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Synthesis of zeolite from steel slag and its application as a support of nano-sized TiO_2 photocatalyst

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Abstract Steel slag, commercial waste material containing silica and alumina which are the chemical components elements of zeolite, was used as a source for synthesis of FAU zeolite (Y-zeolite, X-zeolite). Through acid-treatment to remove CaO species from steel slag and hydrothermal treatment, well-crystallized Na type FAU zeolite was obtained. Furthermore the synthesized FAU zeolite was applied as a support of photocatalyst. It was found that hydrophobic surface property of zeolite enhances photocatalytic activity for decomposition of organic pollutants and the zeolite synthesized from steel slag would be applicable as promising support of TiO_2 photocatalyst.

Introduction

Steel slag is a waste-material generated in steel production and contains SiO_2, Al_2O_3, CaO, and MgO as its main chemical compositions. Steel slag is categorized into blast furnace slag, which is produced in blast furnace, and converter slag, which is produced in converter. Furthermore, blast furnace slag is grouped into water-granulated slag which is cooled by water rapidly and slow cooling slag by the cooling speed. The water-granulated slag is mostly recycled in civil engineering work for concrete or cement and its production in 2005 in Japan was 20 million tons.

It is well accepted that the Si and Al elements contained in the steel slag are also compositional elements of zeolite. Zeolite is an aluminosilicate-type microporous material with large surface area and exchangeable cations in its structure, consisting of SiO_4 and AlO_4 tetrahedral structures. Due to their unique properties, zeolite have been used as adsorbent materials in the industrial fields and have attracted a lot of interests of researchers. Zeolites are conventionally prepared by the hydrothermal method from the gel containing silica, alumina, cation, organic template, and water. However, the organic templates are expensive for large-scale production. On the other hands the practical convenient route for the synthesis of zeolites by utilizing steel slag as a silica source of zeolite should be developed from the aspect of resources problem. Furthermore, the combination of zeolites and nano-sized TiO_2 has been attractive for its adsorption and photocatalytic degradation of organic pollutant diluted in liquid or gaseous phases [1–5].

In the present study, FAU zeolite (Y-zeolite, X-zeolite) was synthesized utilizing the pretreated steel slag and the influences of treatment procedure was evaluated. Furthermore, the synthesized FAU zeolite was applied as the support of TiO_2 photocatalyst. The local structure of titanium oxide species was investigated by X-ray absorption fine structure (XAFS). The influences of zeolite composition and surface chemical property on the crystallization of loaded TiO_2 and the photocatalytic reactivity for degradation of organic pollutants diluted in water were evaluated.

Experimetal

In order to carry out synthesis efficiently an amorphous water-granulated slag material supported from Sumitomo

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Metals Ind., Ltd. was ball milled with 650 rpm for 1 h. The components of slag were, SiO_2: 30.57, Al_2O_3: 15.22, CaO: 38.96, Fe_2O_3: 0.46, MgO: 11.27, TiO_2: 1.14 (wt%). The powdered slag (10 g) was reacted with hydrochloric acid aqueous solution (5 mol/L, 120 mL) with stirring at room temperature for 4 h to remove several elements which inhibit crystallization of zeolite. After drying in air overnight the sample was heated with appropriate amounts of sodium aluminate tablets to form FAU zeolites with desirable SiO_2/Al_2O_3 ratio (2.5) at 623 K in air, followed by adding deionized water and aging for 24 h. The solution was sealed into a teflon capsule and transferred to an autoclave and heated at 373 K for 24 h to carry out crystallization [6]. The synthesized precepitates were centrifuged and dried overnight in air.

A large amount of Na^+ ions contained in the synthesized FAU zeolite in its ion-exchange sites, were exchanged with ammonium ions by stirring in aqueous ammonium hydrate solution (2 mol/L) at room temperature for 6 h, followed by calcinations at 773 K for 5 h in air to form the proton type FAU zeolite named as Slag-FAUzeolite. The proton type Slag-FAU zeolite was stirred in ammonium titanyl oxalate ($(NH_4)_2[TiO(C_2O_4)_2] \cdot nH_2O$) solution of 10 mmol/L at room temperature for 6 h followed by evaporation and drying in air overnight. The sample was calcined at 773 K for 5 h in air to prepare TiO_2-Slag-FAU zeolite [7]. TiO_2 loaded on proton type FAU zeolite were also prepared as reference samples by a similar procedure using FAU zeolites (Y-zeolite: SiO_2/Al_2O_3 = 5,40) and denoted as TiO_2-FAU(5) and TiO_2-FAU(40), respectively.

The structure of products was evaluated by XRD for the measurement on the crystallinity and purity, using Rigaku Mini-flex using Cu Kα radiation of λ = 1.5418 Å. Chemical compositions and SiO_2/Al_2O_3 molar ratios were analyzed by XRF. The crystallinity of obtained TiO_2 loaded zeolite was characterized by XRD and Ti K-edge XAFS analyses. The XAFS spectra were measured at the BL-7C facility of the Photon Factory at the National Laboratory for High-Energy Physics, Tsukuba, Japan. A Si(111) double crystal was used to monochromatize the X-ray from the 2.5 GeV electron storage ring. The Ti K-edge absorption spectra were recorded in the fluorescence mode at 295 K [8, 9].

The hydrophobic or hydroplilic property of samples was determined from H_2O and butane adsorption isotherms. The photocatalytic activities of samples in liquid phase and gaseous phase were investigated from the degradation of 2-propanol diluted in water (2.6×10^{-3} mol/L) and the degradation of acetaldehyde (10 kPa) diluted in air at 295 K under UV-light irradiation (220–600 nm: 1600 W/cm^2 (360 nm)) with TiO_2-zeolite (100 mg).

Results and discussion

After dissolution with hydrochloric acid, only SiO_2 content was remained and most of other contents of steel slag were totally eliminated. The components of treated slag were, SiO_2: 96.88, Al_2O_3: 0.46, CaO: 1.44, Fe_2O_3: 0.15, MgO: 0.33, TiO_2: 0.54 (wt.%). Figure 1 shows the XRD patterns of synthesized FAU zeolites with SiO_2/Al_2O_3 ratio of 2.5 (Slag-FAU zeolite) and its dependence on hydrothermally treated time. After hydrothermal treatment for 6 h, well-crystallized FAU zeolite was obtained. However, no zeolite phase was observed without acid treatment or when synthesized with high SiO_2/Al_2O_3 ratio of over 5.0, suggesting that the presence of CaO and Fe_2O_3 contents might inhibit the nucleation of zeolite crystals and that the precise control in the composition of precursor is an important factor to generate its nucleus growth.

The synthesized Slag-FAUzeolites on each hydrothermal treatment showed the lower H_2O adsorption capacity, as compared to standard FAU zeolite, as shown in Table 1. This result suggests that the well-crystallized FAU zeolite was generated by utilizing steel slag and is applicable to be used as the support of TiO_2 photocatalyst.

Figure 2 shows the results of Ti K-edge XAFS analyses for the TiO_2 loaded zeolite samples. A sharp pre-edge peak was observed at around 4970 eV in the XANES spectrum indicating the existence of isolated titanium

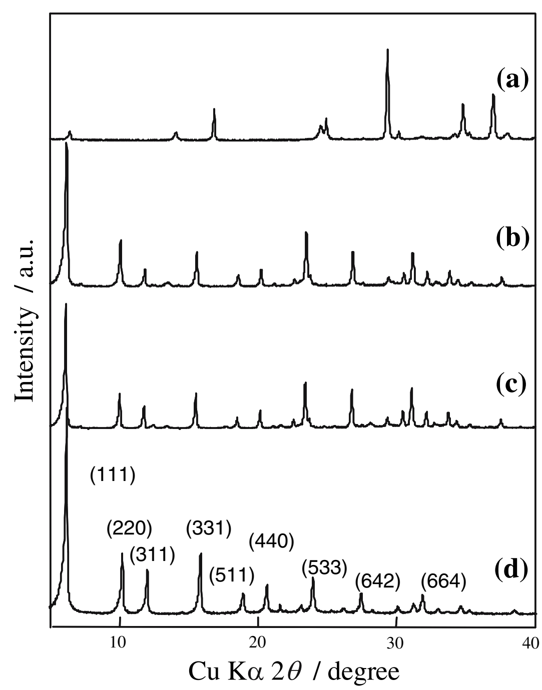

Fig. 1 XRD patterns of FAU zeolite (SiO_2/Al_2O_3 = 2.5) hydrothermally synthesized with the pretreated steel slag materials. Treatment times : (**a**) 0 h, (**b**) 6 h, (**c**) 12 h, (**d**) Reference : FAUzeolite (SiO_2/Al_2O_3 = 5)

Table 1 Crystallinity and H_2O adsorption capacity of the Slag-FAU zeolites synthesized hydrothermally for various times

FAU zeolite (hydrothermal treatment time /h)	Relative intensity of XRD peak (%)	H_2O adsorption capacity (g/zeolite100 g)
Slag-FAU (0 h)	0	5
Slag-FAU (6 h)	48	27
Slag-FAU (12 h)	50	25
FAU (standard)*	100	31

* (SiO_2/Al_2O_3 = 5)

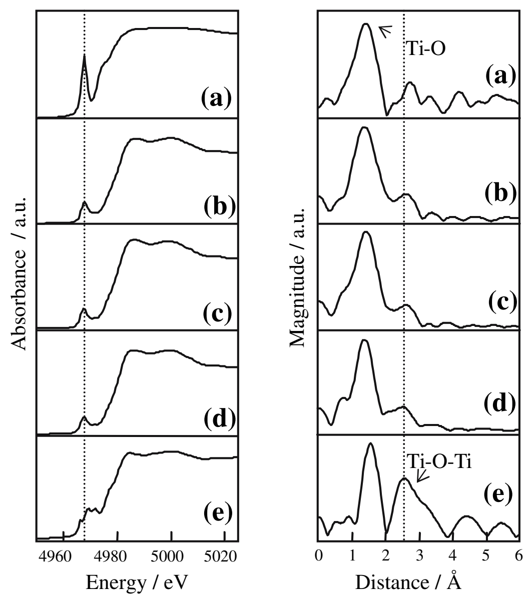

Fig. 2 Ti K-edge XANES and FT-EXAFS spectra of (**a**) Ti(O-^{i}Pr)$_4$, (**b**) TiO_2-Slag-FAU, (**c**) TiO_2-FAU(5), (**d**) TiO_2-FAU(40), (**e**) TiO_2 (Anatase)

oxide species having tetrahedrally coordination. The peak at around 2.5 Å in the FT-EXAFS spectrum is derived from the Ti–O–Ti bonds indicating that the crystalline titanium oxide exists [10–12]. Considering that the pre-edge peak was observed in all samples, it is suggested that the titanium is incorporated into FAU zeolite structure and existed as isolated species mainly in the tetrahedral coordination.

Figure 3 shows the photocatalytic degradation activity of 2-propanol diluted in water and acetaldehyde in gaseous phase per amount of TiO_2 in the samples. TiO_2 loaded on the Slag-FAU zeolite also showed photocatalytic activity. It is clearly shown that the zeolite with higher SiO_2/Al_2O_3 ratio enhanced the photocatalytic activity. It is considered that photocatalytic degradation activity depend largely on the hydrophilic–hydrophobic surface properties of the

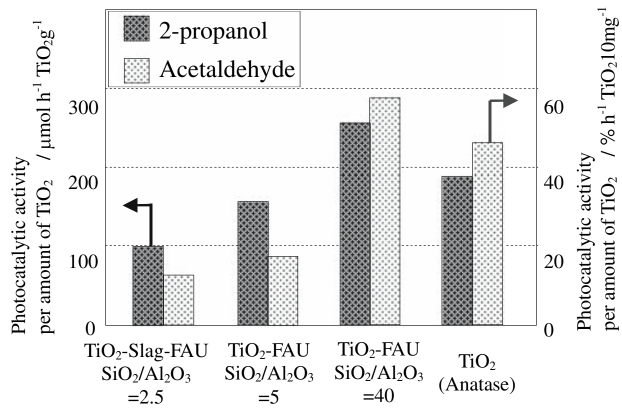

Fig. 3 The photocatalytic activity for degradation of 2-propanol diluted in water and acetaldehyde diluted in air

zeolites, which are related to SiO_2/Al_2O_3 ratio and a factor of adsorption of pollutants into zeolite pores.

Conclusion

Well-crystallized Na type FAU zeolite was synthesized utilizing an acid-treated steel slag through hydrothermal treatment. The acid treatment was an essential procedure to prepare desirable composition of zeolite precursor. The formation of titanium oxide species incorporated in FAU zeolite synthesized from steel slag showed photocatalytic activity for degradation of organic pollutants. It was also demonstrated that the SiO_2/Al_2O_3 ratio of zeolite, which relate to hydrophobic or hydrophilic property plays an important role in degradation of organic pollutants.

Steel slag is a useful material source for the synthesis of FAU zeolite and this zeolite would be applicable as promising support of TiO_2 photocatalyst.

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