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Preparation of cerium-loaded Y-zeolites for removal of organic sulfur compounds from hydrodesulfurizated gasoline and diesel oil

Mei Xue [a,b,*], Ramesh Chitrakar [a], Kohji Sakane [a], Takahiro Hirotsu [a], Kenta Ooi [a], Yuji Yoshimura [c], Makoto Toba [c], Qi Feng [b,*]

[a] *Health Technology Research Center, National Institute of Advanced Industrial Science and Technology (AIST), 2217-14 Hayashi, Takamatsu 761-0395, Japan*
[b] *Department of Advanced Materials Science, Faculty of Engineering, Kagawa University, 2217-20 Hayashi, Takamatsu 761-0396, Japan*
[c] *Research Institute for Green Technology, National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan*

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Abstract

Ce(IV)-loaded Y-zeolites (CeY) were prepared for selective removal of the trace amount of organic sulfur compounds from hydrodesulfurization (HDS)-treated diesel oil. The CeY samples can be obtained from NH_4–Y-zeolite (NH_4Y) using liquid-phase ion-exchange and solid-state ion-exchange methods. The ion-exchange reactions, structures, and selective adsorptions of organic sulfur compounds of the CeY samples were investigated using XRD, IR, XPS, TEM, and GC sulfur analyzer. The organic sulfur compound uptakes strongly depend on the amount and the valency of Ce in the zeolite structure. Ce(IV) shows much higher adsorptive ability than Ce(III). A CeY–S sample prepared by solid-state ion-exchange reaction of NH_4Y and $Ce(NO_3)_3$ with Ce/NH_4 mole ratio of 0.63 at 250 °C showed a maximum sulfur uptake from a model solution of HDS-treated gasoline containing thiophene [$S = 5$ ppm (ppm = mg/L)]. A desulfurization from a HDS-treated diesel oil containing organic sulfur compounds ($S = 1.87$ ppm) and H_2S ($S = 0.73$ ppm) was investigated with a combination of the CeY–S and a CuO adsorbent for removal of H_2S by a batch method. The sulfur content was reduced to below 0.01 ppm for the first time. This method provides a promising desulfurization process to prepare a clean fuel for fuel cells.

Keywords: Thiophene; Cerium; Zeolite; Sulfur removal; Solid-state reaction; Hydrodesulfurization; Diesel oil; Organic sulfur

1. Introduction

Air pollution due to exhaust gas from commercial gasoline and diesel has been a major concern of the public. Since the sulfur compounds in gasoline and diesel are the main source of SO_x in the exhaust gas, the 300 and 500 ppm (parts per million by weight) sulfur limits in gasoline and diesel oil have become worldwide standards. Currently, a new standard has been set up by the Environmental Protection Agency of the United States and the European Commission to reduce the sulfur content to 10–15 ppm by the year 2006. It is expected that similar regulations will be implemented in other countries also. Another reason to reduce sulfur is the application of gasoline and diesel to fuel cells as a fuel to produce hydrogen gas. The sulfur level should be further reduced, close to zero ppm, because the presence of even a trace of sulfur is a poison to the fuel reforming catalysts as well as the electrode catalysts.

At present, hydrodesulfurization (HDS) process is an efficient method for sulfur removal from gasoline and diesel of high sulfur content. In the HDS process, organic sulfur compounds in the liquid fuels are broken down to H_2S using NiMo–CoMo/Al_2O_3 catalysts, followed by the removal of H_2S, and the sulfur content in fuels can be reduced to ∼10 ppm. Yoshimura et al. [1] have reported that Pd–Pt/Yb–USY zeolite catalysts show good performance in the HDS process for diesel oils, and the sulfur content can be reduced from 263 to ∼5 ppm.

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[*] Corresponding authors. Fax: +81 87 869 3551.
E-mail addresses: xue-mei@aist.go.jp (M. Xue), feng@eng.kagawa-u.ac.jp (Q. Feng).

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The remaining sulfur compounds after the HDS process are organic sulfur compounds and H_2S. However, this still cannot satisfy the requirement for fuel cell application, where the sulfur level needs to be reduced to less than 0.1 ppm. Other studies on removal of sulfur from fuels by adsorption have been reported also. Yang et al. [2] reported that Cu^+ and Ag^+ ion-exchanged Na–Y-zeolites adsorb sulfur compounds from commercial fuels, and sulfur content can be reduced from 430 ppm to <0.2 ppm by a column method. Velu et al. [3] have reported that transition metal ion-exchanged NH_4–Y-zeolites (with Cu, Ni, Zn, Pd, Ce) show selective adsorption of organic sulfur from model jet fuel ($S = 507$ ppm). The Ce-exchanged Y-zeolite with a Ce loading of 38 wt% exhibits a higher sulfur adsorption capacity (10 mg/g), and the sulfur content can be reduced to 19 ppm using a column method. These studies suggest that the transition metal ions have a strong affinity for the adsorption of organic sulfur compounds. The reduction of the sulfur content to less than 0.1 ppm, however, has not been reported yet.

We think that the adsorption process is a most effective method for the removal of the trace amounts of residual sulfur in fuels after HDS treatment. In our previous study, we reported the adsorptive properties of Ag^+, Cu^+, and Ce^{3+} ion-exchanged Y-zeolites as adsorbents for selective adsorption of thiophene and 1-benzothiophene in a model solution of HDS-treated gasoline with a markedly low sulfur concentration of 5 ppm [4]. The Ce–Y-zeolite exhibits higher selectivity for the adsorption of the organic sulfur compounds, the sulfur adsorption amount of the Ce–Y-zeolite is strongly dependent on preparation conditions of the adsorbent, and the sulfur contents can be reduced to less than 0.1 ppm by using the adsorbent. In addition, we have developed a microcrystalline CuO adsorbent with high H_2S adsorption capacity for the removal of H_2S in the HDS treated fuel [5].

In the preparation of metal ion-loaded zeolites, conventional ion-exchange reactions in aqueous solution are usually used. Some studies on solid-state ion-exchange reactions of zeolites for loading metal ions have been reported also. Beyer and Karge have reported that Li^+-, Na^+-, and K^+-form ZSM-5 can be prepared by calcination of mixtures of Li, Na, and K chlorides and H–ZSM-5 or NH_4–ZSM-5 at 627 °C in air, respectively [6]. The calcinations of mixtures of Na and Cs chlorides and NH_4^+-form β-zeolite at 550 °C produced the respective cationic forms of zeolites [7]. These results suggest that the solid-state ion-exchange method can be used in the preparation of Ce-loading zeolite as a sulfur adsorbent. This solid-state ion-exchange method is convenient as a preparation procedure as compared to the conventional ion-exchange method in the liquid phase.

In the present study, we develop a solid-state ion-exchange process for the preparation of Ce-loading Y-zeolite (CeY), characterize the organic sulfur adsorption properties from a model solution of HDS-treated gasoline, and compare the properties with those of CeY prepared by the conventional ion-exchange process in the liquid phase. The performance of a combination of the developed CeY adsorbent and the CuO adsorbent in the removal of organic sulfur compounds and H_2S from HDS-treated diesel oil is investigated also.

2. Experimental

2.1. Sample preparation

NH_4–Y-zeolite (NH_4Y, Wako Co. Ltd., Japan, $SiO_2/Al_2O_3 = 7.0$) with an ion-exchange capacity of 1.12 meq/g was used as the starting material for preparation of CeY samples. Liquid-phase ion-exchange and solid-state ion-exchange processes were used in the preparation of CeY samples. In the liquid-phase ion-exchange process, NH_4Y (1 g) was treated with $Ce(NO_3)_3$ solutions of 0.01 M (10, 20, 30 ml) and 0.1 M (200 ml) at ambient temperature for 1 d, respectively. After the Ce^{3+}/NH_4^+ ion-exchange treatments, the samples were filtered, washed, and dried at 80 °C. The Ce loadings of these samples were 0.08, 0.17, 0.26, and 0.42 mmol/g, respectively. The Ce^{3+}-loaded zeolite was calcined at a desired temperature in air or N_2 for 2 h. The calcined samples were designated as CeY–L (0.42–450), etc., where the numbers in the parentheses are Ce content (mmol/g) and calcination temperature, respectively.

In the solid-state ion-exchange process, NH_4Y and $Ce(NO_3)_3 \cdot 6H_2O$ are mixed at a Ce/NH_4 mole ratio of 0.37, 0.63, 0.95, or 1.42 and the mixtures are ground, homogenized, and then calcined at a desired temperature in air for 2 h. The samples prepared are designated as CeY–S (0.63–250), etc., where the numbers in the parentheses are initial Ce/NH_4 mole ratio and calcination temperature, respectively.

2.2. Adsorption experiment

Adsorption experiments were performed by a batch method. Two kinds of liquid feed stocks were used: (i) A model solution consisting of *n*-heptane (99 wt%), toluene (1 wt%), and organic sulfur compound thiophene ($S = 5$ ppm) was used as a model solution of HDS-treated gasoline; (ii) HDS-treated diesel oil was obtained as described in Ref. [8]. The HDS-treated diesel oil contains organic sulfur compounds ($S = 1.87$ ppm) and H_2S ($S = 0.73$ ppm) aromatic compounds (0.32 wt%). The adsorbent was preheated at 200 °C for 1 h to remove the adsorbed water before using in the adsorption experiments. The model solution (20 ml) or the HDS-treated diesel oil (10 ml) was mixed with the adsorbent (0.10 g) and the mixture was stirred in a Teflon tube at 80 °C for 2 h. The liquid phase was separated from the adsorbent, and then the sulfur concentration in the solution was analyzed using a sulfur analyzer. The sulfur uptake was calculated from the decrease of sulfur concentration in the supernatant solution relative to the initial concentration.

2.3. Chemical analysis

The cerium content of CeY–L and CeY–S was determined using a Seiko inductively coupled plasma (ICP) spectrometer (SPS 7800) after the cerium ions were extracted in a 5 M HCl solution. The sulfur concentration in the solutions was determined using a Shimadzu GC2010 sulfur analyzer equipped with a capillary column (DB-1, J & W Scientific, 60 m × 0.319 mm × 5 µm) and a sulfur chemiluminescence detector (SCD, An-