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Regular Article

Promoter effect of heteroatom substituted AlPO-11 molecular sieves in hydrocarbons cracking reaction

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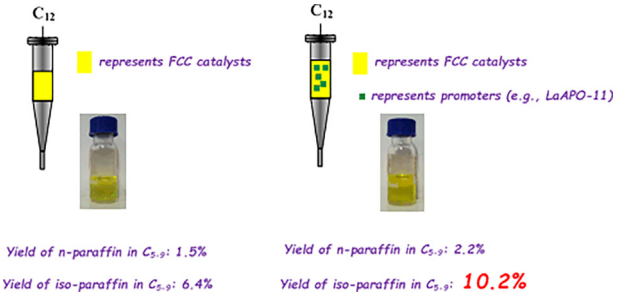
GRAPHICAL ABSTRACT



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ABSTRACT

It is important to develop new promoters of fluid catalytic cracking (FCC) catalyst to increase iso-paraffin yield and avoid the decrease of research octane number (RON) caused by olefin saturation in gasoline hydrofining. SAPO-11 and LaAPO-11 molecular sieves were used as promoters to FCC catalyst to increase gasoline RON and were tested in the cracking reaction of n-dodecane on FCC conditions. LaAPO-11 molecular sieve has less and weaker acidity than SAPO-11 molecular sieve. LaAPO-11's metallic sites polarize the C—H bonds to form carbenium ions for isomerization reaction and weak acid sites make less contributions to the cracking of iso-paraffin. LaAPO-11 promoter increases the yield of iso-paraffin (C_{5-9}) from 6.4% to 10.2%. Besides that, a high yield of arene (2.0%) is caused by the dehydrogenation activity of LaAPO-11 promoter. The new contributions of this paper are the synthesis of a hydrothermal stable LaAPO-11 molecular sieve with isomerization activity and proposing the reaction routes of iso-paraffin. These new contributions are important for developing more effective RON promoters of FCC catalyst.

1. Introduction

The rapid growing economy boosts consumption of energy and causes social issues. For example, vehicle industry increases the demand of gasoline (e.g., 9 millions of barrels per day in USA) [1] but results in combustion emissions to the atmosphere (e.g., SO_3

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from combustion of gasoline) [2]. Besides, air pollution diminishes the quality of life and attracts public's attention due to overwhelming news reports such as the damages to the cultural relics by acid rain [3] and triggered economic loss (e.g., 0.7–2.8% of GDP of USA per year) [4]. Hydrofining is required to remove sulfur compounds from blended gasoline. As the main component of blended gasoline in China, fluid catalytic cracking (FCC) gasoline has a high volume content of olefin (50–65%). Contradiction occurs between increasing gasoline purity by hydrodesulfurization and decreasing FCC gasoline's research octane number (RON) by olefin saturation [5]. Conventional ZSM-5 RON promoter increases RON by generating olefins, which decreases the yield of gasoline and cannot solve the contradiction [6,7]. Also, high olefin content causes excessive emission of nitric oxide (e.g., increasing olefins from 5% to 20% increases NO_x emissions by 6.5% in a fleet of 1989 vehicles) [8], which are toxic and harmful (e.g., causing photochemical smog and forest deterioration) [9]. Compared with increasing olefin, it is an ideal approach to increase the content of iso-paraffin, which is a high RON component.

FCC reaction is a complex system including competitive reactions including cracking, isomerization, hydrogen transfer, aromatization, and cyclization reactions. It is feasible to change product distribution by using promoters of FCC catalyst. Promoters can tune the conversion and selectivity of the main reaction end-products [10] by affecting adsorption properties of the reactants [11] and accessibility of reactants to active sites [12]. For example, aromatization and isomerization reactions are enhanced by using β and ZSM-5 promoters to produce arenes and isomers [13,14]. If a promoter possessing isomerization activity is added to FCC catalysts, it can increase isomerization in the FCC reaction. In our previous research, SAPO-11 molecular sieve promoter effectively increased RON. The pore structure (i.e., one-dimensional 10-membered-ring channel (0.39 nm × 0.64 nm)) was favorable to the isomerization reaction with a 5.0% increase of isohydrocarbon content in the cracking reaction of vacuum gas oil (VGO) [15]. It is also worth noting that rare earth ions can replace Al^{3+} and P^{5+} sites of AlPO-11 and rare earth ions substituted AlPO-11 molecular sieve can preserve its crystal structure at 800 °C for 4 h [16]. Such substitution may break through the limitation of low hydrothermal stability of metal substituted AlPO-11 molecular sieves on FCC conditions and shows potential to be a RON promoter [16]. However, no systematic study has been carried out to explain the role of heteroatoms substituted AlPO-11 molecular sieve in FCC unit.

The objective of this research is to develop and evaluate a novel promoter to increase RON (i.e., LaAPO-11 molecular sieve) and propose reaction routes of iso-paraffin production. This objective is important because LaAPO-11 is a feasible supplement to the design and development of novel promoters with di-functional properties (i.e., isomerization and dehydrogenation) to increase RON values of FCC gasoline.

2. Experimental section

2.1. Preparation and hydrothermal treatment of heteroatom substituted AlPO-11 promoters

Precursor gel was prepared by mixing phosphoric acid (85 wt%, analytically pure, XiRong Petrochemical Co., Ltd), pseudo-boehmite (technical grade, 70 wt% Al_2O_3, Yantai Henghui Petrochemical Co., Ltd), silica solution (technical grade, 30 wt% SiO_2, Qingdao Haiyang Petrochemical Co., Ltd) or lanthanum nitrate (≥99.5%, Sinopharm Chemical Reagent Corporation), template agent of di-propylamine (DPA, ≥99.5%, Sinopharm Chemical Reagent Corporation), and deionized water. Sample names (SAPO-m and LaAPO-n, m and n represent the molar ratios of SiO_2:Al_2O_3 and La_2O_3:Al_2O_3, respectively.) and molar ratios of the resulting gels are shown in Table 1. The solutions were dried to gel in a water bath of 80 °C followed by a drying at 100 °C for 12 h at atmospheric pressure to remove water. Grinded dry gel powders were put in a polyflon container and then placed into an autoclave. Deionized water (0.3 g water per gram dry gel powders) was added into the bottom of the autoclave. The final molecular sieves were obtained after crystallization at 200 °C for 24 h and atmospheric pressure washing with deionized water, drying (110 °C, 12 h) and then calcination (600 °C, 4 h).

The hydrothermal stability of the resulting molecular sieves was tested at 800 °C for 4 h at atmospheric pressure with a flow of deionized water at the rate of 1.0 g/min for 3–5 g samples. Samples were grinded into powders and put into quartz beakers that allow steam transmission through their bottoms.

2.2. Preparation of FCC catalysts (Y-30%) and hybrid catalysts

Catalysts were prepared as follows: ultra-stable Y molecular sieve (technical grade, Zibo Huaqing Co., LTD), alumina solution (technical grade, 30 wt% Al_2O_3, Qingdao Huicheng Pectechnology Co., LTD), and kaolin (technical grade, Weifang Zhengxuan Catalytic materials Co., LTD) were mixed with a mass ratio of 30%:30%:40%. In a typical preparation, 3.0 g Y molecular sieve, 4.0 g kaolin, and 27.4 g alumina solution were mixed in a three-neck flask at 80 °C for 4 h, dried at 110 °C for 12 h, and calcined at 700 °C for 2 h. The products are referred to as Y-30%. The hybrid catalysts are made by mixing Y-30% and promoters (10 wt% of Y-30%) by mechanical mixing method. The hybrid catalyst is named as Y/promoter. For example, Y/LaAPO-0.1 means LaAPO-0.1 is the promoter of hybrid catalysts.

2.3. Characterization

X-ray powder diffraction (XRD) patterns were collected using X, Pert PRO MPD diffractometer (PANalytical B.V. Netherlands) with Cu Kα radiation (λ = 0.15418), operating at 40 kV, 40 mA, and scanning speed of 10° min^{-1}. The crystal size of promoters was calculated by Sherrer equation. The morphologies of samples were observed with a scanning electron microscopy (SEM, S-4800, Japan HQ) at a magnification of 30–800,000 times with an acceleration voltage of 0.5–30 kV. Prior to measurement, samples were treated by gold spraying. The mean particle diameter was calculated based on the results of SEM images. At least 30 particles were selected to calculate the mean particle diameter (D). Particles were randomly selected to reflect their actual size. Samples were measured at three different directions. The finial size was the average of the three values.

$$D = d \pm SE$$

$$SE = \sqrt{\frac{\sum_1^N (x_i - d)^2}{N-1}}$$

d: mean value of selected particles
SE: standard error
N: number of selected particles
x_i: the particle size of selected particles ($i \leq N$)

Table 1
Sample names and synthesis gel composition (molar ratio).

Sample name	Composition of the synthesis gel
SAPO-0.2	1.0 P_2O_5:1.0 Al_2O_3:0.2 SiO_2:0.8 DPA:93 H_2O
SAPO-0.4	1.0 P_2O_5:1.0 Al_2O_3:0.4 SiO_2:0.8 DPA:93 H_2O
LaAPO-0.05	1.0 P_2O_5:1.0 Al_2O_3:0.05 La_2O_3:0.8 DPA:93 H_2O
LaAPO-0.1	1.0P_2O_5:1.0 Al_2O_3:0.1 La_2O_3:0.8 DPA:93 H_2O