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Characterization of coke precursor deposited on the surface of heteropoly acid catalyst in alkylation

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Abstract

The molecular structure of coke precursors deposited on the surface of aged heteropoly acid catalysts in alkylation is determined by various analysis methods, such as IR, NMR, GC–MS, and GC. The physicochemical and surface properties of coke precursor are characterized by BET adsorption, carbon analysis and TGA. It is found that the coke precursors deposited on the aged catalysts are mainly made up of long-chain alkanes, C_{13}, C_{17}, C_{21} and some polynucleo-aromatic hydrocarbons. The coke precursors do not block the pores of the catalysts, but only cover the acid sites of heteropoly acid catalysts, and result in the decrease of acidic strength. It causes the selectivity of the catalysts in alkylation to decline. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Coke precursor; Characterization; Alkylation catalyst

1. Introduction

Alkylation of isobutane with butene is a critical process in the worldwide refining industry [1–3]. The alkylate produced from the process is recognized as a valuable gasoline blending component because of its high octane, low Reid vapor pressure (RVP), and no aromatics or olefins. The liquid acids, concentrated sulfuric acid or hydrofluoric acid, are successfully used as the catalysts in the process for more than half a century. However, liquid acids bring a series of environmental impacts and safety concerns [1–3]. A lot of efforts have been directed to develop solid acid alkylation catalysts for the substitution of the liquid acid [4–9]. In our laboratory, heteropoly acids with superacid characteristics are used as the solid acid catalysts in the alkylation of isobutane with butene [10–16]. A lifetime test of the catalyst, a supported heteropoly acid, in the alkylation under supercritical reaction conditions (T, 137 °C; P, 4.5 MPa; $iC_4/C_4^=$, 20; WHSV, 2.50 l/hr) had been carried out for 1400 h. The activity of the catalysts (conversion of $C_4^=$) remains at 100%, but the octane number (RON and MON) of alkylate decreases about one unit at the end of test. It is believed that the pores or the acid sites on the surface of catalysts are blocked or covered by the deposited coke precursors during the alkylation.

The critical challenge for the substitution of solid acid catalysts for liquid acid, sulfuric acid and hydrofluoric acid, in alkylation is the deactivation of catalysts due to coke [2]. What is the molecular structure of coke precursors deposited on the surface of solid acid alkylation catalysts? What is the physicochemical characterization of coke precursors? Therefore, understanding and answering these questions are becoming more important and urgent for looking for regeneration approaches of the aged or deactivated solid acid alkylation catalysts. The characterization of coke precursor deposited on zeolite catalysts in alkylation has been shown by Guisnet and coworkers

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[17], Weitkamp and Traa [18], and Fan et al. [19]. The purpose of the work is to characterize the coke precursor deposited on supported heteropoly acid catalysts in supercritical alkylation.

2. Experimental

2.1. Preparation of coke precursors deposited on the aged catalyst

The supported heteropoly acid ($H_3PW_{12}O_{40}$, PW_{12}) alkylation catalysts are prepared by impregnation of commercial silicon gel with an aqueous solution PW_{12}, followed by the evaporation until dried samples were obtained. The PW_{12} content for supported catalyst is about 20 wt.%. The catalyst is a solid acid catalyst with superacid characteristics ($H_0 < -13.16$) [15]. The alkylation of isobutane with butene under supercritical reaction conditions was carried out for 1400 h in a continuous fixed-bed reaction system with accurately controlled pressure, temperature and WHSV reaction parameters [16].

The aged catalysts were dissolved in the 40% hydrofluoric acid solution, and then CH_2Cl_2 was added as an extraction solvent, stirred for 25 min at room temperature. The aqueous phase was separated when organic phase and aqueous phase in the solution was stratified. Aqueous phase was extracted with CH_2Cl_2 solvent several times, and the extracted organic phase including the coke precursors and solvent was blended and concentrated.

2.2. Approaches of analysis

The molecular structure of coke precursors in the samples was analyzed by means of IR, ^{1}H-NMR, GC, GC–MS, and physicochemical characterization of aged catalyst was characterized by SEM, BET, carbon analysis and TGA.

3. Results and discussion

3.1. Physicochemical and surface properties of coke precursors

The content and ratio of C/H of coke precursors deposited on the surface of the aged catalysts are obtained by the measurement of TGA and the carbon analyzer respectively. Results include the following.

i. Content of the coke precursors on the surface of the catalysts is 8.11 wt.%
ii. The mole ratio of carbon to hydrogen in the coke precursor equals 0.43 (weight content of C: 6.79 wt.%; H: 1.31 wt.%)

Table 1
C/H mole ratio of hydrocarbons

	Alkene	Alkane	Cyclo-alkane	Benzene	Fuse-ring aromatics
C/H	0.5	<0.5	0.5	1.0	>1.0

Table 1 shows the C/H mole ratio of hydrocarbons obtained by the calculation of molecule formulate. The C/H value gained with the analysis of carbon and hydrogen elements is compared with calculation one in Table 1. It is clear that the C/H mole ratio of the coke precursor obtained by the analysis of elements is less than 0.5. It indicates that the coke precursors deposited on the surface of heteropoly acid alkylation catalyst may be mainly made up of alkanes.

The characterization of surface properties of solid acid alkylation catalysts is analyzed by the BET method. The results of surface area, pore volume, pore diameter of fresh and aged alkylation catalysts are listed in Table 2.

Comparing the fresh and aged catalyst samples, the surface area, pore volume and pore diameter are almost the same. It indicates that the coke precursor deposited on the surface of the aged catalyst does not block the pores of the catalyst support, but only cover the acid sites during the alkylation. When acid sites of the catalyst are covered with the coke precursor, its superacid properties will be changed. It shows that the catalyst is aged, and octane number of alkylate decreases during the alkylation.

Table 2
Surface properties of the catalysts

Catalyst	Surface area (m^2/g)	Pore volume (ml/g)	Pore diameter (Å)
C-1[a]	286	0.60	70
C-2[b]	281	0.59	66

[a] C-1, fresh catalyst.

[b] C-2, aged catalyst after the test of 1400 h life-time.

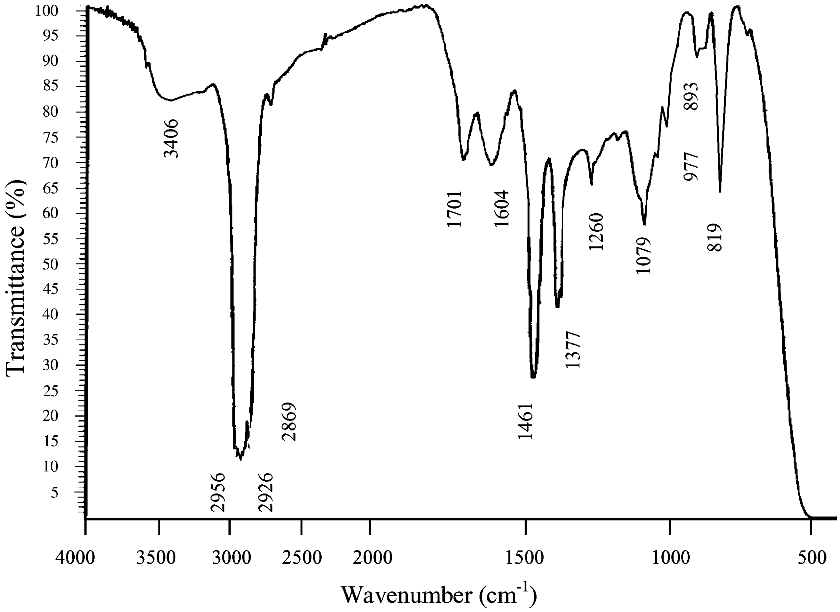


Fig. 1. IR Spectrum of the coke precursors.

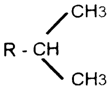
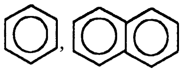
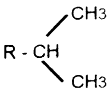
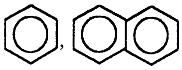
3.2. Molecular structure of coke precursors

3.2.1. Infrared spectroscopy characterization

The IR spectroscopy of the coke precursors is shown in Fig. 1. The wave numbers, type of vibration and possible organic structures are listed in Table 3.

According to the result of IR spectroscopy, the molecular structure of coke precursor may be speculated roughly. The coke precursors are mainly made up of long-chain alkanes and polynucleo-aromatic hydrocarbons. The adsorption peaks of IR, which stand for the aromatic hydrocarbons, are much weaker than

Table 3
Possible molecular structure of the coke precursors

Wave numbers (cm^{-1})	Type of vibration (v)	Organic structure
2926	CH_2 asymmetrical stretching (v_{as})	–$(CH_2)_n$–
2956	CH_3 asymmetrical stretching (v_{as})	
2869	CH_3 symmetrical stretching (v_s)	C–CH_3, 
1701, 1604	Frame vibration of benzene	
1260	CH_2 out of plane blending	–$(CH_2)_n$–
1461, 1377	CH_3 asymmetrical blending, CH_3 symmetrical blending	C–CH_3, 
893, 819	Out of plane blending, for C–H of benzene	

the peaks for the long-chain alkanes. Therefore, there is only a small amount of aromatic hydrocarbons in the coke precursor.

3.2.2. GC analysis

The samples of the coke precursors are analyzed by HP-5890 gas chromatography with 50 m ov-1 capillary column. The retention time of the main GC peak, which stands for components of the coke precursor, compares with one of the standard samples. It is clear that the coke precursors are mainly long-chain alkanes with carbon number greater than 13. There are also some weak adsorption peaks representing unknown substances.

3.2.3. GC–MS characterization

Fig. 2. shows the GC spectrograph of coke precursors in the GC–MS analysis. There are mainly four peaks. The MS spectra of different peaks in GC–MS analysis are indicated in Fig. 3. It is well known that the MS analysis is a powerful tool for identification of organic compounds. According to the result of GC–MS analysis, the coke precursors deposited on the catalyst may be identified roughly. There are mainly four constitutions in the sample of coke precursor. They are C_{13} (2,5,6-trimethyl decane), C_{19} (2,6-dimethyl heptadecane), C_{21} (2,6,10,14-tetramethyl heptadecane), dodecamethyl cyclohexasiloxane, respectively. Why do those alkanes with the odd number are formed during the alkylation, and deposited on the surface of superacid catalyst under the condition of the super critical reaction, not C_{12}, $C_{18}\ldots$ with the even number? This is an interesting and amazing result. Complementary work is needed to solve the mystery.

When the aged catalysts were dissolved in the 37% hydrofluoric acid solution, SiO_2 support will react with hydrofluoric acid, and dodecamethyl cyclohexasiloxane is found in the analysis of GC, GC–MS and NMR. When the aged catalysts were extracted with CH_2Cl_2 solvent several times, not dissolved in hydrofluoric acid, no siloxanes were found with the measurements of GC–MS, NMR and GC. It indicates that the siloxanes are formed during preparing the sample of the coke precursor with hydrofluoric acid solvent.

3.2.4. NMR characterization

The NMR spectroscopy of coke precursor sample is indicated in Fig. 4, and the chemical shifts of NMR peaks and corresponding structure of organic molecules are listed in Table 4.

According to the result of NMR analysis, the NMR peak with about chemical shift 1.0 ppm stands for the long-chain alkanes, and the chemical shift of NMR peak expressed for the aromatic hydrocarbons is about 7.6 ppm. It is obvious that the coke precursors are

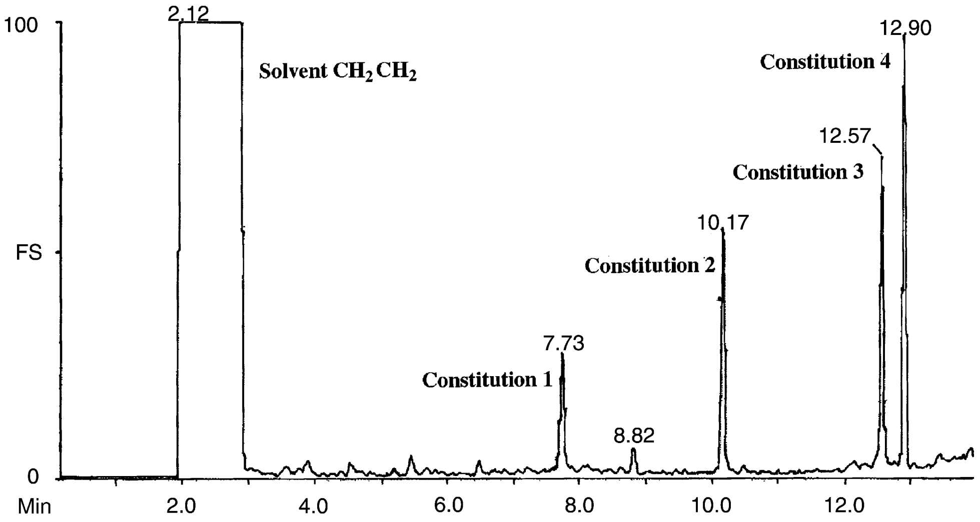
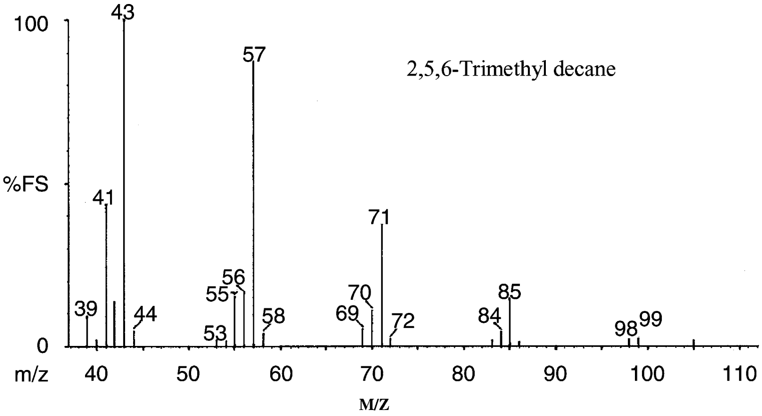
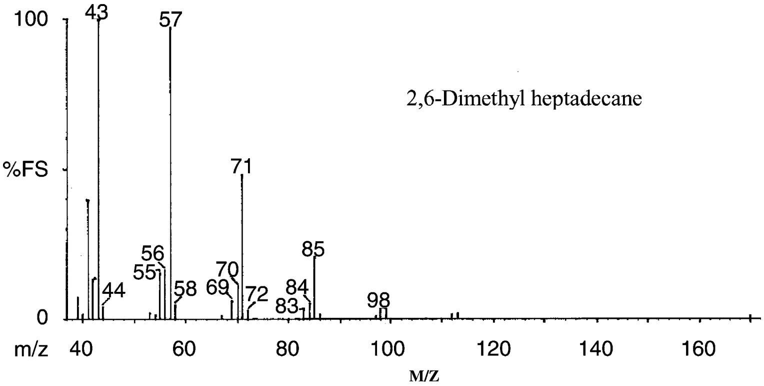


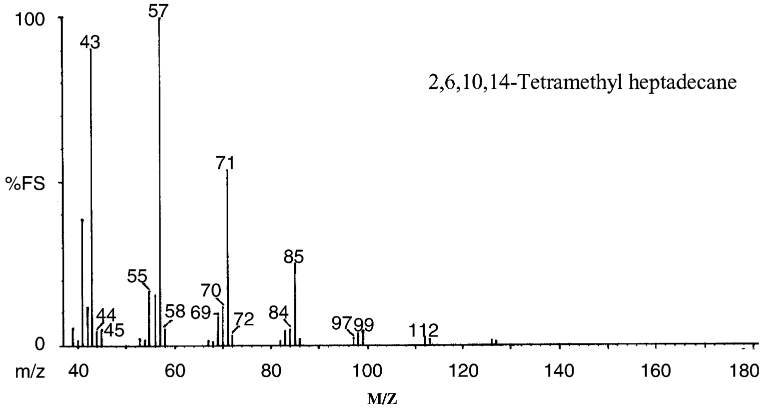
Fig. 2. GC profile of the coke precursor in GC–MS analysis.



a. Constitution 1 (7.73)

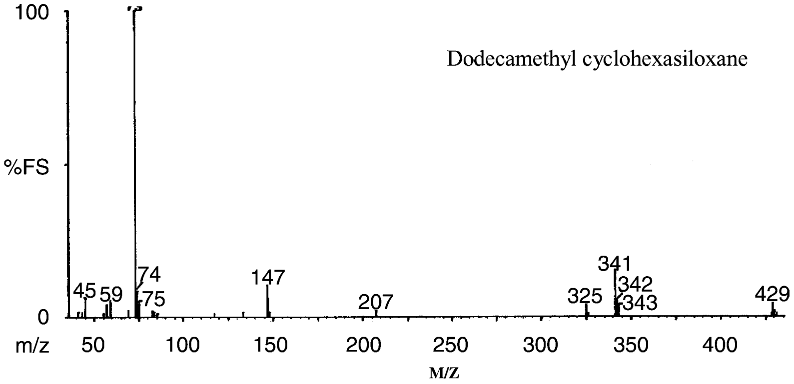


b. Constitution 2 (10.17)



c. Constitution 3 (12.57)

Fig. 3. Mass spectra of the coke precursors.



d. Constitution 4 (12.97)

Fig. 3. (*Continued*).

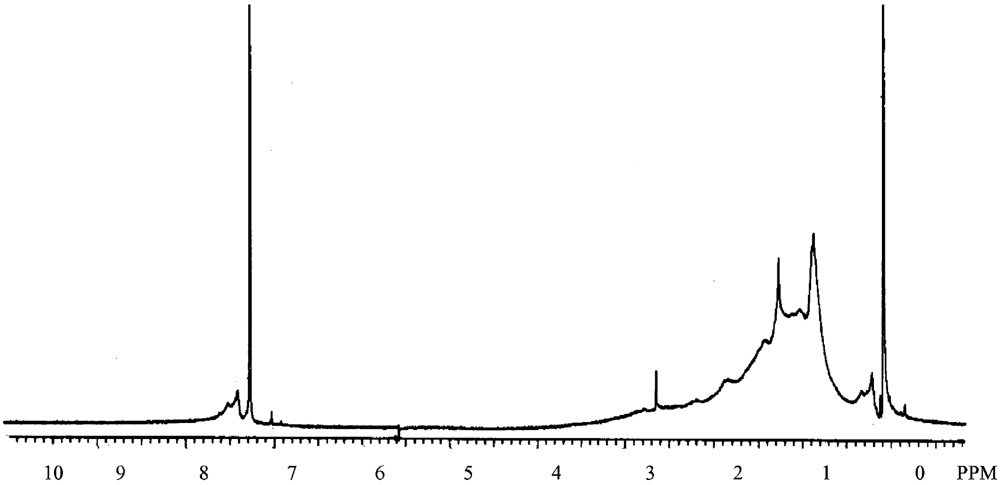
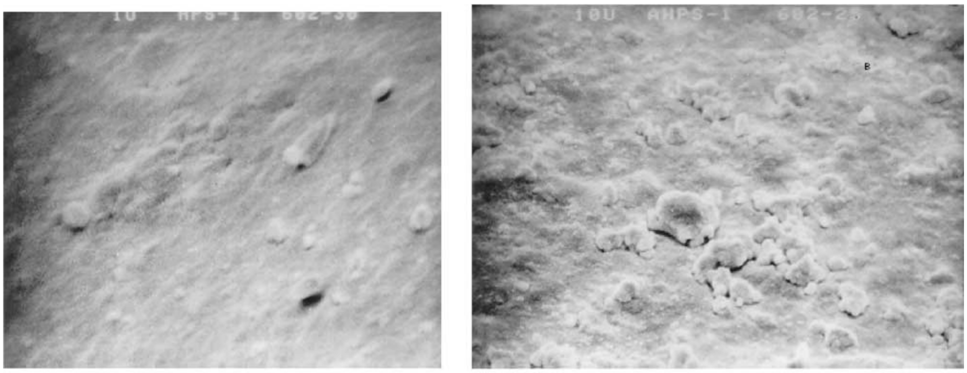


Fig. 4. NMR spectrum of the coke precursors.



a. b.

Fig. 5. Surface appearance of the catalysts: a, fresh catalyst; b, aged catalyst

Table 4
The corresponding molecular structure to the chemical shift

Chemical shift (PPM)	Molecular structure
0.1–0.4	Cyclohexasiloxane
0.8–1.2	CH_3–R
7.5–7.7	Ar–H

made up of long-chain alkanes with carbon number greater than 10 and aromatic hydrocarbons.

3.3. Surface appearance

The surface appearance of the catalysts determined by SEM is shown in Fig. 5. There is no conspicuous difference between the surface of fresh catalyst and aged catalyst. This is another evidence that the coke precursor on the surface of aged catalyst does not block the pores, but only cover the acid sites of heteropoly acid catalysts.

4. Conclusions

1. According to the characterization results of IR, NMR, GC and GC–MS, the coke precursors deposited on the surface of the supported heteropoly acid alkylation catalysts are mainly made up of long-chain saturated hydrocarbons and a small amount of polynucleo-aromatics.
2. The coke precursors deposited on the surface of the heteropoly acid catalysts do not block the pores of the catalysts, but only cover the acid sites of catalysts, and result in the decrease of strength of acid sites. It causes the selectivity of the catalysts in alkylation to decline.
3. The coke precursors composed of long-chain saturated hydrocarbons indicate that the supported heteropoly acid alkylation catalysts have very strong ability for hydrogen transfer between large carbonium $C_n{}^+$ and isobutane. This is because of the high acidic strength of the catalysts.

Acknowledgements

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