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In situ infrared study of *n*-heptane isomerization over Pt/H-beta zeolites

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Abstract

The isomerization of *n*-heptane over hydrogenated (H-) and Pt-loaded (Pt/H-) beta zeolites was observed directly by in situ infrared spectroscopy for investigation of the reaction mechanism and coking process. Carbonaceous species produced in the reaction are identified as either highly branched polyolefins (1485 cm^{-1} band) or coke (1600 cm^{-1}). The former can be readily removed by O_2 treatment at moderate temperatures (>573 K), whereas complete removal of the latter requires higher temperatures (>723 K). The formation of coke is successfully inhibited by the presence of H_2 in the reaction stream. The hydrogenation and dehydration functionality of Pt particles in this catalyst system has been confirmed through H/D isotope exchange experiments.

Keywords: In situ IR; *n*-Heptane; Isomerization; Coke; Isotope exchange

1. Introduction

A fundamental problem in heterogeneous catalysis research is the difficulty in performing in situ measurements of the reaction system. Such measurements involve monitoring the reactants in the gas stream under appropriate temperatures and pressures. It is accepted that characterization results obtained under working conditions provide invaluable information for understanding the reaction process. Despite great efforts in recent years to identify the active sites of catalysts and elucidate the reaction mechanism by in situ spectroscopy, further application of the spectroscopic approach has been hindered by the lack of suitable spectroscopic cells and the complexity of data analysis [1].

Among various characterization techniques used to date, in situ infrared (IR) spectroscopy has attracted much attention, particularly for the zeolite and zeolite/adsorbate systems, as a facile and sensitive technique for studying zeolite acidity, the nature of adsorbed species, and the interaction between reactants and catalysts [2]. In situ nuclear magnetic resonance (NMR) analysis, another powerful characterization method, suffers quenching problems and thus is limited in the range of applicable temperature. In contrast, in situ IR can be used over a broad temperature range, from temperatures suitable for the study of cryogenic interaction between probe molecules (e.g., CO or N_2) with zeolite acidity to those of industrial processes, often above 573 K [3,4]. Some interesting applications of in situ IR spectroscopy have been reviewed recently [5].

The isomerization of *n*-heptane over Pt-loaded beta zeolites has become more important as the demands for octane-enhancement processes have increased. The catalytic isomerization of *n*-heptane, with a research octane number (RON) of zero, into more valuable products, such as mono-branched isomers (42–65 RON) and multibranched isomers (80–112 RON) using a solid catalyst remains an important research topic in industrial refinement [6]. In the isomerization process, *n*-heptane is converted in the presence of H_2 to suppress catalyst deactivation and increase the yield of desired branched products. Matsuda et al. recently examined various catalysts in *n*-heptane isomerization and found that Pt/H-beta zeolite catalyst exhibited the most promising catalytic performance of those tested, possibly due to the unique structure of three-dimensional interconnected channels of BEA-type zeolite [7]. With respect to the mechanism of action, it has been suggested that the skele-

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tal isomerization of alkanes proceeds over Pt/zeolites through a bifunctional reaction mechanism involving Pt-catalyzed dehydrogenation of alkane to alkene and reversible hydrogenation of alkene to alkanes, where the acidity of the zeolites promotes protonation of the intermediate alkene and subsequent rearrangement [8]. But recent experiments have cast doubt on this model, suggesting instead that the reaction is initiated solely by Brønsted acidity through carbocation, and that the Brønsted acidity facilitates subsequent rearrangement while Pt catalyzes alkene hydrogenation [9].

Various characterization methods have been applied to investigate this reaction system [10,11]; however, there are no reports of in situ IR studies of *n*-heptane isomerization over beta zeolites, despite the advantages of such a sensitive vibrational spectroscopy technique in gaining a more comprehensive understanding of the reaction mechanism. As Pt/beta zeolite catalysts are increasingly used for selective catalytic reduction of NO_x with hydrocarbons, knowledge of the intrinsic properties of Pt/H-beta zeolite is expected to aid the understanding of other reactions [12].

The present work used in situ IR spectroscopy to study the isomerization of *n*-heptane over H/beta zeolite and the Pt/H-beta zeolite catalyst in the high-temperature reactant stream (to 723 K). The investigation focuses on the inhibition of coke formation by the presence of H_2 and the role of Pt particles in the isomerization process.

2. Experimental

2.1. Catalyst preparation

NH_4-beta zeolite (Si/Al = 25) was kindly provided by Zeolyst (USA). H/beta zeolite was prepared by calcination of NH_4-beta zeolite at 773 K for 5 h. The Pt/H-beta zeolite catalyst was prepared by a conventional aqueous ion-exchange method involving the addition of 5 g of NH_4-beta zeolite to 100 mL of dilute aqueous tetraammineplatinum(II) chloride $[Pt(NH_3)_4]Cl_2$ solution containing 25 mg of Pt. The solution was stirred vigorously at 373 K for 12 h to promote the ion-exchange reaction. The resultant ion-exchanged zeolite was filtered and washed thoroughly with deionized water at room temperature before being dried at 343 K overnight. The dried sample was heated from 273 to 773 K at a rate of 0.5 $K\,min^{-1}$ and then held at the maximum temperature for 5 h. (This slow heating rate was applied to avoid the agglomeration of Pt species and to obtain a good dispersion of Pt particles on the catalyst surface.) Inductively couple plasma optical emission spectroscopy (ICP-OES) confirmed that the catalyst was loaded with 0.5 wt% Pt, as expected. Experience indicates that NH_4-beta zeolite is a better precursor for the ion exchange than H-beta zeolite in terms of dispersion.

2.2. Catalytic reactions

The catalytic isomerization of *n*-heptane was carried out in a U-shaped fixed-bed quartz tube reactor under atmospheric pressure. The catalyst bed was supported in the center of the reactor by quartz wool. Gas flow rates were controlled by mass flow controllers, and the reactor was heated in a furnace. *n*-Heptane was introduced by syringe pump to the reaction feed at a H_2-to-*n*-heptane molar ratio of 5. The contact time (W/F) of *n*-heptane was approximately 3 $g\,h\,mol^{-1}$. The catalyst was reduced under H_2 at 673 K for 1 h before reaction. The reaction products were monitored by gas chromatography (Shimadzu GC-12A) with an ID Petrocol™ DH fused silica capillary column and flame ionization detector. The product selectivity reported herein is based on the carbon mass balance.

2.3. In situ IR characterization

The in situ IR cell used to investigate the reaction mechanism at elevated temperature and pressure is shown in Fig. 1. The cell was fabricated from stainless steel and included two CaF_2 windows in Teflon holders sealed by Kalrez O-rings [13,14]. Four KBr windows were placed inside the cell to minimize dead space, allowing the IR cell to operate as a microreactor with an optical path length of ca. 2 mm. The sample holder was fixed in the center of the cell, with gas inlet and outlet ports located on opposite sides to guarantee exposure of the catalyst sample to the pretreatment gas or reactants. A thermocouple was set in contact with the sample wafer to monitor the cell temperature. The gas inlet port was connected to a gas flow controlled by mass flow controllers, and the gas outlet port was connected to the gas chromatograph for detection of the reaction products. The tubing of the reaction system was heated throughout the reaction, to avoid condensation of heavy product molecules and thereby guarantee complete detection. Such an in situ cell is expected to be suitable for reactions at temperatures up to 773 K and pressures up to 1 MPa. The present measurements were carried out at atmospheric pressure.

Approximately 10 mg of the catalyst was pressed into a self-supporting wafer and mounted in the center of the cell for reaction and IR measurement. All IR spectra were recorded on a Fourier transform (FT) IR spectrometer (JASCO 7300) fitted with a mercury–cadmium–telluride (MCT) detector. The resolution of the spectrometer was 4 cm^{-1} over 64 scans. Before measurement, the wafer was heated at 673 K under H_2 for 1 h to reduce the catalyst and desorb water. The sample was then cooled to the desired reaction temperature and exposed to the flow of H_2/*n*-heptane or He/*n*-heptane at a molar ratio of 5. The flow of H_2 or He was maintained at 6.4 $mL\,min^{-1}$ during IR measurements, which were performed in the reactant atmosphere.

H/D isotope exchange experiments were conducted to investigate the role of Pt particles in the isomerization process. In these experiments, the proton in the zeolite was replaced with deuterium and D_2 was used in place of H_2 as the feed gas. The catalyst, either H-beta or Pt/H-beta zeolite, was first reduced under 50% H_2/He (60 $mL\,min^{-1}$) at 673 K for 2 h, and then exposed to 50% D_2/He (60 $mL\,min^{-1}$) at 673 K for a further 1 h. After the catalyst was cooled to the desired reaction temperature (498–573 K), the sample cell was purged with pure D_2 (60 $mL\,min^{-1}$) for 30 min. The sample was then exposed to

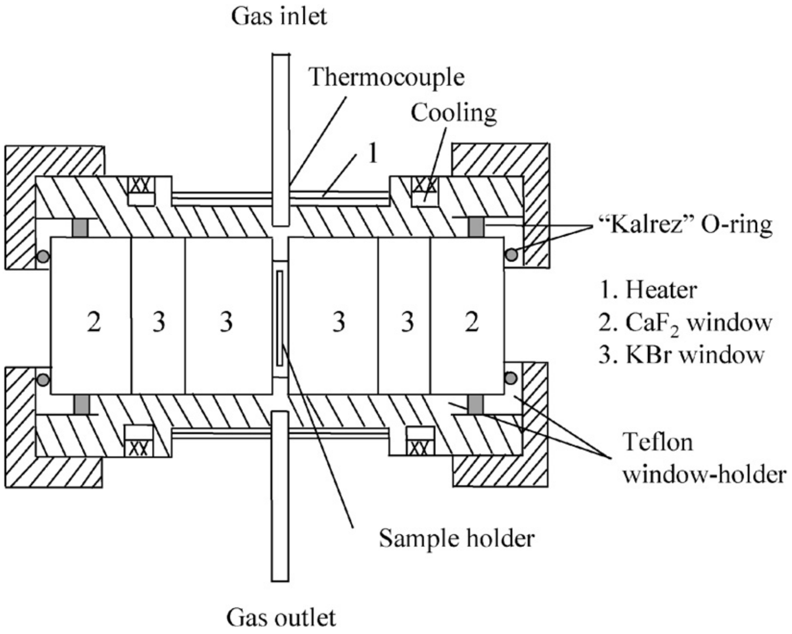

Fig. 1. Schematic view of IR cell for in situ monitoring of flow reactions.

n-heptane flow for reaction measurements (D_2/*n*-heptane = 5; D_2, 6.4 mL min^{-1}).

3. Results and discussion

Fig. 2 shows representative reaction results for the isomerization of *n*-heptane over the nonloaded and Pt-loaded H-beta zeolite catalyst in a fixed-bed reactor. The conversion of *n*-heptane over H-beta zeolite was observed at 523 K and above, affording the desired product (C_7 isomers) and byproducts (propane and butane) due to cracking. The lack of active centers for hydrogenation and dehydrogenation allowed the cracking reaction over acid sites to proceed relatively strongly in the transformation of *n*-heptane over H-beta zeolite. The selectivity for isomers decreased with increasing reaction temperature until only cracking products were observed above 673 K. Over Pt/H-beta zeolite, however, both the conversion of *n*-heptane and the selectivity for isomers were substantially higher, and the reaction proceeded at temperatures as low as 513 K, at which virtually no reaction products were detected over H-beta zeolite. The activity of the Pt/H-beta zeolite catalyst decreased from 40 to 20% in the first hour of reaction, after which the activity remained stable for almost 4 h. The isomerization products were dominant (ca. 80%) in the reaction over Pt/H-beta zeolite, consistent with results reported in the literature [6].

Clearly, the presence of Pt on the H-beta zeolites enhanced the catalytic activity for *n*-heptane isomerization and inhibited the cracking reaction, affording the desired isomers as the major product. The conversion increased to 40% at 593 K with decreasing isomerization selectivity to 50%. Of the isomer products, 2-methyl-hexane constituted the majority (82%), with the remainder (18%) afforded as multibranched isomers. The reaction conditions in the fixed-bed and in situ cell experiments are considered sufficiently similar to allow direct comparison of the above reaction results with the IR results obtained using the in situ cell.

The inset in Fig. 3A shows FT-IR spectra for the Pt/H-beta zeolite at 293 K. Numerous bands due to the stretching vibration of hydroxyl groups are distinguishable in the range of 4000–3200 cm^{-1}. A sharp adsorption band at 3745 cm^{-1}, ascribed to external SiOH groups of beta zeolite, and another broad band centered at 3676 cm^{-1} can be seen. The band at 3676 cm^{-1} is assigned to the hydroxyl groups attached to the extra-framework Al of the zeolite, which possibly act as Lewis acid sites. The band at 3613 cm^{-1} is commonly associated with the Brønsted acid sites of zeolites, assigned to the proton covalently bonded to oxygen-bridging Si and Al in the zeolite.

The function of H_2 in the isomerization of alkanes is an important aspect of the reaction mechanism, and in situ IR measurements provide good information on the adsorbed hydrocarbon species. The effect of H_2 on the surface species on the zeolite under reaction conditions were observed directly by exposing Pt/H-beta zeolite to *n*-heptane at room temperature, followed by purging with H_2 or He at elevated temperature. Differential spectra, obtained by subtracting the prereaction spectra, are shown in Fig. 3. Negative bands indicate consumption of the corresponding functional group, and positive bands correspond to generated adsorbed species. The interaction of *n*-heptane over Pt/H-beta zeolite at room temperature results in negative bands for hydroxyl groups (3500–3800 cm^{-1}), indicating hydroxyl consumption, and a complex feature between 2800 and 3000 cm^{-1} accompanied by the appearance of bands at 1457 and 1379 cm^{-1}. The overlapping bands at 2800–3000 cm^{-1} are associated with the C–H bond stretching vibrations of $-CH_3$ and $-CH_2-$ groups, whereas the bands at 1457 and 1379 cm^{-1} are related to the C–H bond deformation vibrations of $-CH_2-$ and $-CH_3$ [15]. Thus, it is concluded that *n*-heptane-related hydrocarbon species are present on the Pt/H-beta zeolite catalyst after exposure to *n*-heptane. This conclusion is supported by the

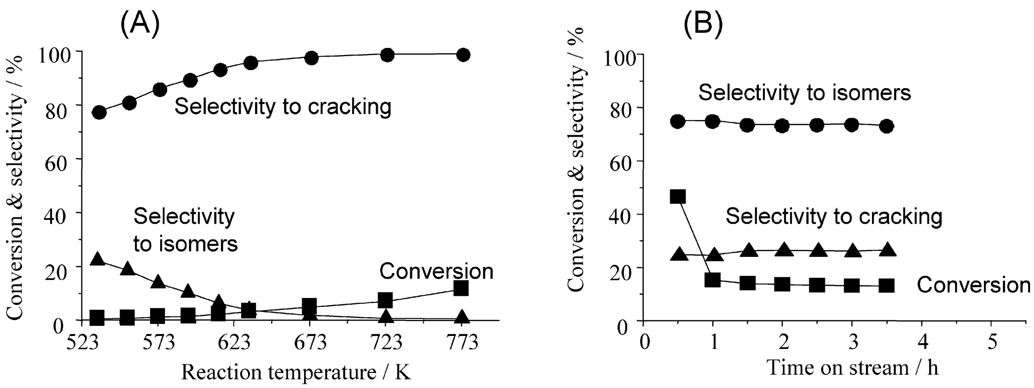

Fig. 2. Comparison of reaction performance of H-beta and Pt/H-beta zeolite catalysts: (A) temperature dependence of reaction over H-beta at 1 h of the reaction, and (B) time course of reaction over Pt/H-beta at 513 K.

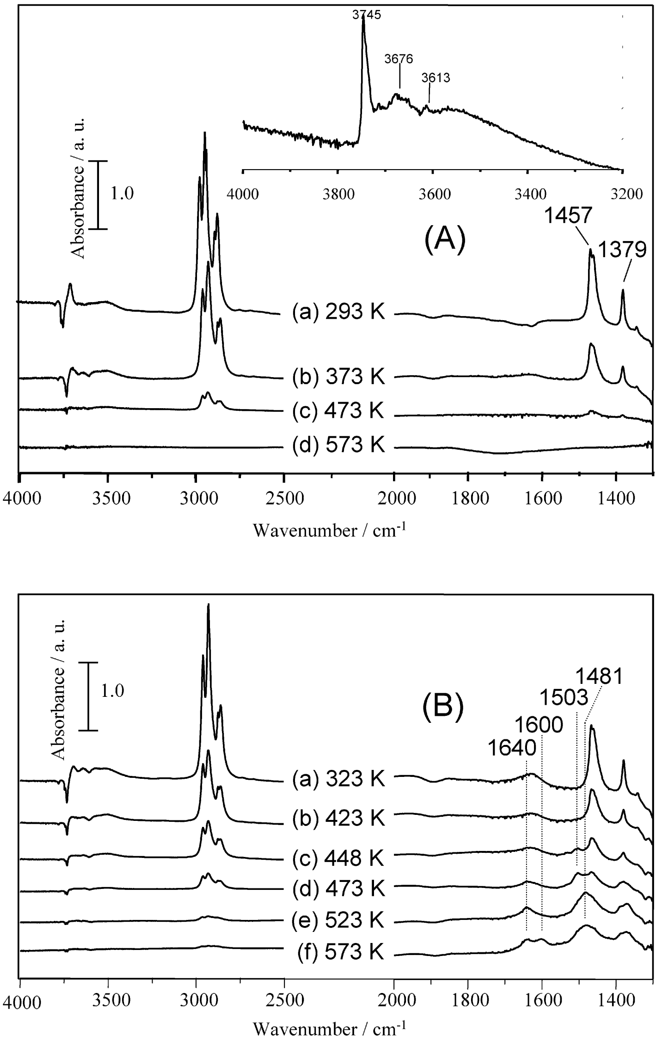

Fig. 3. Comparison of in situ IR spectra of *n*-heptane adsorbed on Pt/H-beta catalyst under (A) H_2 flow at (a) 293, (b) 373, (c) 473, and (d) 573 K, and (B) He flow at (a) 323, (b) 423, (c) 448, (d) 473, (e) 523, and (f) 573 K. *n*-Heptane was adsorbed at room temperature followed by exposure to H_2 or He flow at the same temperature then gradually heating of the sample at the indicated temperatures. The inset in the figure (A) shows the zeolite spectrum at 293 K after dehydration. Differential spectra are obtained by subtracting the corresponding zeolite spectra at the reaction temperatures.

appearance of a broad band at 3500 cm^{-1} assigned to hydrogen bonding between the hydroxyl group and the adsorbed hydrocarbons [16]. The intensity of the characteristic bands associated with –CH_3 and $\text{–CH}_2\text{–}$ decrease with increasing temperature under H_2, indicating a decrease in the amount of adsorbed *n*-heptane-related species. No adsorbed species were detected on the catalyst at 573 K, suggesting complete disappearance of the adsorbed *n*-heptane due to cracking, isomerization, or simple desorption as *n*-heptane. Under purge with He, an inert gas in this reaction, a remarkable change in the 1300–1700 cm^{-1} region appeared with increasing temperature. In addition to the characteristic bands at 1457 and 1379 cm^{-1} due to $\text{–CH}_2\text{–}$ and –CH_3 groups, a broad band at 1580–1700 cm^{-1} can be seen. Several broad bands centered at 1640, 1600, 1503, and 1481 cm^{-1} are clearly distinguishable on further increases in temperature under He flush. The band at 1640 cm^{-1} is considered to correspond to the stretching vibration of the C=C bond, which is useful as an indicator of olefinic species [17]. The broad band at 1600 cm^{-1} is widely reported to be assignable to coke and thus is attributed to carbon–carbon stretching vibration in aromatic rings [18,19]. The band at 1503 cm^{-1} is assigned to alkenyl carbenium ions; that at 1481 cm^{-1}, to deformation vibration of the C–H bond of adsorbed polyolefins [20,21]. Bands characteristic of coke and carbonaceous species in the 1300–1700 cm^{-1} region are clearly observed at 573 K, indicating substantial coke and carbonaceous species formation in the absence of H_2. The increase in coke formation is accompanied by a decrease in the yield of adsorbed *n*-heptane, as indicated by the decreased intensity of the CH stretching bands between 2800 and 3000 cm^{-1} and the deformation bands due to $\text{–CH}_2\text{–}$ and –CH_3 groups. Thus, clearly the presence of H_2 inhibits coke formation on the hydrocarbon-adsorbed catalyst surface.

In situ IR measurements allow concurrent detection of the species adsorbed on the catalyst surface and the gas-phase reactants. The contribution of gas-phase hydrocarbons to the IR spectra was investigated by capturing the spectra of the reactant mixture (H_2/*n*-heptane = 5) in the absence of the catalyst under otherwise identical reaction conditions (not shown). The intensity of the gas-phase peaks was $<10\%$ of that observed during adsorption or reaction. Blank measurements for other isomer products (e.g., 3-methyl-hexane, 2,3-methyl-pentane)

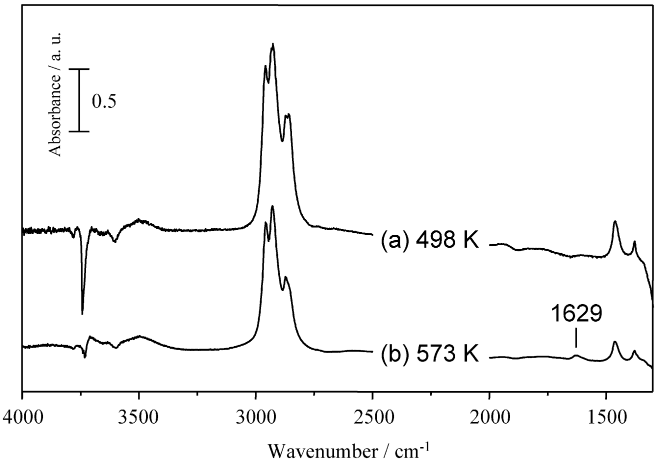

Fig. 4. IR spectra of surface species on Pt/H-beta zeolite under working conditions at (a) 498 and (b) 573 K.

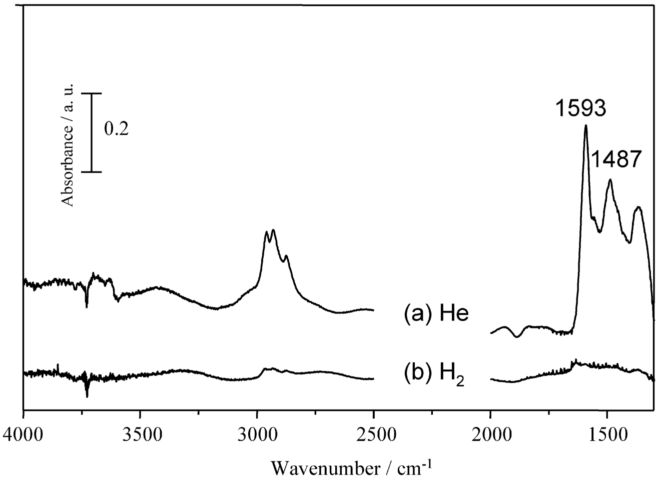

Fig. 5. Effect of (a) He and (b) H_2 purge after *n*-heptane isomerization over Pt/H-beta zeolite at 573 K.

confirmed that the species adsorbed on the catalyst during the reaction dominate the IR absorption spectrum. Thus finding indicates that the contribution of gas-phase chemicals produced under in situ conditions is negligible.

Fig. 4 shows differential IR spectra for surface species on Pt/H-beta zeolite under working conditions (H_2/*n*-heptane flow). The spectra were measured after reaction for 60 min. At 498 K, a negative band appeared in the OH stretching region, indicating participation of the hydroxyl groups in the reaction. Under these conditions, 5% *n*-heptane conversion was obtained with 98% selectivity for isomers. The adsorbed hydrocarbon species generated overlapping features of $–CH_3$ and $–CH_2–$ stretching vibrations between 2800 and 3000 cm^{-1}, accompanied by the appearance of $–CH_3$ and $–CH_2–$ deformation vibrations at 1460 and 1380 cm^{-1}. No aromatics were observed in this reaction, as demonstrated by the lack of C–H vibrations at frequencies >3000 cm^{-1} [22]. Moreover, the appearance of a broad band centered at 3500 cm^{-1} indicates the interaction of physically adsorbed hydrocarbons with the hydroxyl groups, leading to the shift of –OH groups to low frequencies. Increasing the reaction temperature to 573 K resulted in slightly lower rates of *n*-heptane conversion to isomers (71%) and isomer selectivity (71%). The negative bands near 3750 cm^{-1} were weaker at 573 K, indicating less aggressive replacement of hydroxyl groups by adsorbed hydrocarbon complexes, and a weak band emerged at 1629 cm^{-1}, identified as a characteristic band of olefinic species. Neither the characteristic broad band of coke centered at 1600 cm^{-1} nor that of adsorbed polyolefin species (1485 cm^{-1}) were observed. These results suggest that polyolefin species may be the precursors of coke. The presence of H_2 in the reaction appeared to suppress coke formation, yet produced olefinic species.

Catalyst deactivation in hydrocarbon reactions occurs primarily due to the formation of coke, which is generally considered a carbonaceous deposit consisting of a mixture of highly unsaturated polyaromatics (although the exact composition remains a matter of some debate) [22]. In situ IR spectroscopy is effective for investigating the formation of coke and has been used in many previous studies for this purpose [18,19]. Fig. 5 shows differential IR spectra illustrating the effect of H_2 and He on the adsorbed species formed during *n*-heptane isomerization in the presence of H_2 at 573 K. Conversion of adsorbed hydrocarbon species to coke can be clearly observed under He flow, as evidenced by the strong band centered at 1593 cm^{-1}. Coke formation is accompanied by the emergence of a broad band at 1487 cm^{-1} characteristic of adsorbed polyolefins. The adsorption of such polyolefins on the catalyst generates $–CH_3$ and $–CH_2–$ groups, which produce a characteristic C–H stretching vibration in the 2800–3000 cm^{-1} region (the exact assignment of adsorbed species is difficult). The appearance of a broad band due to C–H stretching vibration at wavenumbers above 3000 cm^{-1} indicates the presence of polyaromatics, which are likely to be the main constituents of coke. This is in contrast to the case for H_2 purge (Fig. 4b), in which the peaks due to adsorbed hydrocarbon species are substantially weaker and the peaks indicating polyolefin (1487 cm^{-1}) and coke (1593 cm^{-1}) are negligible.

The present in situ IR measurements offer clear evidence that the presence of H_2 in the reaction stream inhibits the formation of “hard coke” (i.e., alkylaromatics and polyaromatics) and thereby extends the useful life of the catalyst, whereas post-treatment with H_2 readily reduces “soft coke” (i.e., paraffinic and olefinic species) at medium temperatures [22].

Coke combustion was monitored by in situ IR spectroscopy as a method frequently used for the regeneration of isomerization catalysts. Fig. 6 shows time courses of O_2 treatment of a coked Pt/H-beta zeolite catalyst. The IR spectra include contributions from both the parent catalyst and the adsorbed hydrocarbon species (as-observed spectra). The bands at 1589 and 1487 cm^{-1} are assigned to coke and polyolefin, respectively, with corresponding C–H stretching vibrations in the range of 2800–3000 cm^{-1}. After calcination of the catalyst for 10 min at 573 K, the band at 1487 cm^{-1} became substantially weaker, whereas the band at 1589 cm^{-1} weakened only slightly. Calcination for 60 min resulted in the near-complete desorption of polyolefins, leaving a moderate amount of coke (1589 cm^{-1}). The decreased intensity of the bands in the 2800–3000 cm^{-1} region confirms that the C–H stretching vibration contained

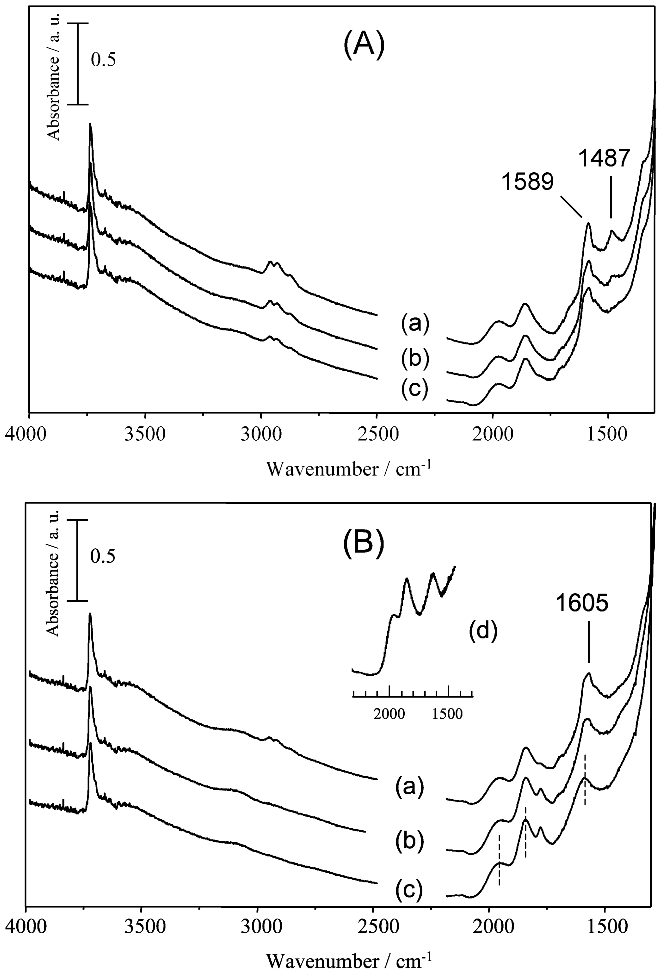

Fig. 6. Effect of O_2 treatment on coked Pt/H-beta zeolite (as-observed IR spectra). (A) O_2 treatment at 573 K for (a) 0 (coked sample), (b) 10, and (c) 60 min. (B) O_2 treatment for 60 min at (a) 623, (b) 673, and (c) 723 K. The spectrum (d) inset is a background H-beta catalyst before reaction. The peaks at the dotted lines are attributed to H-beta zeolite.

contributions from both coke and adsorbed polyolefins. The characteristic coke peak at 1589 cm^{-1} shifted to 1604 cm^{-1} on calcination, indicating that this peak is assignable to a resilient coke fraction. An increase in the calcination temperature to 723 K resulted in the effective removal of almost all coke from the catalyst surface, as evidenced by the decreased intensity of the band at 1605 cm^{-1}. Although a small amount of coke may have remained (probably related with the new band at 1750 cm^{-1}), the CH stretching bands near 3000 cm^{-1} became almost undetectable on treatment at 723 K.

It should be noted that three bands highlighted with dotted lines are attributed to zeolite sample compared with spectrum (d). Therefore, O_2 treatment at elevated temperature appears to be an efficient method for the removal of coke, particularly the resilient "hard coke" fraction.

The results of isotope-exchange experiments are shown in Figs. 7 and 8. IR measurements of isotope-exchanged reaction systems are widely used to study reaction mechanisms and identify reaction intermediates [23,24]. The conversion of OH groups on the catalysts to OD groups by exposure to D_2 at 673 K for 1 h is shown in Fig. 7. The majority of OH groups on Pt/H-beta zeolite were successfully converted to OD, despite the persistence of a small amount of neutral silanol (–SiOH) groups. H-beta zeolite was similarly converted to D-beta zeolite by this treatment. The differential in situ IR spectra for *n*-heptane isomerization over Pt/D-beta and D-beta zeolite in the presence of D_2 are shown in Fig. 8. The exposure of Pt/D-beta zeolite to the reactant mixture at elevated temperature resulted in the emergence of intense bands in the 2800–3000 cm^{-1} region (CH stretching bands), indicating the presence of enriched hydrocarbon species on the catalyst surface. A broad band centered at 2170 cm^{-1} also appeared, attributable to the stretching vibration of C–D bonds. The appearance of a positive band in the OH group stretching vibration region (3600–3700 cm^{-1}) indicates that a fraction of the O–H hydroxyl bond population had been regenerated. The regeneration of OH groups was caused by the isotope exchange of –OD groups with either H_2 produced by the dehydrogenation of *n*-heptane to its related alkenes, or hydrogen atoms in the adsorbed hydrocarbon species. The C–D bond was produced by D_2 hydrogenation of alkenes, leading to a scrambled deuterium distribution in *n*-heptane and its isomers (see below). The broad band at 3500 cm^{-1} is suggested to correspond to hydrogen–OH groups associated with adsorbed hydrocarbons. The sharp negative band at 2750 cm^{-1} indicates the consumption of OD groups due to transformation of the OD bond to OH by H_2 or surface hydrocarbons. At higher temperature (573 K), the bands decreased in intensity, due to adsorbed hydrocarbons, accompanied by the appearance of a small band at 1627 cm^{-1} characteristic of olefinic species. The increased abundance of olefinic species at elevated temperature is consistent with the proposal that the first step of *n*-heptane isomerization is dehydrogenation of *n*-heptane to heptene at Pt centers [8].

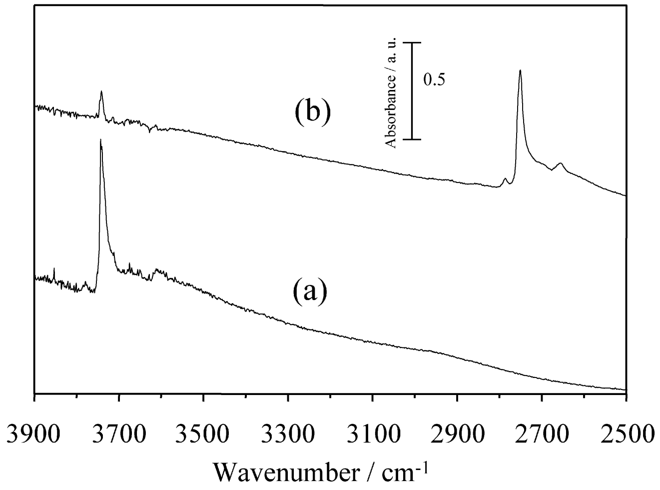

Fig. 7. Comparison of background IR spectra of (a) Pt/H-beta and (b) Pt/D-beta. The measurements are performed at 673 K.

The D-beta zeolite catalyst exhibited markedly different spectral features than the Pt/D-beta zeolite, the most interesting of which was the absence of CD stretching absorption at 2000–2250 cm^{-1}, indicating no isotope exchange between hydrocarbon species and D_2 or OD groups. The incorporation of D atoms into hydrocarbons can be done only in the presence of

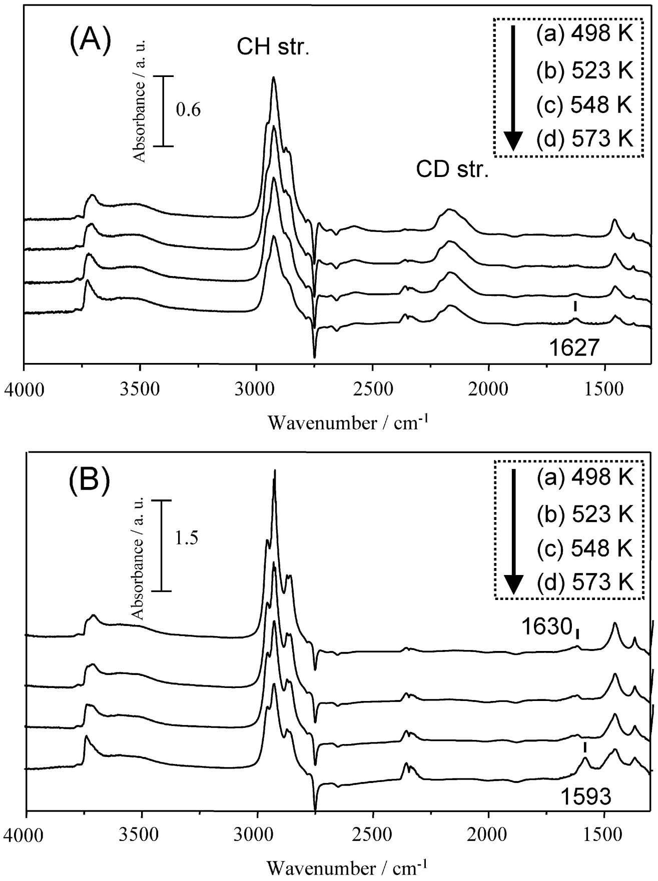

Fig. 8. IR spectra of surface species formed by *n*-heptane isomerization in the presence of D_2 on (A) Pt/D-beta and (B) D-beta zeolite at (a) 498, (b) 523, (c) 548, and (d) 573 K.

Pt, and direct H/D exchange between D_2 and hydrocarbons cannot proceed. It is well known that Pt is the most efficient catalyst for the dissociation of H_2 molecules and the subsequent hydrogenation reaction; therefore, CD bond formation (Fig. 7A) is attributed to the hydrogenation of alkenes with D_2 at Pt metal centers. The absence of Pt particles prevents the hydrogenation and dehydrogenation reactions. Thus, the protonation of *n*-heptane was the predominant reaction over Pt/D-beta zeolite, whereas the subsequent cracking of *n*-heptane into propane and butane were the main reactions over D-beta zeolite. Regeneration of OH groups was observed on the D-beta zeolite, indicating that H_2 also was produced in the coking process. This conclusion is supported by the subsequent formation of coke (band at 1593 cm^{-1}) at elevated temperature (573 K) even under a D_2 atmosphere. Therefore, the coke-inhibiting effect of H_2 also requires the presence of Pt for the dissociation of H_2, which is a prerequisite for sequent hydrogenation.

In the bifunctional reaction mechanism of *n*-heptane isomerization over Pt/beta zeolite, the dehydrogenation, protonation, isomerization, deprotonation, hydrogenation, and cracking processes are determined by the distribution of Pt particles and acidic sites on the catalyst. The present isotope-exchange reaction supports this conclusion, particularly for the hydrogenation function of Pt. Considering the reversibility of the hydrogenation and dehydrogenation steps, dehydrogenation at Pt particles is also concluded to play an important role in isomerization. The acidic sites of zeolite participate in hydrogen transfer and methyl shift, leading to isomerization of hydrocarbons in the presence of Pt. However, in the absence of Pt, the isomerization is quenched and cracking becomes dominant, resulting in propane and *n*-butane.

4. Conclusion

In situ IR spectroscopy was used to monitor the isomerization of *n*-heptane over Pt/H-beta zeolite. It was found that the presence of H_2 in the reaction system efficiently inhibited the formation of coke during the reaction process. The carbonaceous products were distinguished into highly branched polyolefins and coke. The former can be readily removed by O_2 treatment at moderate temperature (573 K), whereas the latter can be removed only by combustion at higher temperature ($>$723 K). Whereas C–D bonds did not form on exposure of the deuterated beta zeolite to *n*-heptane and D_2, H/D exchange occurred rapidly in the presence of Pt, leading to scrambling of the deuterium distribution in *n*-heptane and its isomers. These results clearly support a bifunctional reaction pathway for this reaction system.

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