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Editor's choice paper

The effective silylation of external surface on H-ZSM5 with cyclic siloxane for the catalytic cracking of naphtha

S. Akiyama[a,b], H. Mochizuki[b], H. Yamazaki[b], T. Yokoi[b], T. Tatsumi[c], J.N. Kondo[b,*]

[a] Mitsui Chemicals, Inc., 580-32 Nagaura, Sodegaura, Chiba, 299-0265, Japan
[b] Laboratory for Chemistry and Life Science, Institute of Innovative Research, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, 226-8503, Japan
[c] National Institute of Technology and Evaluation, 2-49-10 Nishihara, Shibuya-ku, Tokyo, 151-0066, Japan

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ABSTRACT

Acid sites existing on the external surface of zeolites are the main cause of the formation of coke materials, resulting in decreasing the catalytic activity. For the durability of the reaction, silylation of external acid sites was adopted. Among various silylation reagents, cyclic siloxanes were effective silylation compounds for the deactivation of the acid sites on external surface on zeolite without prohibiting the objective reaction, cracking of naphtha. The effect of silylation was confirmed not only by the reaction but also by infra-red analysis.

1. Introduction

Light olefins (ethene, propene, butenes and butadiene) and aromatic compounds represented by benzene, toluene and xylene are indispensable elemental chemicals for the production of such principal chemicals as plastics, synthetic fibers, synthetic rubbers, paints, synthetic detergents, medicines, and so on. These source chemicals are mainly produced by thermal cracking of naphtha at 1073 K and above because of the low reactivity of these components. Practically, the temperature range, where profitable product yield is gained, is very much limited. Since the product distribution of naphtha cracking solely depends on the cracking temperature, it is very difficult to selectively produce desirable chemicals for the demand. Nowadays, around middle-east, less expensive ethane is the most competitive feed stock of ethene than naphtha, and ethene and its derivatives flow in enormous Asian market. On the other hand, this process, starting with ethene, does not produce so much propene that it cannot supply the propene demand sufficiently. The demand for propene and its derivatives increases rapidly and exceeds that for ethene and its derivatives. This tendency is regarded accelerated from now on. Under such circumstances, any naphtha cracking processes that can control the product distribution so as to meet the demand has been desired. In particular, the catalytic cracking of naphtha has been expected as one of the valuable technologies. In comparison to conventional "energy-consuming" naphtha cracker, this technique suppresses the generation of carbon dioxide remarkably and limits the consumption of fossil resource efficiently [1].

The use of acidic zeolites have been proposed as precedent technology for naphtha cracking catalysts, and the temperature of cracking by using zeolites are decreased to 873–973 K [2–7]. In addition, the ratio of propene to ethene in total products can be increased due to the lower reaction temperature range. Not only the yield of ethene and propene but also the yield of other valuable chemicals was controllable by this catalytic process. However, opened techniques of catalytic cracking of naphtha are not mature

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* Corresponding author.
E-mail address: jnomura@res.titech.ac.jp (J.N. Kondo).

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enough to substitute the conventional thermal cracking process. In fact, because the temperature of cracking has not been controlled well, primary products react sequentially and carbon material, so-called coke, is produced. Coke materials deposited on the surface of zeolite catalysts block pores or acidic sites, resulting in decreasing the catalytic activity. In order to idealize the process at the industrial level, durability of catalysts must be improved by suppressing the coke formation. The durability of catalyst also decreases both the fluctuation in product distribution and the cost of purification.

Coke is considered being produced by sequential side reactions of objective light olefin products, such as oligomerization, cyclization, dehydration, and so on. The coke formation becomes remarkable at temperatures above 873 K, where the catalytic cracking of naphtha is operated. In general, when zeolites are used as heterogeneous catalysts, objective products are generated by structurally selective reactions at acid sites in the zeolite pores. Nevertheless, acid sites also exist on the external surface of zeolite, and the non-selective reactions without restriction by porous structure are promoted, resulting in coke formation. It is reported that the selective deactivation of acid sites on the external surface leads to the suppression of coke formation and increases the selectivity of objective products, because coke formation proceeds mainly on the surface of zeolite [8–10]. As one of the deactivation methods of acid sites on the external surface of zeolite, silylation covering method of those sites is often adopted using silyl compounds [11–18]. Silylation compounds, which have steric hindrance represented by alkoxysilanes, alkylsilanes, halosilanes, polysiloxanes and so on, are generally often used. After silylation, simple calcination in air leads to the formation of silica species covering acid sites on external surface. Acid sites of zeolite exist uniformly on internal and external surfaces. In order to encourage shape selective reactions over active sites on the internal surface, it is necessary to selectively deactivate acid sites on the external surface by silylation using silyl compounds, whose molecular sizes are larger than zeolite pores. If the molecular size of silyl compounds is similar to that of zeolite pores or if silyl compounds possess any side chains, which are inserted in pores, the compounds cover the inlet of zeolite pores to narrow the apparent pore size, resulting in the disturbance of diffusion of reactants. Therefore, silyl compounds whose molecular size are sufficiently larger than zeolite pores are desirable. On the other hand, if the size of silyl compounds is too large, the steric hindrance leads the decrease in efficiency of silylation [13]. In addition, large silicon oxide phase formed on the external surface of zeolite during calcination after silylation blocks zeolite pores. To evade those problems the selection of appropriate silylation compounds, which adapt to the number of member ring, pore size and pore shape of zeolites are required.

Based on the above considerations, typical sylilation compounds include polysiloxanes, orthosilicates and chlorosilanes. For example, Mobil reported that bulky polysiloxanes as silylation compounds were effective for toluene disproportionation with a high selectivity to *p*-xylene on MFI type zeolite [15–17]. On the other hand, evaluation of acid amount on the external surface of zeolites is indispensable to perform silylation. The conventional evaluation methods were indirect: it was estimated by the change of the objective reaction or cracking reaction of 1, 3, 5-triisopropylbenzene before and after silylation [19]. Recently, Kubota, et al. reported the direct evaluation of the amount of acid sites on the external surface not by reactions but using infrared (IR) spectroscopy [20]. In this paper, various new types of silylation compounds were employed to efficiently suppress coke formation without decreasing the catalytic performance of naphtha cracking over H-ZSM5. In addition, the location of acid sites on H-ZSM5 before and after silylation was confirmed by IR spectroscopy using adsorption of probe molecules with various sizes.

2. Experimental

2.1. Synthesis of H-ZSM5 zeolite

Tetraorthosilicate (TEOS, Wako Pure Chemical Industries, Ltd., >95%) was added to tetrapropylammonium hydroxide (TPAOH, 25% aqueous solution, Tokyo Kasei). The resulting mixture was stirred at 353 K for 24 h. Thereafter, the solution containing water, $Al(NO_3)_3 \cdot 9H_2O$ (Wako, 99.9%) and NaOH (Wako, 97%) was added to the mixture and stirred at 298 K for 1 h. Thus, prepared mother gel was crystallized at 443 K for 24 h. The molar composition of the final gel was 1 SiO_2: 0.0067 Al_2O_3: 0.25 TPAOH: 0.033 Na_2O: 8.3 H_2O. Then, the solid product was collected by filtration. The Na-ZSM5 sample was obtained by calcination of the as-synthesized sample in an oven at 823 K to remove TPA^+ species. The NH_4-ZSM5 sample was obtained by the treatment of Na-ZSM5 samples with 1 M NH_4NO_3 (Wako, 99%) aq. at 353 K for 12 h twice. The H-ZSM5 samples were obtained by calcination of the NH_4-ZSM5 samples at 823 K for 10 h.

2.2. Silylation

Silylation of the H-ZSM5 was performed with each silylation compound in xylene. To 120 ml of xylene was added 6.0 g of H-ZSM5. After 4.0 mmol of 1, 3, 5, 7-Tetramethylchyclotetrasiloxane (TMCTS) was added dropwise under a nitrogen atmosphere at 298 K, the mixture was stirred at 343 K for 17 h, filtered, washed by *n*-hexane and dried. The dried sample was calcined at 823 K for 10 h to obtain silylated H-ZSM5 (TMSCT). In the same way, silylations of H-ZSM5 were perfomed with other silylation compounds (shown in Table 1); 1, 3, 5, 7, 9-pentamethylcyclopentasiloxane (PMCPS), Tris (trimethylsiloxy) silane (TTMSS), Tetraethoxysilane (TEOS), Dichlorotetramethylsiloxane (DCTMSLX), Diphenyldichlorosilane (DPDCS), and Dichlorotetramethylsilane (DCTMS), to obtain silylated H-ZSM5 (PMCPS), H-ZSM5 (TTMSS), H-ZSM5 (TEOS), H-ZSM5 (DCTMSLX), H-ZSM5 (DPDCS), and H-ZSM5 (DCTMS), respectively.

2.3. N_2 adsorption

Nitrogen adsorption-desorption isotherms were measured to obtain information on the micro- and *meso*-porosities at 77 K on a Belsorp-max (Microtrac-Bel). The BET specific surface area (S_{BET}) was calculated from the adsorption data in the relative pressure ranging from 0.04 to 0.2. External surface area (S_{EXT}) was estimated by the *t*-plot method.

2.4. NH_3 TPD

Temperature-programmed desorption of ammonia (NH_3-TPD) spectra were recorded on Belcat-A (Microtrac-Bel). Typically, 25 mg catalyst was pretreated at 773 K in He for 1 h and then was cooled to adsorption temperature at 373 K. Prior to the adsorption of NH_3, the sample was evacuated. Approximately 5 vol% of NH_3 was allowed to contact with the sample for 30 min. Subsequently, the sample was evacuated to remove weakly adsorbed NH_3 for 15 min. Finally, the sample was heated from 373 to 973 K at a ramping rate of 10 K min^{-1} with the He flow passed through the reactor. A mass spectrometer (mass number 17) was used to monitor desorbed NH_3. The amount of acid sites was determined by using the area of the so-called *h*-peak in the profiles.

2.5. Si NMR and Al NMR

Solid state ^{27}Al magic-angle spinning (MAS) NMR spectra were obtained with $\pi/2$ pulse width of 6 μs and pulse delay of 5 s on a JEOL ECA-400 spectrometer. Al resonance frequency employed was