JOURNAL OF CATALYSIS **138**, 750–753 (1992)

Activation of Molecular Hydrogen into Protonic Acid Sites over Metal-Free H-ZSM-5 Catalyst

The acid character (protonic and Lewis sites) is the origin of the activity of zeolites for a great number of hydrocarbon transformations (*1–3*). Among the zeolites, H-ZSM-5 zeolite attracts much attention because of its unique activity and shape selectivity. The H-ZSM-5 contains both protonic and Lewis-acid sites, and their concentration is dependent on the calcination temperature (*4*), the degree of dealumiantion (*5*), the location of the aluminium (*6*), and aluminium content in unit cell (*7*). In order to obtain the desired catalytic performances, modification of the zeolites has been extensively performed by treatment of the zeolites with molecules such as $(CH_3O)_3P$ (*8*) and $Si(OCH_3)_4$ (*9*).

Besides the parameters mentiond above, the modification of the acid properties of the metal-free H-ZSM-5 catalyst due to the interation with molecular hydrogen in the vapor phase has been postulated (*10*). This arises from the suppression of the catalytic activity for toluene disproportionation in the presence of hydrogen (*10*). This suppression has been explained as shielding of the Lewis-acid sites by hydrogen atoms. However, the spectroscopic evidence demonstrating the modification of the acid properties of the metal-free H-ZSM-5 catalyst have not been presented yet. In this note, we report the results which demonstrate the dynamic modification of the acid properties of the metal-free H-ZSM-5 catalyst with molecular hydrogen by means of infrared (IR) spectroscopy of adsorbed pyridine (*11*). The formation of the protonic acid sites from molecular hydrogen and reversible change by evacuation are presented in this note.

Na-ZSM-5 was prepared following the procedure of Yoshimura *et al.* (*12*). The resultant Na-ZSM-5 was ion-exchanged in 1 *N* HCl (aq.) and washed with distilled water until no Cl^- ions could be detected. More than 99% of the sodium ions were exchanged into protons. The Si/Al atomic ratio of the H-ZSM-5 is 49. The surface area of the sample calcined and evacuated at 773 K was ca. 430 m^2/g. The content of iron in the sample was analyzed to be 3640 ppm by atomic absorption spectrometry.

A self-supported wafer placed in an *in-situ* quartz IR cell with CaF_2 windows was heated in oxygen (ca. 200 Torr) at 773 K for 20 min and evacuated at 773 K for 10 min. This treatment was repeated three times. Then, the wafer was exposed to less than 1 Torr of pyridine (purified by repeated freeze–thaw degassing cycles) at 423 K for 1 h to allow pyridine to permeate the sample, followed by evacuation at 423 K for 10 min. Then, the pyridine-covered sample was exposed to 400 Torr of hydrogen at room temperature. The sample was heated stepwisely from 373 to 523 K by 50-K increments. The hydrogen was purified by passing through a hydrogen diffusion purifier (Japan Pure Hydrogen Co., Ltd.), molecular sieves (13X), and a liquid-nitrogen trap. The sample was successively evacuated stepwisely at temperatures from 373 to 673 K by 50-K increments. All IR spectra were recorded on IR-700 infrared spectrometer (Japan Spectroscopic Co., Ltd.) at room temperature. In a typical IR measurement, eight spectra were accumulated.

To determine the fraction of adsorbed pyridine on the protonic-acid site (pyridinium ion, at 1540 and 1490 cm^{-1}) or Lewis-acid sites (coordinated pyridine, at 1490 and 1440 cm^{-1}), the extinction coefficients (ε) were obtained by comparing the IR peak

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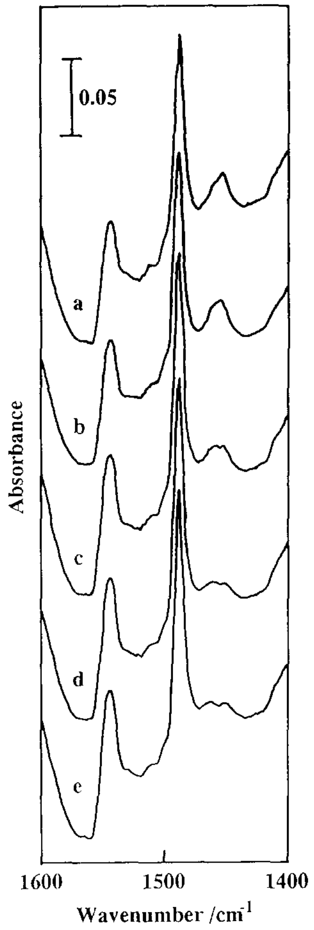

FIG. 1. The IR spectra of pyridine adsorbed on H-ZSM-5 after heating in the presence of hydrogen (400 Torr) at different temperatures: (a) before heating, (b) 373 K, (c) 423 K, (d) 473 K, and (e) 523 K. The pretreated sample was exposed to pyridine at 423 K and evacuated at 673 K before the introduction of hydrogen.

areas before and after adsorption of a known amount of pyridine on the sample. The extinction coefficient ratio, $\varepsilon^{P}(1490)/\varepsilon^{L}(1490)$ was 2.5, where $\varepsilon^{P}(1490)$ and $\varepsilon^{L}(1490)$ refer the protonic component and Lewis component of the band at 1490 cm^{-1}, respectively. The obtained ratio was close to that (2.74) reported by Sayed *et al.* (*5*). The extinction coefficient ratio, $\varepsilon^{P}(1490)/\varepsilon(1540)$ was 1.1, where $\varepsilon(1540)$ refers the coefficient due to the pyridinium ion of 1540 cm^{-1}. The total amount of the pyridine which remained on the H-ZSM-5 sample after 673 K evacuation was 48.9 μmol/g. The amount was estimated by comparing the intensities of the IR bands with those for the sample on which known amounts of pyridine were adsorbed.

Figure 1 shows the IR spectra of adsorbed pyridine on the H-ZSM-5 followed by heating in the presence of hydrogen at different temperatures. After evacuating the H-ZSM-5 at 673 K and before introduction of hydrogen, the bands at 1440, 1490, and 1540 cm^{-1} were observed. Heating in the presence of hydrogen (Figs. 1b–1e) caused

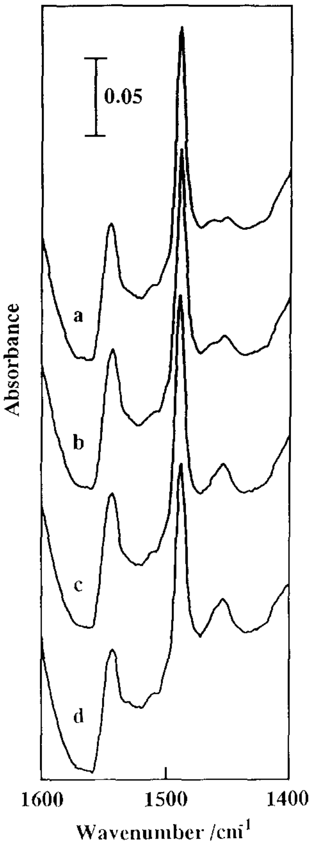

FIG. 2. The IR spectra of pyridine adsorbed on H-ZSM-5 after evacuation at different temperatures: (a) 373 K, (b) 473 K, (c) 573 K, and (d) 673 K. The pretreated sample was exposed to pyridine at 423 K and evacuated at 673 K, then exposed to hydrogen (400 Torr) stepwisely at the temperature from 373 to 523 K by 50-K increments.

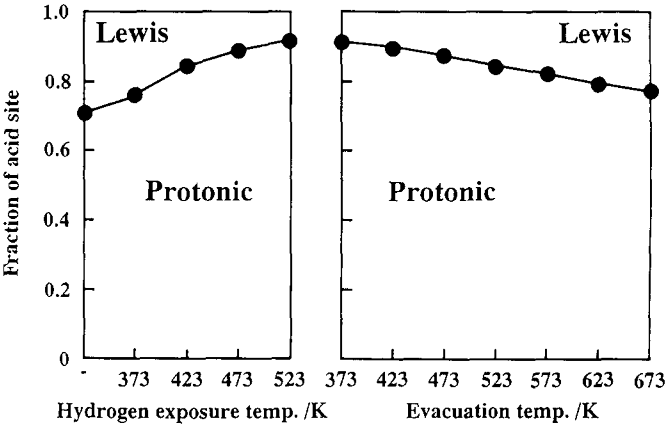

FIG. 3. The fractions of acid sites after heating in the presence of hydrogen (400 Torr) and successive evacuation at different temperatures.

the peak intensity at 1440 cm^{-1} (due to coordinated pyridine) to decrease and those at 1490 and 1540 cm^{-1} (due to pyridinium ion) to increase. This result strongly indicates that the formation of the protonic-acid sites originating from molecular hydrogen on the surface of the metal-free H-ZSM-5 catalyst.

The IR spectra of adsorbed pyridine on the H-ZSM-5 followed by evacuation at different temperatures, which were measured successively after heating in the presence of hydrogen at 523 K, are shown in Fig. 2. Evacuation caused the peak intensity at 1440 cm^{-1} to increase and those at 1490 and 1540 cm^{-1} to decrease. The initial IR spectrum (before heating in the presence of hydrogen, Fig. 1a) almost recovered by evacuation at 673 K (Fig. 2d). This implies that the hydrogen-induced modification of the acid properties of the H-ZSM-5 catalyst is reversible.

The fractions of protonic and Lewis-acid sites after heating in the presence of hydrogen and evacuation at different temperatures are shown in Fig. 3. The initial fraction of the protonic-acid sites was ca. 70%. The dominance of the protonic-acid sites on the surface of the H-ZSM-5 catalyst with a large Si/Al ratio has been already reported by Sayed *et al.* (*5*). On heating in the presence of hydrogen, the fraction of the protonic-acid sites increased and that of the Lewis-acid sites decreased. By evacuation, the hydrogen-induced acid properties of the H-ZSM-5 catalyst was recovered its original state. The acid properties of the H-ZSM-5 catalyst dynamically change with heating in the presence of hydrogen and evacuation. However, the degree of fractional change of the acid sites occurring on the H-ZSM-5 catalyst was smaller than that occurring on the Pt/SO_4^{2-}–ZrO_2 catalyst, where the hydrogen molecule was converted into the protonic-acid sites via a hydrogen spillover mechanism (*13*).

Since the H-ZSM-5 catalyst used in the present study contained 3640 ppm iron, the same type of experiment was performed on the other H-ZSM-5 catalyst which contains 360 ppm iron and is commercially available. The result was essentially the same, regeneration of protonic-acid sites being observed on heating in the presence of hydrogen.

The above results clearly demonstrate that the activation of the hydrogen molecule into the protonic-acid sites occurs on the metal-free H-ZSM-5 catalyst. It has been reported that the metal-free zeolites are capable of activating the hydrogen molecule (*14, 15*). The activation of the hydrogen molecule on the metal-free H-ZSM-5 catalyst might occur on the polar aluminosilicate surface and/or the electrostatic field within the zeolite cavities (*16*).

Sano *et al.* have reported that the metal-free H-ZSM-5 can hydrogenate ethylene into ethane at 623–823 K in the presence of molecular hydrogen (*17*). The ethylene hydrogenation activity of H-ZSM-5 was greatly enhanced by the hydrogen molecule; the activity was scarcely observed when the reaction was carried out in the presence of helium. This observation by Sano *et al.* indicates that the metal-free H-ZSM-5 can activate the hydrogen molecule and the activated hydrogen can hydrogenate ethylene into ethane. Recently, Kanai *et al.* have commented on the mechanism of ethylene hydrogenation over the metal-free zeolites and suggested the important role of the protonic-acid sites of the zeolites (*3*). According to Kanai *et al.*, the ethylene hydrogenation over the metal-free zeolites proceeds via a pentacoordinated carbocation intermediate which is formed by the insertion of a hydrogen molecule into the ethyl carbenium ion. The hydrogen activation into protonic-acid sites observed in this study might correspond to the higher ethylene hydrogenation activity of the metal-free H-ZSM-5 catalyst in the presence of molecular hydrogen (*17*). The nature (structure and reactivity) of the new protonic-acid sites originating from molecular hydrogen and hydrogen activation mechanism (mode) over the metal-free H-ZSM-5 catalyst are still matters for further investigation.

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Received February 26, 1992; revised June 25, 1992

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