was charged in a quartz tubular reactor, and pretreated at 550 °C under Ar flow for 1 h, and then cooled to 50 °C. Ammonia (20% $NH_3$ in He) with a flow rate of 30 mL $min^{-1}$ was introduced at 50 °C for 0.5 h. Then, He stream was fed in until a constant TCD signal obtained, and the physisorbed ammonia was removed by flowing He at 100 °C for 1 h. The chemically adsorbed ammonia was determined by raising temperature up to 650 °C with a heating rate of 10 °C $min^{-1}$. Py-IR (Pyridine Adsorbed Infrared) spectra