Comparison of steaming stability of Cu-ZSM-5 with those of Ag-ZSM-5, P/H-ZSM-5, and H-ZSM-5 zeolites as naphtha cracking catalysts to produce light olefin at high temperatures

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ABSTRACT

We performed n-heptane cracking over Cu-ZSM-5, Ag-ZSM-5, and P/H-ZSM-5 before and after steaming under various conditions. The reduced Cu-ZSM-5 and Ag-ZSM-5 exhibited similar n-heptane cracking activities to H-ZSM-5 due to generation of Brønsted acid sites by reduction of metal cations. The order of steaming stabilities in the presence of O_2 was Cu-ZSM-5 > Ag-ZSM-5 ≫ P/H-ZSM-5, which was the reverse order of cumene cracking activities in the presence of O_2. Cumene cracking activity is a function of Brønsted acidity. Therefore, these findings indicate that the steaming stability of a catalyst is strongly related to its Brønsted acidity. Cu^{2+} and Cu^+ cations in the 194%Cu-ZSM-5 were not reduced to Cu^0 at a high temperature of 1023 K in the presence of O_2 and, therefore, 194%Cu-ZSM-5 exhibited an ultra-high steaming stability in the presence of O_2. The Brønsted acidity of 95%Ag-ZSM-5 was extremely low, almost equal to 194%Cu-ZSM-5. However, the thermal reduction of Ag^+ took place during steaming even in the presence of O_2 at a high temperature of 1023 K and, therefore, the steaming stability of 95%Ag-ZSM-5 in the presence of O_2 was much lower than that of 194%Cu-ZSM-5.

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1. Introduction

Light olefins, such as ethylene, propylene, and butene, are important raw materials for various polymers and petrochemicals. Ethylene is the major product of the naphtha thermal cracking process, while propylene is a byproduct in this process [1]. The petrochemical industry is currently facing a major squeeze in propylene availability as a result of the increasing demand for propylene derivatives (*e.g.*, polypropylene). However, the naphtha thermal cracking process is not sufficient to meet the demand for propylene since it is difficult to control its selectivity for specific olefins (propylene/ethylene weight ratio is 0.5–0.6). Moreover, this process, which is usually performed at high temperatures (>1073 K), requires a large amount of energy [2]. Therefore, much attention is now focused on the naphtha catalytic cracking process as an alternative to naphtha thermal cracking, because of its superior ability to obtain a propylene/ethylene weight ratio higher than 0.6 at a reduced reaction temperature. Most of the model compounds of naphtha in the literature are n-paraffins

because naphtha is a mixture of hydrocarbons and its main components are C_{5-8} n-paraffins. Zeolite is a typical catalyst used for the cracking [3–21]. Specifically, ZSM-5 zeolite is one of the most efficient catalysts for the naphtha catalytic cracking process at high temperatures (873–923 K) [13–21]. Unfortunately, a considerable amount of coke forms during the cracking over the zeolite catalyst and it fouls the catalytic surfaces and blocks the micropores, resulting in deactivation of the catalyst. Therefore, the regeneration of H-ZSM-5 by calcination in air is necessary. However, a small amount of steam is generated during the regeneration, because coke contains a small amount of hydrogen [22]. It is widely known that permanent deactivation related to dealumination from the zeolitic framework occurs in a hydrothermal atmosphere.

Phosphorus impregnation is known to be an effective method for improving the steaming stability of H-ZSM-5. Blasco et al. have reported that the optimum P/Al molar ratio is 0.5–0.7. They proposed a model involving a phosphorus-zeolite interaction in which cationic species of phosphorus, formed by protonation of orthophosphoric acid, neutralize one of the acid sites corresponding to a framework Al pair, stabilizing this aluminum while its neighbor preserves its acidity toward steaming [23]. However, the phosphorus impregnated H-ZSM-5 (P/H-ZSM-5) exhibits lower

activity for catalytic cracking than H-ZSM-5, because the Brønsted acidity of P/H-ZSM-5 is lower than that of H-ZSM-5 in the catalytic cracking [21,23]. Sano et al. reported that a proton catalyzes dealumination of H-ZSM-5 [24]. Fujita et al. reported that the steaming stability of H-ZSM-5 is improved by adding alkaline earth metals [25]. A catalyst with a lower Brønsted acidity may exhibit higher steaming stability, but lower activity for catalytic cracking. The regeneration is carried out in the presence of O_2; however, the cracking over H-ZSM-5 at high temperatures takes place in a reductive atmosphere, due to the formation of a considerable amount of H_2. Therefore, if the catalysts have a low Brønsted acidity in an oxidative atmosphere and a high Brønsted acidity in a reductive atmosphere, they will exhibit a high steaming stability and a high catalytic activity.

We previously reported that the copper cation exchanged ZSM-5 (Cu-ZSM-5) (exchange degree of copper cation: 194%) and silver cation exchanged ZSM-5 (Ag-ZSM-5) (exchange degree of silver cation: 95%) zeolites had low Brønsted acidities in the presence of O_2 and high Brønsted acidities in a reductive atmosphere (The exchange degrees of copper and silver cations were defined as the percentage charge compensation of Al in ZSM-5 by Cu^{2+} ions and Ag^+ ions, respectively.). These catalysts exhibited high steaming stabilities in the presence of O_2 and higher cracking activities in a reductive atmosphere than P/H-ZSM-5 and H-ZSM-5. Cu-ZSM-5 exhibited an ultra-high steaming stability [17].

In this study, we expect to clarify why the order of steaming stabilities is Cu-ZSM-5 > Ag-ZSM-5 ≫ P/H-ZSM-5. We carried out the cracking of n-heptane over Cu-ZSM-5 and Ag-ZSM-5 with various cation exchange degrees and P/H-ZSM-5 before and after steaming under various conditions.

2. Experimental

2.1. Catalyst preparation

Na-ZSM-5 zeolite was synthesized by a hydrothermal synthesis using tetrapropylammonium bromide as a structure directing agent, water glass as a silicon source, aluminum sulfate as an aluminum source, sulfuric acid, and sodium chloride [26]. The Si/Al atomic ratio of the preparation gel for hydrothermal synthesis was 50. The resultant gel was placed in an autoclave at 433 K for 20 h. The obtained product was washed with pure water and dried at 383 K for 16 h in air. The as-prepared Na-ZSM-5 zeolite was calcined at 803 K for over 3.0 h in air or until the product was whitened to remove the organic template. The sodium cations were then exchanged for protons by treatment with 1 M hydrochloric acid at 333–353 K for 1 week. The hydrochloric acid solution used for cation exchange was replaced every day. The cation exchanged zeolite was washed with pure water and dried at 383 K for 16 h in air. Cu-ZSM-5 and Ag-ZSM-5 were prepared by a conventional cation exchange procedure using the H-ZSM-5 as follows. The exchange of copper cations was carried out with 0.001, 0.01, or 0.1 M copper (II) acetate aqueous solutions for 24 h at 298 K. The exchange of silver cations was carried out with 0.01, 0.1 M, or 1 M silver nitrate aqueous solutions. In the case of 0.01 or 0.1 M silver nitrate aqueous solution, a 24 h exchange was carried out once at 298 K. In the case of 1 M silver nitrate aqueous solution, a 2 h exchange was carried out three times at 343 K. The metal cation exchanged zeolites were washed with pure water and dried at 383 K for 16 h in air, and then finally calcined at 803 K for 4 h in air. P/H-ZSM-5 with the P/Al atomic ratio of 0.5 was prepared by an impregnation method. An aqueous solution of phosphoric acid was added to the H-ZSM-5. The mixture was evaporated on a water bath at 373 K. The resultant material was dried at 383 K for 16 h and then finally calcined at 803 K for 4 h in air.

2.2. Characterization

X-ray diffraction (XRD) patterns for the catalyst were obtained by an X-ray diffractometer (RINT2000, Rigaku) using Cu Kα radiation (40 kV, 30 mA) with a scanning range of 2θ from 5° to 50° at a scanning rate of 2° min^{-1}. The N_2 adsorption measurements were carried out at liquid N_2 temperature using an Accelerated Surface Area and Porosimetry Analyzer (ASAP2010C, Micromeritics). The specific surface areas of the catalysts were calculated using the Langmuir equation. External surface areas and micropore volumes were estimated by the t-plot method. The concentrations of aluminum in the H-ZSM-5, copper cation in the Cu-ZSM-5, and silver cation in the Ag-ZSM-5 were measured by an inductively coupled plasma - atomic emission spectrometer (ICP-AES, SPS3500, SII NanoTechnology). The exchange degrees of copper and silver cations were defined as the percentage charge compensation of Al in ZSM-5 by Cu^{2+} ions and Ag^+ ions, respectively.

Temperature-programmed desorption of ammonia (NH_3-TPD) experiments were carried out using a mass spectrometer (M-200GA-DM, Canon Anelva) as a detector of desorbed ammonia ($m/e = 16$). The sample weight was 50 mg. The pretreatment and oxidation treatment for the catalysts were carried out in flowing He at 973 K for 1 h and in flowing O_2 at 923 K for 0.5 h, respectively. Ammonia adsorption on Cu-ZSM-5 and Ag-ZSM-5 was carried out after the pretreatment followed by the oxidation treatment, while ammonia adsorption on H-ZSM-5 was carried out after the pretreatment. Ammonia was introduced into the cell at 373 K for 0.5 h. After purging by He to remove weakly adsorbed ammonia at the same temperature for 0.5 h, NH_3-TPD was carried out at a heating rate of 10 K min^{-1} in flowing He (60 mL min^{-1}) from 373 to 1023 K.

The cracking of cumene ((1-methylethyl)benzene) is widely known as a simple and typical reaction solely catalyzed by Brønsted acids [27–29]. Thus, Brønsted acidities of catalysts can be evaluated from the catalytic activities for the cracking of cumene. The cracking of cumene was performed in a conventional fixed bed flow reactor under atmospheric pressure at 573 K. The catalysts were placed into a quartz reactor of 8 mm i.d. Cumene (Wako Pure Chemicals) was fed into the reactor by a plunger pump. N_2 was used as a carrier gas. The cumene/N_2 ratio was 1/19 mol mol^{-1}. The ratio of catalyst weight to total flow rate (W/F_{total}) was 0.58 g_{-cat} h mol^{-1}. The pretreatment, oxidation, and reduction treatments for the catalysts were carried out in flowing N_2 at 973 K for 1 h, in flowing O_2 at 923 K for 0.5 h, and in flowing H_2 at 923 K for 1 h, respectively. The catalytic activities of Cu-ZSM-5 and Ag-ZSM-5 for the cracking of cumene were measured after only the pretreatment, or the pretreatment followed by the oxidation or reduction treatment. In the case of the reduced Cu-ZSM-5 and reduced Ag-ZSM-5, the cracking of cumene was carried out in the presence of H_2 (cumene/N_2/H_2 = 1/9.5/9.5). The catalytic activities of the H-ZSM-5 and P/H-ZSM-5 for cumene cracking were measured after the pretreatment.

H_2-temperature programmed reduction (H_2-TPR) measurements were carried out using H_2 (1%)/Ar (60 mL min^{-1}) at a heating rate of 10 K min^{-1}. The pretreatment and oxidation treatment for the catalysts were carried out in flowing He at 973 K for 1 h and in flowing O_2 at 923 K for 0.5 h, respectively. The change of the H_2 concentration in the effluent gas was monitored with a TCD detector. Water produced during the reduction process was removed by an adsorbent before entering the TCD detector.

Diffuse reflectance UV–vis spectra of catalysts were recorded in a UV–vis spectrometer (V-550, JASCO) equipped with an in situ flow cell with a quartz window [30]. $BaSO_4$ was used to collect a background spectrum. In situ UV–vis spectra were measured in flowing steam at 773 K between 200 and 600 or 800 nm ranges at a step of 0.5 nm. The carrier gas was N_2 or O_2. The water was introduced by a bubbler (298 K).