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Preparation of MCM-41 supported phosphoric acid catalyst for thiophenic compounds alkylation in FCC gasoline

Rong Wang, Yonghong Li *

Key Laboratory for Green Chemical Technology, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, PR China

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ABSTRACT

The alkylation of thiophenic sulfur compounds with olefins in FCC gasoline followed by distillation of heavy compounds is a good alternative to classical desulfurization technologies. In this study, the preparation condition of MCM-41 supported phosphoric acid catalyst was optimized and the activity tests in real gasoline proved that the optimal catalyst was promising to be applied in the alkylation transfer process of thiophenic sulfurs compared to the HY zeolite previously studied. Moreover, characterization results obtained by XRD and NH_3-TPD revealed that the factors affecting on catalytic activity such as surface acid properties and crystallinity were greatly influenced by preparation conditions.

1. Introduction

New regulations aim to achieve very low sulfur concentration (less than 10 ppm by weight) that will be in full force in 2011. However, fluid catalytic cracking (FCC) gasoline represents almost 40% of the total gasoline pool and it is the major sulfur contributor to the environment, with up to 85–95%. Consequently, many approaches to deep desulfurization for ultra-clean gasoline have been proposed [1]. Olefinic alkylation of thiophenic sulfur (OATS) process as one of these approaches can be handled under relatively mild conditions with a minimal loss of octane number and without any hydrogen consumption, it can be seen as a good alternative to the conventional catalytic hydrodesulfurization process [2,3].

Many publications have proposed different catalysts to catalyze the alkylation reaction of thiophenic sulfurs with olefins, such as zeolites (Hβ, HY, USY etc.) [4–7] and supported heterogeneous acids [8,9]. However, most of them were carried out in a simple simulation system which could not fully represent the complex real gasoline. Furthermore, the catalyst life was greatly reduced by products generated by side reactions (olefins polymerization or aromatics alkylation) in OATS process. Therefore, it is essential to evaluate the catalyst reactivity in real gasoline and choose carefully the catalyst nature to limit the secondary reactions and improve the catalytic stability.

A solid phosphoric acid (SPA) catalyst has been used industrially for polymer gasoline through the oligomerization of light olefins, owing to its higher acid strength, thermal stability and environmentally benign properties [10,11]. Considering that olefins polymerization and thiophene alkylation are both acid catalyzed reactions. It seems to be potential to utilize it as the acidic catalyst in OATS process by improving preparation methods. Virginie et al. [12] synthesized a Grace Davison silica (specific surface area 320 m^2/g) supported phosphoric acid with a loading of 11 wt.% (SPA-11) to evaluate its catalytic properties in the alkylation of 3-methylthiophene with 2-methyl-2-butene. SPA-11 appeared to be less active than USY zeolite but better selective towards monoalkylated products to reduce the olefins consumption.

In this work, we selected a purely siliceous MCM-41 zeolite as the support of SPA catalyst in view of its enormous specific surface area (954 m^2/g), and aimed to obtain a MCM-41 supported phosphoric acid catalyst (SPAM), with the maximum catalytic activity for thiophene and its derivatives alkylation in FCC gasoline, by optimizing preparation conditions. And the optimal SPAM was compared with the previously studied HY zeolite by designed activity tests. Additionally, the active structures of SPAM under different conditions were studied by characterizations to study the effect of preparation on reactivity. And the relationship between the active structures and reactivity was also investigated, for it was beneficial for the further improvement and industrial application of SPAM in catalytic distillation process [13].

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* Corresponding author. Tel.: +86 22 27406795; fax: +86 22 27403389.
E-mail address: yhli@tju.edu.cn (Y. Li).

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2. Experimental

2.1. Catalysts and feedstock

The SPAM was prepared by impregnating the MCM-41 silica zeolite made by ourselves [14] (specific surface area 954 m^2/g and mean pore diameter 3.54 nm) with a mixture of H_3PO_4 and $H_4P_2O_7$ in an appropriate proportion. After impregnated at 353 K for 18 h, the admixture was dried at 473 K until it could be crushed into particles between 20 and 60 mesh. Finally, the catalyst used in this experiment was obtained by roasting the particles at a setting temperature for 4 h. HY zeolite (Si/Al = 8) was obtained by Catalyst Company of Nankai University and it needed to be pretreated at 823 K for 5 h. The Properties and fraction ranges of FCC gasoline used in the experiments were listed in Table 1.

2.2. Evaluation of the catalyst

The activity test was carried out in a 100 mL stirred batch reactor. The reactor was charged with 4.0 g fresh catalyst and 80 mL fresh FCC gasoline in each test. Time zero was taken arbitrarily when the optimum reaction temperature was reached and the system pressure was changed with temperature. The stirring speed was keeping at 400 rpm in reaction process. After 1 h the product was obtained and analyzed to evaluate the catalyst activity in the alkylation reaction of sulfur compounds. It should be noted that the experiment results had revealed the optimal activity temperatures of SPAM and HY in this alkylation reaction were 423 K and 393 K, respectively.

Analyses were performed on a FULI9790 gas chromatograph (produced in Zhejiang of China) that was equipped with two detectors (FID, Column OV-101: 30 m × 0.25 mm × 0.50 μm; FPD, Column OV-101: 60 m × 0.25 mm × 0.50 μm). Meanwhile, different sulfur species in samples were identified by a Hewlett–Packard model HP5975 gas chromatograph equipped with a capillary column (HP5-MS, 30 m × 0.25 mm × 0.25 μm) and a FID detector, which was coupled to a mass spectrometer (series 6890), GC–MS. The analysis conditions of GC and GC–MS were both programmed from 308 to 533 K by heating at a rate of 5 K/min, and the initial and final temperatures were hold for 10 min, respectively.

2.3. Characterization of the catalyst

The ratio of silicon ortho- to pyrophosphate and the crystallinity were determined by X-ray diffraction (XRD) analysis utilizing a Rigaku D2500 equipped with a monochromator of Cu Kα. radiation (λ = 0.154056 nm).

The surface acidity was investigated by NH_3-TPD (temperature-programmed desorption). The sample was prepared at 573 K for 1 h in flowing argon. After that the sample was cooled to 323 K and saturated with ammonia. Then the program was carried out from 323 to 1073 K at a rate of 10 K/min. The desorbed ammonia was monitored continuously with a gas chromatograph equipped with a TCD detector. In this work, the amount of total surface acid was expressed by the molar quantity of NH_3 adsorbed on per gram of the catalyst (mmolNH_3/gcat), though the corresponding relation of desorption peak areas between the sample and 1 mL NH_3.

Table 1
Properties and fraction range of FCC gasoline in the experiments.

Properties	Datum
The concentration of sulfurs (mg L^{-1})	288.99
The constitutors of hydrocarbons (w) (%)	
Aromatics	15.3
Olefins	37.4
Saturated hydrocarbons	47.3
Distillation (K)	
Initial boiling point	307
50 vol.%	357
90 vol.%	428
Final boiling point	453

The nitrogen adsorption isotherms were measured on ASAP 2010 Micromeritics equipment after preliminary treatment of samples under vacuum at 423 K for 15 h. Specific surface areas were calculated according to the BET equation. Pore size distribution was determined from the isotherm desorption branch by the BJH formula.

2.4. Determination method of pH value in the gasoline sample

The pH value of gasoline sample was measured by a digital pH meter of pHS-25 to determine whether there were free acids lixiviated from the acidic catalyst in the organic liquid phase. Specific procedures were as follows: a certain volume of gasoline sample was taken by adding the same volume of deionized water, then the mixture was put aside for layering after sufficiently stirring, finally the water was extracted to determine its pH value with the meter. The pH valve of the water was considered to be that of the above gasoline sample.

3. Results and discussion

3.1. The distribution of sulfur compounds before and after catalyzed by SPAM

As shown in Fig. 1, the major sulfurs in FCC gasoline are thiophene (T), 2-methylthiophene (2MT), 3-methylthiophene (3MT), and small amount of tetrahydrothiophene (THT), C_2- and C_3-thiophenes. For the alkylation reaction will redistribute the sulfur compounds in gasoline fraction. Fig. 1 displays the distribution of thiophenic compounds after the activity test, revealing that most of sulfur compounds in the feed were transformed into much heavier formulation, except C_3-T.

Moreover, the boiling point of 2,3,5-trimethylthiophene (C_3-T) is very close to the final boiling point of the gasoline used in experiments (453 K), the molecular sulfur compound which is heavier than C_3-T can be removed from gasoline fraction by distillation. Thus the efficiency for the catalytic alkylation would be calculated by the amount of sulfur compounds converted to the heavier than C_3-T in this work. The chromatograms in Fig. 1 indicate that the

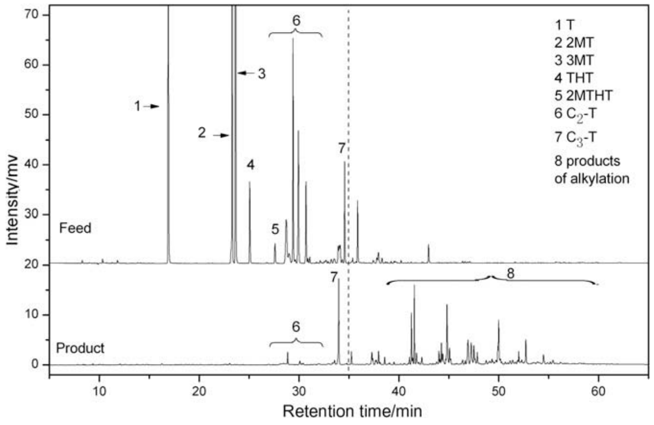

Fig. 1. Distribution of sulfur compounds in gasoline before and after catalyzed by SPAM under the optimal preparation conditions.