Solid phosphoric acid catalyst for propene oligomerization: Effect of silicon phosphate composition

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Jichang Zhang, Yaru Yan, Qi Chu, Jie Feng *

Key Laboratory of Coal Science and Technology (Taiyuan University of Technology), Ministry of Education, Shanxi Province, Taiyuan 030024, PR China
Training Base of State Key Laboratory of Coal Science and Technology Jointly Constructed by Shanxi Province and Ministry of Science and Technology, Taiyuan 030024, PR China

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ABSTRACT

Solid phosphoric acid catalysts have been industrially used for propene oligomerization to improve the gasoline quality. However, solid phosphoric acid catalysts will lose their mechanical strength in the presence of water which is used to hydrolyze silicon phosphates to produce free phosphoric acids for maintaining the catalytic activity. In this case, to harmonize the catalyst lifetime and activity of solid phosphoric acid catalysts, the properties of silicon phosphate were investigated to achieve the maximum catalytic performance. A solid phosphoric acid catalyst was prepared with kieselguhr and concentrated phosphoric acid. Trace water was used to promote the release of active components from silicon phosphates during the reaction. Free phosphoric acid content, as a vital property of a solid phosphoric acid catalyst, was measured by ammonia temperature-programmed desorption. The crystal phase composition of silicon phosphates in a solid phosphoric acid catalyst was analyzed by X-ray diffraction. The catalytic performance was evaluated in a fixed bed under the conditions of 210 °C and 4 MPa. A solid phosphoric acid catalyst with relative content of 51% $Si_5O(PO_4)_6$ and 49% SiP_2O_7 showed the best performance in improving catalytic activity and lifetime, and the conversion of propene was above 99% for nearly 70 h.

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1. Introduction

In the process of high and low temperature Fischer–Tropsch synthesis, a light olefin mixture is obtained from the tail gas. It will cause more investment in fixed assets and consume much more energy if the mixture is separated. Not only can light olefin oligomerization avoid this disadvantage, but it can also produce high value-added products and increase the profit [1].

Since the early 1930s, solid phosphoric acid catalysts have been industrially used for light olefin oligomerization to produce polymer gasoline [2], which is an important step in the promotion of gasoline quality. The catalyst is usually produced by mixing kieselguhr with concentrated phosphoric acid followed by calcination at high temperature. The main crystalline phases of the catalyst are silicon phosphates: $Si_5O(PO_4)_6$ and SiP_2O_7. Water is necessary for the solid phosphoric acid catalyst to hydrolyze silicon phosphates to produce free phosphoric acid, a mixture of ortho-phosphoric acid and pyro-phosphoric acid [3], which are the active components in catalyzing olefin oligomerization. Previous studies have shown the relationship between free phosphoric acid and its catalytic performance [4]. With the decomposition of silicon phosphates, it is inevitable to result in the catalyst mudding and the decrease of crushing strength, which lead to a short lifetime of the solid

phosphoric acid catalyst. Therefore, the acidity and its catalytic performance are based on the fundamental silicon phosphate composition. Zhu [5] discussed the component variation in the preparation process especially the free phosphorus variation, Coetzee [6] focused on the variation of SiP_2O_7 in different preparation conditions because SiP_2O_7 is beneficial to mechanical strength and the lifetime of the catalyst. But both of them didn't supply the effect of component variation on catalytic performance. The analysis of the silicon phosphate composition helps to recognize the reason for the variation of the catalytic performance and guide the design and the optimization of the solid phosphoric acid catalyst.

The variation of silicon phosphate composition and its effect on catalytic performance were studied in this paper. With regard to oligomerization, propene from the light olefin mixtures is less active [7], so propene is selected as the feed material.

2. Experimental

2.1. Catalyst preparation and activation

The solid phosphoric acid catalyst was prepared by kneading dried kieselguhr (Shengzhou Huali Diatomite Products), concentrated phosphoric acid, which was prepared by phosphoric acid (Tianjin Kemiou Chemical Reagent, ≥85.0%) and phosphorus pentoxide (Tianjin Damao Chemical Reagent, ≥98.0%), and some bleaching clay as the

additive at a temperature of 170 °C followed by calcination under 400 °C for 4 h. The main components of the catalyst are silicon phosphates. Catalysts A–E with different silicon phosphate compositions were prepared and the preparation conditions are shown in Table 1.

Before catalytic performance tests, the solid phosphoric acid catalyst needs to be activated because the active components of the catalyst are free phosphoric acids spread over the catalyst hydrolyzed from silicon phosphates. We grind the calcined catalyst into 0.85–1.18 mm and treat them with water at a rate of $0.05 \ mol \ g_{cat}^{-1} \cdot h^{-1}$ carried by nitrogen under 200 °C for 3.5 h. The catalyst (about 4 mL) was then activated and ready for oligomerization reaction.

2.2. Catalytic performance test

The laboratory equipment for the catalytic tests was a fixed-bed reactor, containing about 3.5 g solid phosphoric acid catalysts. A simplified flow diagram of the reactor system is shown in Fig. 1. The propene was quantitatively fed to the reactor by a double plunger pump. The propene oligomerization catalyzed by free phosphoric acid was carried out at $8.7 \ h^{-1}$ LHSV (liquid hourly space velocity), 4.0 MPa and 210 °C. We took liquid and gas samples at regular times when the oligomerization reaction was stabilized. Both the liquid product condensed with ice-water and the exhaust gas were analyzed qualitatively by gas chromatography–mass spectrometry with DB-5 and quantitatively by gas chromatography with a HP-PONA, programmed temperature and FID detector. Propene conversion, as the catalytic activity measurement, and the product selectivity are calculated by the following equations.

$$Propene \ conversion = \frac{(liquid + gas_{total})_{out} - (gas_{propene})_{out}}{(liquid + gas_{total})_{out}} \times 100\%$$

$$C_i \ selectivity = \frac{C_i}{liquid_{out}} \times 100\%$$
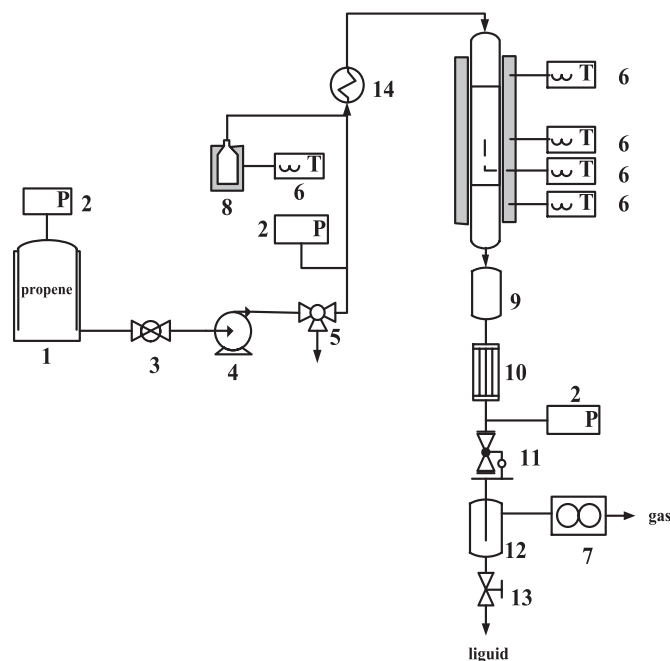
where $i = 6, 9, 12$.

2.3. Catalyst characterization

The crystal structure of the silicon phosphate was studied by X-ray diffraction (XRD) Rigaku RU 200 automated diffractometer with Cu Kα radiation. The X-ray source was a rotating anode operating at 40 kV and 30 mA with a copper target [8]. Data were collected between 5° and 65° in 2θ with a step of 4° per minute.

The amount of acid was detected by ammonia temperature-programmed desorption (NH_3-TPD) in a Micromeritics Autochem 2920 instrument. The tests were carried out in a flow apparatus with helium as carrier gas (50 cm^3/min). The samples were firstly flushed with helium at 350 °C for 1 h. Then the ammonia (15 vol.% NH_3) adsorption was pulsed at 40 °C. After a period of 2 h at this temperature, samples were heated to 900 °C at a heating rate of 10 °C/min. The ammonia desorption was recorded with the increase of temperature.

The crushing strength (force required to break a tablet by compression) was measured in weights of force using a Tablet Hardness Tester (Model ZQJ-500N, Dalian).
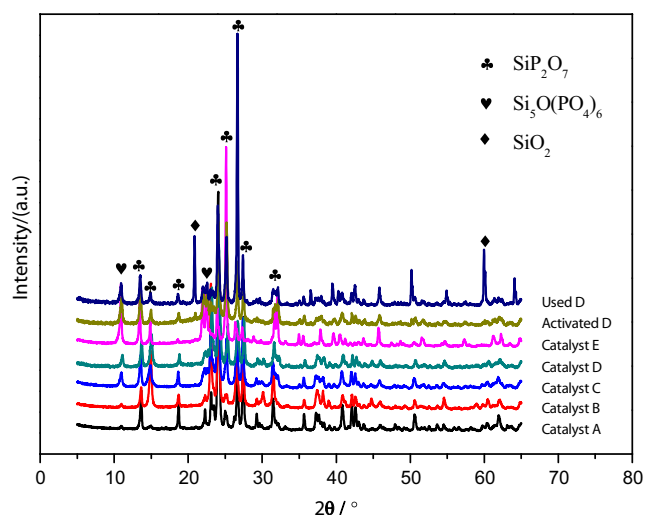

Fig. 1. Simplified flow diagram of lab-scale reactor system. 1—Propene tank, 2—pressure gage, 3—ball valve, 4—pump, 5—triple valve, 6—temperature controller, 7—flowmeter, 8—water evaporimeter, 9—buffer tank, 10—condenser, 11—back pressure valve, 12—back pressure valve, 13—stop valve, 14—preheater.

3. Results and discussion

3.1. Effect of compositions on activity

Phosphoric acid concentration and process temperature affected the silicon phosphate composition [6]. Changing the preparation parameters, solid phosphoric acid catalysts with different compositions were obtained. Fig. 2 shows different silicon phosphate compositions in catalysts.

After the same activation condition, solid phosphoric acid catalysts with active component-free phosphoric acids were evaluated in the fixed bed reactor. The results of propene conversion are shown in Table 2. According to the results of activity evaluation, catalyst D showed the highest activity in catalyzed propene oligomerization. Certain amounts of free phosphoric acids hydrolyzed from silicon

Table 1
Preparation conditions of different catalysts.

Catalyst	Concentration of phosphoric acid/%	Kneading temperature/°C	Calcination temperature/°C	The ratio of additive/%
A	104	190	400	1
B	104	170	450	1
C	115	170	400	1
D	104	170	400	1.5
E	85	180	315	0

Fig. 2. XRD spectra of catalysts with different silicon phosphate compositions.