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Hydrocarbon Reformer Trap by Use of Transition Metal Oxide-Incorporated Beta Zeolites

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Abstract The concept of a hydrocarbon reformer trap is proposed as a novel technology for cleaning up automobile emissions. Zeolite beta with/without metal species such as iron, manganese, or cobalt is synthesized through a solid phase transformation of mesoporous (metallo)aluminosilicate MCM-41 along with tetraethylammonium cations for structure direction to zeolite beta. The microporosity of zeolite functions as a hydrocarbon trap, and the metal species inside the pores provide a reforming site.

Keywords Hydrocarbon reformer trap · Zeolite beta · Oxidation · Acidity · Automobile catalyst

1 Introduction

Automobile emissions containing unburned hydrocarbons, carbon monoxide, and nitrogen oxides still constitute one of the most significant impacts on the environment and on human society. In order to meet strict emission regulations, three-way catalysts (TWC) have been developed and used on cars with gasoline-burning engines [1]. Since the first introduction of emission control devices in automobiles in the 1970s, much effort has been made to continuously improve automotive catalysis in order to satisfy the stricter legislation regarding engine emission control [2]. However, it is sometimes accepted that more than 70% of the total amount of emitted hydrocarbon is released at the engine's initial running period, that is, within the first 30 s to a few minutes following the engine's start-up, the so-called cold start, when the TWC is inactive [3].

In order to assist the ability of TWC especially against hydrocarbons during cold start, a well-known process called hydrocarbon (HC) trap has been adopted. In this system, microporous and crystalline zeolites are utilized because of their thermodynamic affinity to HCs. Many reports has focused on the trapping properties of silicalite [4], ZSM-5 [5, 6], beta [5, 7], Ag-ZSM-5 [8], mordenite [9], and faujasite [6]. In devices using these elements, hydrocarbons are trapped temporarily, and the HC molecules are gradually desorbed out of the porous structure accompanied by the increasing temperature of the exhaust. Therefore, this system shows a novel concept of catalysis, by dividing the catalytic process into diffusion, adsorption, and a surface reaction, along with a time axis. When we investigate a catalyst, we have to consider two types of time: one is contact time during which the catalyst performs at its optimum if the surface reaction limits the intrinsic reaction rate, and the other is the life time during which the catalyst shows its original activity. In the case of the hydrocarbon trap, another time factor must be taken into account: transient holding time. The longer the HC is held, better the HC trap system performs, because the TWC needs time to become activated by heat. Previously, we have found that SSZ-33, a new type of zeolite which is composed of an interconnected pore system of 10- and 12-membered rings, requires a longer time to diffuse throughout the crystal [10]. In this case, controlling the molecular traffic in the interior of the zeolite crystal might be a uniquely effective way to contain HCs. By use of SAPO, silicoaluminophosphate series zeolitic microporous materials, we have found that smaller exit pores resulted in

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better performance from the viewpoint of diffusion through the crystal, though the adsorption capacity was lower. On the other hand, larger pores were more effective from the viewpoint of adsorption amount [,though] the trapped HC eluted more quickly out of the particles [11]. Consequently, a mixture of micropores having different sizes in SSZ-33 is considered to demonstrate a unique HC holding capacity.

Here we define the concept of an HC reformer trap, in reference the HC trap. Nothing happens to HC while inside the micropores of zeolitic HC trap materials; therefore, the trapped HC is released as it reaches higher temperatures. As a result, the task of the TWC is not changed, or rather a larger amount of HC has to be treated all at once. Therefore, the same or a higher level of oxidation and reduction of the emitted components is required of the TWC. In contrast, HC is reformed to an active species via isomerization, cracking, or partial oxidation by the reformer trap. Between the low-temperature stage of HC adsorption and the higher-temperature stage of desorption, such HC reforming is performed inside the microporous structure of the zeolite trapping materials. This system will lighten the duty of the TWC, and lessen the quantity of precious metals contained in the TWC's construction. A similar effect has been previously proposed using a physical oxide mixture of Cr, Co, Fe, and Al, and ZSM-5 zeolite [12]. In our case, two functions of trapping and reforming HC are performed in identical micropores of zeolite beta, which is expected to increase the reaction rate because of the concentrated HCs within the confined microporous structure. Although silver loaded H–Y zeolite has been shown to be effective for a dual functional adsorbent/catalyst system [13], silver and Y with a high Al content are known to be weak against (hydro)thermal conditions, and degradation might occur with their repeated usage.

Here we will discuss the preliminary results of an HC reformer trap system using high silica beta zeolite, which is a candidate for a practical use in an HC trap system, along with metal oxides. Toluene and 2,2,4-trimethylpentane are used as typical hydrocarbons, which are present in high concentrations in gasoline engine-based exhaust.

2 Experimental

2.1 Preparation of Metal-Containing MCM-41

Aluminum-containing MCM-41, Al-MCM-41, was prepared as an aluminosilicate source for Al-beta. Cetyltrimethylammonium bromide, CTAB, was used as a templating surfactant. Tetramethylammonium hydroxide was selected as an alkaline source. The chemical composition of hydrogel for Al-MCM-41 was SiO_2: $0.01Al_2O_3$: 0.61CTAB: 0.5TMAOH: $60H_2O$. The resultant SiO_2/Al_2O_3 ratio was 100.

When incorporating metal species in the structure, acetate salts were used as a starting reagent of each metal species as Me^{2+}. Iron, manganese, and cobalt were selected since these metal oxides have been reported to show high catalytic performances in the elimination/partial oxidation of volatile organic compounds or diesel soot at relatively low temperatures [14–16]. The chemical composition of hydrogel for Me-Al-MCM-41 is SiO_2: $0.01Al_2O_3$: 0.02MeO: 0.61CTAB: 0.5TMAOH: $60H_2O$. The resultant SiO_2/Al_2O_3 and Si/Me ratios were 100 and 50, respectively. When pure silica Si-MCM-41 and Me-Si-MCM-41 were prepared, the same procedure except for the addition of the Al source was conducted.

The hydrogel containing silicate-surfactant compound was heated at 100 °C in a 100 cc polypropylene bottle without stirring, then filtered, washed, and dried at 100 °C overnight. The X-ray diffraction pattern of the obtained precipitate was collected by an RINT 2100 (Rigaku) to confirm the mesophase. The mesoporous aluminosilicate material was calcined at 540 °C for 12 h to remove the templating CTAB. Then the mesostructural periodicity of the material was confirmed again by the XRD pattern and the nitrogen adsorption isotherm at the temperature of liquid nitrogen, 77 K. Prior to the adsorption of nitrogen, the mesoporous samples were heated at 150 °C while the microporous samples were heated at 300 °C in order to allow dehydration. The isotherms were recorded by a Belsorp 28 SA (Nippon Bel Corp.).

2.2 Synthesis of Metal-Loaded Beta Zeolite Through the Phase Transformation of Metal-Containing MCM-41

The phase transition of amorphous MCM-41 into crystalline zeolite was carried out according to the method reported by Takewaki et al. [17]. Three-tenths g of 35% tetraethylammonium (TEA) hydroxide aqueous solution was dropped on 0.1 g of the calcined Me-Al-MCM-41 samples prepared as described above. The samples were dried at room temperature for more than 12 h. The dried sample was put into a 50 cc SUS Teflon-lined container, and kept at 150 °C under autogenous pressure without the addition of water unlike the dry gel conversion method [18]. After more than 5 days, or typically 7 days, the sample was cooled down and XRD measurement was performed to confirm its crystallinity to zeolite beta. The zeolites obtained were then calcined at 540 °C for 5 h to remove TEA cations occluded in the micropores. The microporosity and crystallinity of the calcined samples were evaluated by nitrogen adsorption and XRD. The morphology of the samples was observed by a FE-SEM

S-4500 (Hitachi). UV–vis spectra were recorded by a JASCO V-650 in order to determine the coordination state of the metals involved in the samples.

2.3 Evaluation of the HC Reformer Trap by the Use of Toluene and 2,2,4-trimethylpentane

Acting as an HC trap, the microporous samples trap HCs and hold them until they reach high temperatures. Furthermore, as an HC reformer trap, they are expected to show catalytic activity regarding the trapped HCs activated under such a low temperature before their passage through the micropores. Here, toluene and 2,2,4-trimethylpentane (TMP) were selected as a standard aromatic compound and as an alkane in automobile exhaust. Toluene is known to be difficult to pyrolyze, while TMP is difficult to oxidize, so that they are released intact in automobile exhaust even though they pass through a TWC. A total of 50 mg of the zeolite sample were placed in a glass tube with a 4 mm inner diameter, heated at 300 °C in the chamber of a gas chromatograph in order to remove physisorbed water, and cooled to 50 °C. Toluene or TMP was pulsed until the peak area of the thermal conductivity detector (TCD) signal at the sample's exit was saturated. The sample was flashed for 30 min by helium to remove weakly-adsorbed hydrocarbons. The temperature of the chamber was then ramped at 20 K/min and the eluted hydrocarbons were monitored by the TCD directly connected from the glass tube without a gas chromatograph (GC) column. He as the carrier gas was flown at the rate of 50 cm^3/min. To identify the eluted hydrocarbons, the eluted gas from the TCD outlet was inserted into a flame ionization detector (FID) inlet directly, and monitored with GC column filled with α-Al_2O_3, whose species were evolved.

As a reference material, H-beta with Si/2Al ratios of 39, 110, and 1540 were used as supplied from Tosoh Corp. Fe ion exchange was also carried out with the H-beta having a Si/2Al of 39 using an $Fe(NO_3)_3$ aqueous solution aimed at the level of 10 or 100% ion exchange as $[Fe(OH)_2]^+$, denoted as Fe(10)/H-beta and Fe(100)/H-beta, respectively.

3 Results and Discussion

Figure 1 shows typical low-angle XRD patterns of the metallosilicate samples. All the samples showed three apparent diffraction patterns: a maximum diffraction appeared at around 2 deg by CuKα radiation, and two other peaks were detected at around 3.5 and 4 degs. These peaks could be assigned as 100, 110, and 200 of the 2d-hexagonal mesophase, meaning that mesoporous (metallo)aluminosilicate MCM-41 was obtained. A slight difference in diffraction intensity was observed, though it strongly depended on the preparation procedure, and we could finally obtain a sample with much higher periodicity, regardless of the metal species.

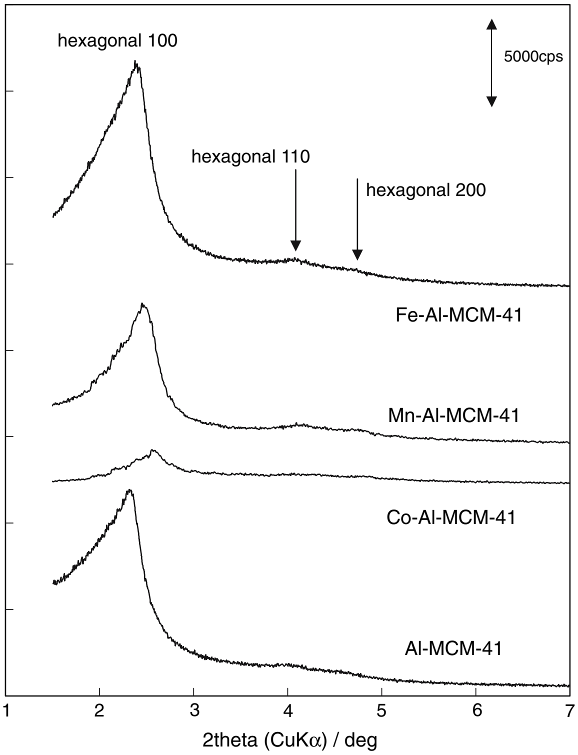

Fig. 1 XRD patterns of the products synthesized in SiO_2–Al_2O_3–MeO–CTAB–H_2O system

Diluted TEAOH aqueous solution was then dropped on calcined Me-Al-MCM-41, and the samples were dried at room temperature, followed by heating at 150 °C for several days under autogenous pressure. The XRD patterns of the products obtained after 7 days revealed that the mesophase was transformed into microporous, crystalline beta zeolite, as summarized in Fig. 2. The diffraction at 7–8 deg was a characteristic broad peak, indicating that the sample could be assigned as BEA* which involves polymorphs A and B. The peaks at 21 and 22 degs were not as clearly split compared to commercialized aluminosilicate or high silica beta zeolites. Like the zeolite sample synthesized by the dry gel conversion technique [18], the beta zeolites obtained here are comprised of tiny crystallites.

The nitrogen adsorption isotherm of the beta zeolite presently obtained also showed its porous properties. Figure 3 exhibits the isotherms of Fe-Al-beta obtained by solid state phase transformation from Fe-Al-MCM-41, and Fe ion-exchanged beta zeolite, Fe/H-beta. The latter showed a type I isotherm, typically observed on microporous materials. Capillary condensation of nitrogen occurred at high relative pressure on the former sample, which is due to its interparticle mesoporous structure. SEM images of these beta zeolites are shown in Fig. 4. Amorphous-like particles without any uniformity in size or morphology

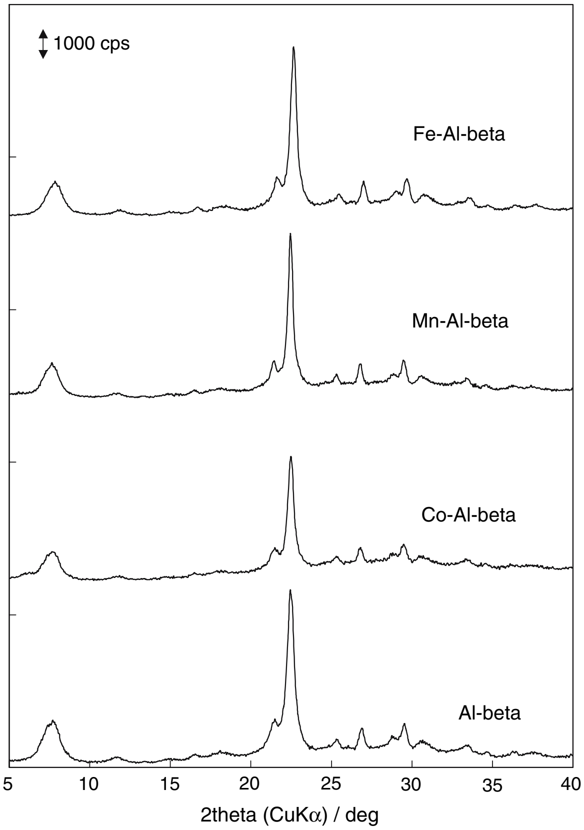

Fig. 2 Typical XRD patterns of the products by solid state phase transformation at 150 °C for 7 days of Me–Al-MCM-41 immersed with TEAOH aqueous solution

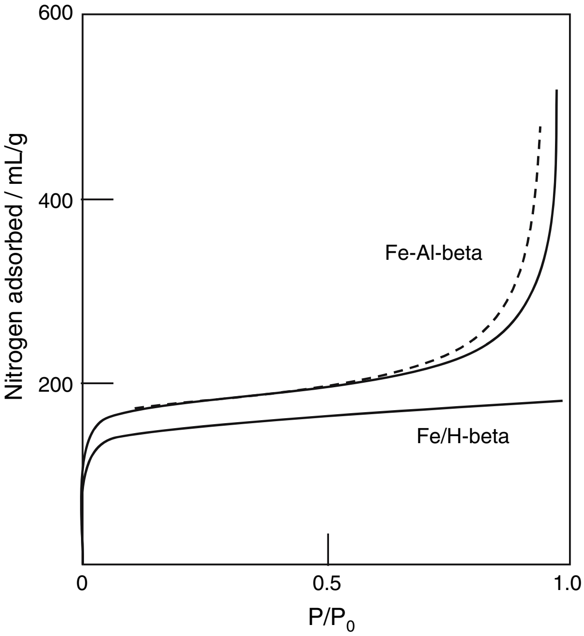

Fig. 3 Nitrogen adsorption isotherms of Fe–Al-beta synthesized from Fe–Al-MCM-41 and Fe ion exchanged H-beta

were given in Fe-Al-beta derived from Fe-Al-MCM-41. The morphology of amorphous mesoporous silica might be preserved during the solid state phase transformation. A lesser amount of water than that in the steam-assisted crystallization technique [18] was utilized when the transformation was carried out. Saturated water vapor plays a critical role in changing the morphology of the silica source. In contrast, particles having a uniform size of 500 nm were observed in the Fe/H-beta. In regard to surface morphology, Fe–Al-beta was composed of tiny, discrete particles 20 nm in size, while 30–50 nm particles were agglomerated into a larger clusters in the case of Fe/H-beta. The size of a particle deposited from a homogeneous solution is thermodynamically determined by the balance of the surface tension of the silicate in aqueous media according to Ostwald ripening. During the solid phase transformation, a continuous liquid phase does not exist in the synthesis medium; therefore, the size of this particle size would be totally different from the hydrothermally synthesized one. As observed in the sample crystallized by the dry gel conversion method [18], a higher concentration of nuclei in the dried solid phase leads to rapid crystallization into a tiny particle.

The trapping capacity of HCs was evaluated for Me–Al-beta using the temperature-programmed desorption of toluene, which is commonly used as a test for HC traps. The desorption profiles of toluene emitted from the Me–Al-beta samples along with H-beta are illustrated in Fig. 5. The elution curve from H-beta was observed to be steep as reported previously [10]. Broad spectra were, on the other hand, obtained from Me–Al-beta samples. HC trapping capacity was estimated based on both by the amount of trapped HC, and by the temperatures where toluene starts to desorb and where desorption ends. Typically, the amount of adsorbed toluene was 0.11 cm^3 (STP) per gram of Fe–Al-beta. The amount of adsorbed HC on the trap materials relates closely to the micropore volume, decreasing with the decrease in volume caused by hydrothermal treatment for example [10, 11]. The adsorption capacities of H-beta and Fe–Al-beta appear comparable, with the micropore volumes of those samples being 0.13 and 0.15 cm^3 per gram, respectively. Trapping capacities differed among the metal species involved in MCM-41, and Fe-Al-beta showed a stronger capacity to trap toluene among Me–Al-beta. It is interesting to note that elution from Fe–Al-beta was slow, and that half of the adsorbed toluene was retained in the micropores until temperatures reached as high as 200 °C. Fe–Si-beta from Fe-containing pure silica Si-MCM-41 was also tested for HC trap, but such a broad desorption profile was not obtained. Therefore, acidity is quite important to trap and hold HCs until high temperatures are reached under our experimental conditions. Niwa's group has recently reported that Na^+

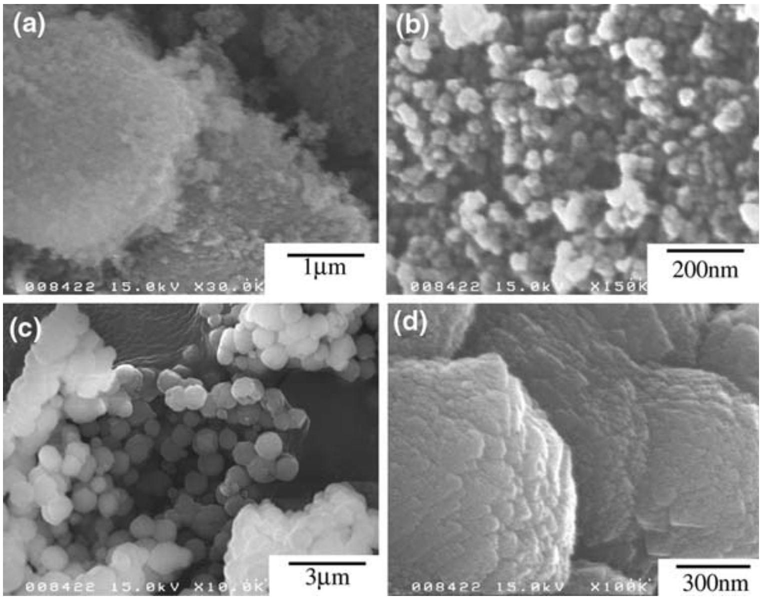

Fig. 4 SEM images of (**a**) Fe–Al-beta from Fe–Al-MCM-41, (**b**) the higher magnification of (**a**), (**c**) Fe/H-beta, and (**d**) the higher magnification of (**c**)

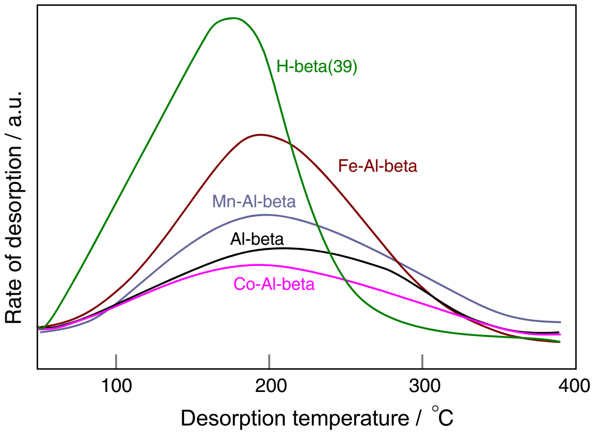

Fig. 5 Profiles of temperature-programmed desorption of toluene from H-beta and Me–Al-beta

plays a quite interesting role in holding HC due to the electrostatic interaction with aromatic pi electrons [19]. High silica zeolites are applied in such an adsorbent owing to their hydrophobic interaction and micropore filling. In any case, some interaction between adsorbent and adsorbate is required to hold HC in order for the HC trapping material to fulfill one of its roles.

After the evaluation of HC trapping capacity, the color of all the samples turned gray or black. These samples were oxidized in a TG-DTA chamber under a flow of air, but no obvious weight loss or exothermic peak were detected even though the color of the sample was returned to as it was before the trapping experiment. This means that the color of the sample after its use as an HC trap did not derive from carbon deposited on the sample, but from the change in the state of the metal oxide included in the sample.

The elutant composition was monitored by a GC-FID directly connected to the TCD detector used in the former experiments. At a starting temperature of 50 °C, a small amount of toluene, which can be recognized as weakly physisorbed toluene, was detected. The peak intensity of toluene in the exhaust gas increased with increasing the temperature, and at 200 °C a trace amount of elutant at a much later time of retention could be detected by the GC column of FID, indicating a highly polarized product. At a higher temperature the peak corresponding to the product was then diminished at all but toluene remained. Judging from the retention time, the product was assigned as benzaldehyde, an oxidized product of toluene. Niwa's group has reported that benzaldehyde and benzoic acid were detected when a Pd catalyst was utilized for the oxidation catalyst of toluene along with Na-zeolite as the toluene trapping material [20], so that benzaldehyde could be regarded as the oxidized product of toluene on Fe-Al-beta. Further oxidation to CO_2 might take place at higher temperatures, which was not detectable by the GC-FID.

In order to evaluate the oxidation ability of Fe-Al-beta, temperature-programmed reduction by hydrogen was conducted on the samples, where various types of Fe species were involved. As can be seen in Fig. 6, three types of hydrogen consumption were observed on the sample; the first started at 200 °C with a maximum reduction rate at around 300 °C, a second sharp peak was observed between 300 and 400 °C, and a last one at over 800 °C. Fe–Al-beta synthesized from Fe–Al-MCM-41 showed the three peaks with the major species being the last, most difficult to reduce, while Fe/H-beta possessed two relatively reducible species without the last one which was observed on Fe–Al-beta. The major reduction peak was detected at 800 °C on

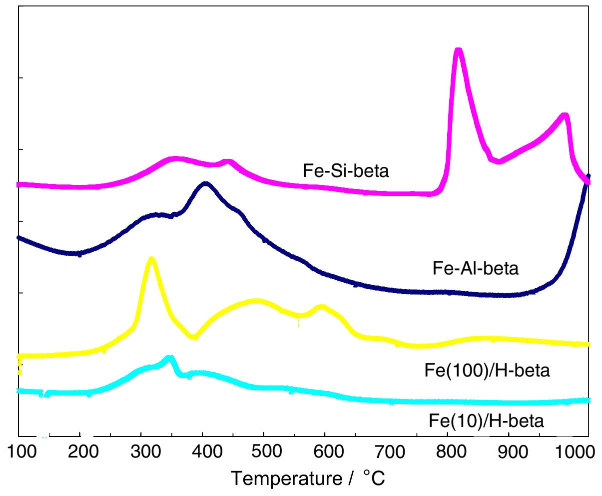

Fig. 6 Temperature programmed reduction of Fe–Al-beta, Fe–Si-beta, and Fe/H-beta at the ion exchanged levels of 10 and 100%. 5% H_2/Ar was used as a reductant

Fe–Si-beta from Fe–Si-MCM-41. The color of the samples changed after the TPR measurements; Fe–Al-beta and Fe–Si-beta were gray, while Fe(100)/H-beta was dark brown and Fe(10)/H-beta was pale. Judging from these results along with those reported in the literature, the most common and reducible Fe species was assigned as Fe_2O_3 [21, 22], and Fe_3O_4 was formed by the reduction. This was followed by the reduction of Fe in the ion-exchanged site of zeolite, Fe^{3+} to Fe^{2+}, which was detected mainly on Fe/H-beta, and also to a minor extent on Fe–Al-beta. The Fe species inside the zeolite framework was the most difficult to reduce and was finally reduced to FeO, which is black in color. In particular, the Fe ion-exchanged species in zeolite is known to be difficult to fully reduce to metal Fe [22]; therefore, Fe^{2+} might be stabilized on Fe/H-beta. The result that toluene was partially oxidized at a relatively low temperature of 200 °C indicates that the toluene trapped inside the micropores of Fe–Al-beta is oxidized by Fe_2O_3 on the extraframework of beta zeolite.

Isooctane, 2,2,6-trimethylpentane (TMP), is known as an additive to control the total octane number of gasoline. In turn it is often recognized as another target to be trapped because of its low reactivity and conversion by use of TWC. Figure 7 summarizes the desorption profiles of TMP from the H-beta samples with various Al contents, along with Fe–Al-beta from Fe–Al-MCM-41. In every case, the desorption profile appears to contain two kinds of elutant: one is broad and starts to desorb from a low temperature up to more than 200 °C, while the other is sharp at around 150 °C. Fe–Al-beta showed a larger and wider desorption profile than any other sample, possibly due to the physisorption of TMP in its wider mesopores. The amount of adsorbed TMP was 0.30 cm^3 (STP) per gram of Fe–Al-beta, which was a much higher value than that of the micropores.

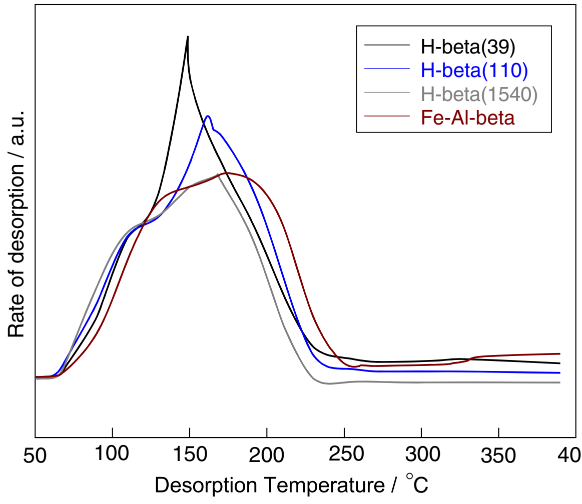

Fig. 7 Desorption profiles of 2,2,4-trimethylpentane from H-beta with Si/2Al ratios of 39, 110, and 1540, and Fe–Al-beta synthesized from Fe–Al-MCM-41

The component of the elutant was detected as a function of temperature during desorption. Isomolar components of isobutane and isobutene, the cracked products of TMP, were detected along with a minor propylene and isopentane, at the temperature where the sharper elution was observed. At other temperatures, only TMP was detected as a component of the elutant. The cracking of TMP to isobutane and isobutene was derived from the catalytic activity and acidity of the trapping material, since the cracked products apparently decreased when the Si/Al ratio increased. This indicates that acidity enhances not only the trapping capacity till higher temperatures, but the cracking activity of the trapped HC to lighter HCs.

The catalytic activities of Pt/Al_2O_3 and Pd/Al_2O_3 for the oxidation of toluene and benzaldehyde are demonstrated in Fig. 8. It was observed that benzaldehyde was oxidized

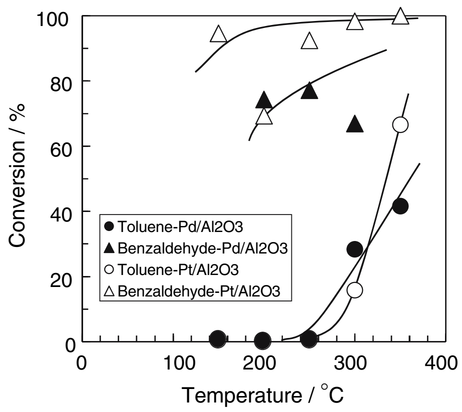

Fig. 8 Catalytic activities of Pt/Al_2O_3 (open) and Pd/Al_2O_3 (closed) for oxidation of toluene (circle) and benzaldehyde (triangle)

completely at a much lower temperature of 200 °C on Pt/Al_2O_3 than was toluene which started to oxidize at 300 °C, a difference of almost 100 K. Pd/Al_2O_3 showed slightly lesser catalytic performance for total oxidation, but even though benzaldehyde was not totally removed, its oxidation was larger than that of toluene. The catalytic activities of Pt and Pd were also investigated using three HCs of TMP, isobutane, and isobutene, and among them isobutene can be oxidized at a lower temperature than can isobutane and TMP on Pt/Al_2O_3. From these results, Fe–Al-beta and acidic beta can be concluded to perform as a HC reformer trap; the trapped HC was accelerated to react in the limited space of micropores to form more reactive HCs, which can be easily removed by oxidation on the three-way catalyst. This is the meaning of "reformer", which catalyzes the trapped HC to obtain a more reactive one for a subsequently easier reaction.

4 Conclusions

The concept of an HC reformer trap is proposed in this study; HC is temporally stored in the micropores of zeolite, and within the pores the HC is partially reformed, oxidized, or cracked, into a more reactive HC species, and is then released. Mesoporous silica containing oxides such as Co, Mn, or Fe is utilized as resources for Si, Al, and metal oxides for zeolite beta. Calcined Me-MCM-41 is immersed into diluted TEAOH aqueous solution, which directs to beta zeolite. A solid state phase transformation without the addition of water, as is the case with the dry gel conversion technique, is carried out to successfully obtain metal oxide-incorporated beta zeolite. The trapped toluene and TMP inside the micropores of Me-beta are confirmed to be reformed into benzaldehyde and isobutene/isobutane, respectively. TWC catalyzes the oxidation of the reformed HCs at much lower temperatures than oxidation of HC as trapped, indicating that Me-beta can perform as an HC reformer trap.

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