The Reaction Mechanism of C_6 Hydrocarbons over Acid–Base Bifunctional Catalysts, TiO_2–ZrO_2

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This study examined the relation between the acid–base properties of a binary oxide, TiO_2–ZrO_2, and the reaction behavior of various C_6 hydrocarbons over this mixed oxide. Based on experimental results, both the strong acid sites and the strong base sites performed as cracking sites and could be poisoned by doping a small amount of K_2O and B_2O_3, respectively. It was demonstrated that the paired acid–base sites played most important roles on dehydrogenation of cyclohexane and cyclization of *n*-hexane and hexene. Both the yield and selectivity of benzene increased with the relative paired acid–base amount. The results of isomerization of 1-hexene showed that the yield of the molecular isomerization increased at the expense of the double bond migration as the relative acid/base ratio increased. The results also showed that 2-hexene had a much higher aromatization rate than 1-hexene over TiO_2–ZrO_2 catalysts. A detailed reaction mechanism of the aromatization C_6 hydrocarbons over an acid–base bifunctional catalyst is proposed, which was different from the mechanism of a conventional metal–acid bifunctional catalysts. © 1996 Academic Press, Inc.

INTRODUCTION

Catalytic reforming over metal–acid bifunctional catalysts involves complex reactions such as cracking, dehydrogenation, isomerization and dehydrocyclization. The mechanism of those reactions were described in detail by Pines (1) and Gates *et al.* (2). In general, cracking reactions proceed via a carbenium ion and free radical intermediates catalyzed by acid and metal surfaces, respectively. Dehydrogenation reactions occur mainly on metal surfaces, while isomerization reactions take place on acidic surfaces. Dehydrocyclization reactions, which include dehydrogenation, cyclization and isomerization reactions follow the scheme described by Mills *et al.* (3). Active sites of both the metal and acidic surfaces are important to achieve high performance of the reforming process. Recently, the acid–base bifunctional catalysts showed the pronounced catalytic activities (4–6). However, the precise reaction mechanism of reforming reactions over the acid–base bifunctional catalyst has not yet been fully elucidated.

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Studies on dehydrocyclization of C_6–C_8 *n*-paraffins over the acid–base bifunctional catalysts, TiO_2–ZrO_2, were reported previously (7). The results (7) showed that the aromatization rate could be well correlated with the site density of the paired acid–base sites on the catalysts. In addition, TiO_2–ZrO_2 catalysts cyclized the *n*-paraffin through a direct six-membered ring mechanism, while reactions using the commercially available catalyst Pt–Re/γ-Al_2O_3 catalysts went through a five-membered ring intermediate (7). Thus, these two catalysts have significantly different reaction pathways. The purpose of this study was to correlate the acidity and basicity of a TiO_2–ZrO_2 catalyst with its catalytic activities of cracking, dehydrogenation, isomerization, and cyclization by using cyclohexane, 1-hexene, 2-hexene, and *n*-hexane as the reactants.

EXPERIMENTAL

Preparation and Characterization of Catalysts

The mixed oxides TiO_2–ZrO_2 (molar ration 1:1) were prepared using a coprecipitation method described previously (7). The dry precipitate were calcined in air at 823 K for 2 h at a step rate of 50 K/0.5 h. K_2O/TiO_2–ZrO_2 and B_2O_3/TiO_2–ZrO_2 were prepared from TiO_2–ZrO_2 by the incipient wetness method with potassium hydroxide (KOH) and orthoboric acid (H_3BO_3). The commercial catalyst, R-62 with 0.22% Pt and 0.44% Re on γ-Al_2O_3, was provided by Chinese Petroleum Corporation.

The amounts of acid and base sites on the catalysts were measured by the ammonia and acetic acid temperature program desorption (TPD) method. Ammonia adsorption temperature was set to 303 K, and desorption temperature ranged from 303 to 823 K at a slope of 10 K/min. Acetic acid adsorption temperature was set to 393 K, and desorption temperature ranged from 393 to 823 K at a slope of 10 K/min. The details of these measurements will be described elsewhere (8).

Reaction Equipment and Experimental Procedure

Reactions were performed in a continuous flow fixed-bed microreactor as described previously (7). The catalyst

was pretreated with air at 813 K for 2 h. The reaction was studied under the following conditions: temperature, 813 K; total pressure, 101.2 KPa; hydrocarbon partial pressure, 6.66 KPa; nitrogen partial pressure, 94.57 KPa; and gas hourly space velocity (GHSV), 6000 v/v/h. Both feed and product were analyzed by a HP fused silica capillary column crosslinked methylsilicone with a column length of 25 m.

RESULTS AND DISCUSSION

Dehydrogenation of Cyclohexane

Prior to 1970, MoO$_3$–Al$_2$O$_3$ and Cr$_2$O$_3$–Al$_2$O$_3$ mixed oxides were the preferred catalysts for cyclohexane dehydrogenation. A dual-function mechanism (9) was proposed. It claimed that the hydrogenation–dehydrogenation activities were associated with the properties of transition metal ions, although the function of acid sites was not clearly defined within the oxides. However, the mixed oxides catalysts are much less active than metal Pt catalysts. The mechanism of cyclohexane dehydrogenation over Pt metal involves the adsorption of cyclohexane, with either simultaneous or rapid subsequent dissociation of six hydrogen atoms. The above mechanism was believed to be mediated by electrons of the aromatics interacting with d orbital of metals (10).

Chang and Wang (11) first studied the dehydrogenation of cyclohexane over an acid–base bifunctional catalyst. TiO$_2$–ZrO$_2$–V$_2$O$_5$. A stepwise dehydrogenation function mechanism was proposed. This research attempts to further investigate the relationship between the acid–base amount and the dehydrogenation activity of cyclohexane over TiO$_2$–ZrO$_2$ catalysts.

As shown in Table 1, the amount of acid and base sites of TiO$_2$–ZrO$_2$ could be changed by impregnation of K$_2$O and B$_2$O$_3$ on catalysts. The acid and base amount of catalysts were measured by the ammonia and acetic acid TPD method (8). The relative acid and base amount of original TiO$_2$–ZrO$_2$ was defined as unity (1.00). It shows the relative acid amount decreased with increasing K$_2$O doping content. Similarly, the relative base amount decreased with increasing B$_2$O$_3$ doping content. However, TiO$_2$–ZrO$_2$ gave the highest relative paired acid–base amount, and increas-

TABLE 2

Dehydrogenation of Cyclohexane over Acid–Base Bifunctional Catalysts^a

Catalyst	Conversion^b (wt%)	Product yield (wt%)			
		C$_1$–C$_5$	1-, 2-, 3-C$_6^{2-}$	i-C$_6^{2-}$	Benzene
TiO$_2$–ZrO$_2$	10.68	0.65	0.25	1.21	8.57
0.5% K$_2$O/TiO$_2$–ZrO$_2$	5.72	0.07	0.12	1.02	4.51
2.0% K$_2$O/TiO$_2$–ZrO$_2$	2.22	0.40	0.29	0.78	0.75
0.5% B$_2$O$_3$/TiO$_2$–ZrO$_2$	8.50	0.32	0.09	1.35	6.74
2.0% B$_2$O$_3$/TiO$_2$–ZrO$_2$	7.58	0.73	0.12	1.74	4.99

^{a} Reaction conditions: $P_{C_6H_{12}} = 6.66$ KPa; $P_{N_2} = 94.57$ KPa; $T = 793$ K; GHSV = 6000 h^{-1}.
^{b} Time on stream: 5 h.

ing K$_2$O and B$_2$O$_3$ doping content decreased the relative paired acid–base amount.

Table 2 shows the total conversion of cyclohexane decreases when increasing the doping content of either K$_2$O or B$_2$O$_3$. The yield of benzene increases with increasing the relative paired acid–base amount of catalysts, as shown in Fig. 1. It implies that both acid and base sites are important for cyclohexane dehydrogenation. Figure 2 gives the relation between the yield of benzene and the relative acid/base ratio of catalysts. A volcano-shaped curve was obtained and the maximum yield located at the relative ratio was near unity. It further indicates that neither the acid site nor the base site alone can effectively dehydrogenate cyclohexane. Hydrogenolysis the C–C bond of cyclohexane is the necessary step for ring opening and cracking reactions and it needs strong acid or base sites. However, the strong acid or strong base sites of TiO$_2$–ZrO$_2$ catalysts were poisoned by K$_2$O or B$_2$O$_3$. As shown in Table 2, the yield of cracking (C$_1$–C$_5$) and i-hexene products were reduced by doping a small amount of K$_2$O of B$_2$O$_3$ (0.5 wt%) on original TiO$_2$–ZrO$_2$. A further increase of the doping amount of K$_2$O to 2.0 wt% would generate new strong base sites resulting on increasing yield of cracking products (C$_1$–C$_5$). Increasing the doping amount of B$_2$O$_3$ to 2.0 wt%, both the cracking and i-hexene products yield increased. Besides,

TABLE 1

Acid and Base Amounts of Catalysts Measured by TPD of Ammonia and Acetic Acid

Catalyst	Acid amount (mmol/g)	Base amount (mmol/g)	Relative acid amount	Relative base amount	Relative acid–base amount^a	Relative acid/base ratio
TiO$_2$–ZrO$_2$	0.203	0.553	1.00	1.00	1.00	1.00
0.5% K$_2$O/TiO$_2$–ZrO$_2$	0.158	0.539	0.78	0.97	0.78	0.80
2.0% K$_2$O/TiO$_2$–ZrO$_2$	0.066	0.568	0.33	1.03	0.33	0.32
0.5% B$_2$O$_3$/TiO$_2$–ZrO$_2$	0.219	0.529	1.08	0.96	0.96	1.13
2.0% B$_2$O$_3$/TiO$_2$–ZrO$_2$	0.215	0.414	1.06	0.75	0.75	1.41

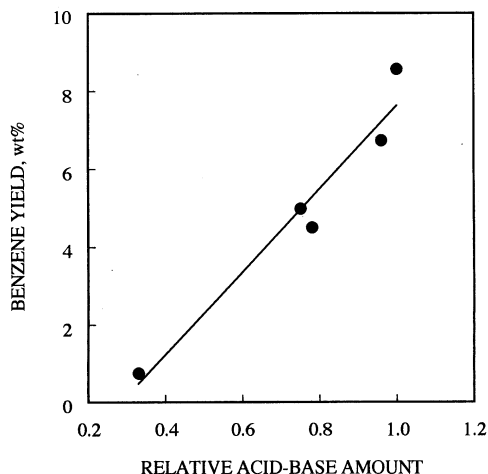^{a} The amount of relative acid or base sites, whichever is lower.

FIG. 1. Correlation between the relative acid–base amount and the benzene yield of cyclohexane dehydrogenation. Reaction conditions as in Table 2.

methylcyclopentane was not observed among the products, proving that TiO_2–ZrO_2 catalysts could not isomerize cyclohexane to methylcyclopentane in accordance with observation reported earlier (7).

Based on our results, we propose the reaction pathway of cyclohexane over an acid–base bifunctional catalyst, as shown in Fig. 3. (I) Ring opening of cyclohexane: The cyclohexane is adsorbed on either strong acid sites or strong base sites, where the $C_6H_{11}^+$ carbenium ion intermediate or $C_6H_{11}^-$ carbanion intermediate are formed. The $C_6H_{11}^+$ carbenium ion adsorbed on strong acid sites precedes C–C bond hydrogenolysis, and gives hexene. The $C_6H_{11}^-$ carbanion intermediate adsorbed on strong base sites proceeds through ring opening to get hexene. (II) The cyclohexane is adsorbed on paired acid–base sites, where it goes through a dehydrogenation reaction. First, the acid sties abstract one
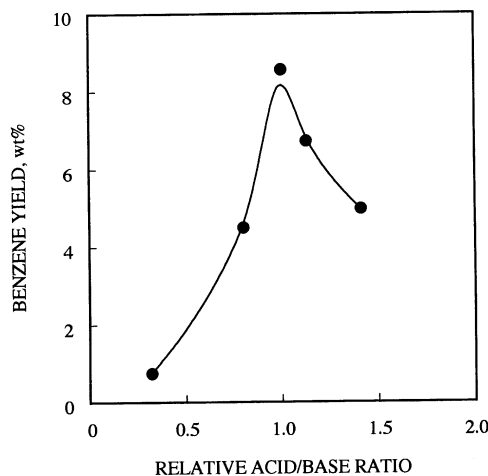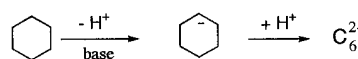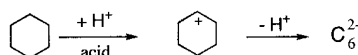

FIG. 2. The benzene yield of cyclohexane dehydrogenation as a function of relative acid/base ratio. Reaction conditions as in Table 2.
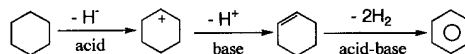

FIG. 3. The proposed reaction pathway of cyclohexane over an acid–base bifunctional catalyst.

H^- ion of cyclohexane, and the carbenium ion is formed. Then, the base sites abstract on H^+ ion of the carbenium ion and the cyclohexene is formed. The cyclohexene still remains adsorbed on the paired acid–base sites and proceeds through a dehydrogenation reaction to benzene. Furthermore, Table 2 shows that cyclohexane gave a much higher benzene yield than C_1–C_5 yield. It demonstrates that the amount of Lewis acid sites are much higher than the amount of Brønsted acid sites on the TiO_2–ZrO_2 surface. It suggests that the Lewis acid sites are the active sites on acid–base bifunctional catalysts in the dehydrogenation reaction as reported in a earlier paper (12).

Dehydrocyclization of 1-Hexene

Olefin (hexene) can be easily cracked, isomerized or cyclized by acid and base catalysts. The product selectivity depends on the catalysts, and several reaction schemes have been proposed (1, 13, 14). It is of particular interest to know the active sites of acid–base bifunctional catalysts for 1-hexene reactions. Table 3 shows the total conversion and product yield of 1-hexene dehydrocyclization, with a

TABLE 3

Dehydrocyclization of 1-Hexene over Acid–Base Bifunctional Catalysts[a]

Catalyst	Conversion[b] (wt%)	Product yield (wt%)			
		C_1–C_5	2-, 3-C_6^{2-}	i-C_6^{2-}	Benzene
TiO_2–ZrO_2	92.80	14.84	42.34	15.53	20.09
0.5% K_2O/TiO_2–ZrO_2	90.21	10.71	57.30	9.10	13.10
2.0% K_2O/TiO_2–ZrO_2	83.10	11.14	64.55	4.60	2.81
0.5% B_2O_3/TiO_2–ZrO_2	91.06	12.82	48.08	13.26	16.90
2.0% B_2O_3/TiO_2–ZrO_2	91.96	18.11	34.03	28.07	11.75

[a] Reaction conditions: $P_{1-C_6} = 6.66\,KPa$; $P_{N_2} = 94.57\,KPa$; $T = 793\,K$; GHSV = 6000 h^{-1}.
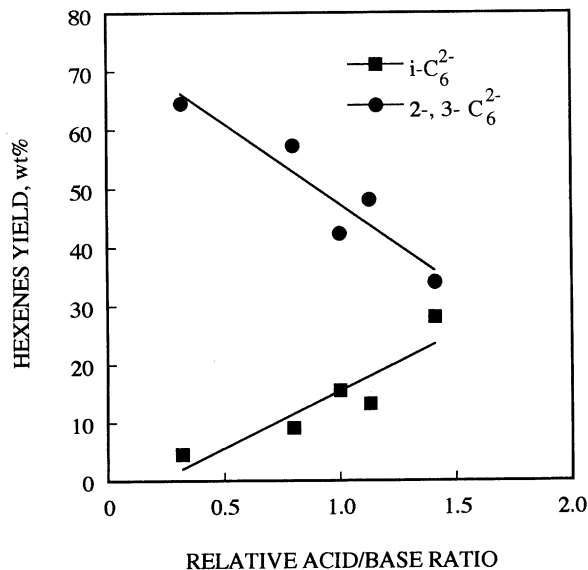[b] Time on stream: 0.5 h.

FIG. 4. The yield of (2-hexene + 3-hexene) and *i*-hexene of 1-hexene isomerization as a function of relative acid/base ratio. Reaction conditions as in Table 3.

reaction time of 0.5 h. The total conversion of 1-hexene decreased slightly with increasing K$_2$O doping, but doping B$_2$O$_3$ had no effect on the conversion of 1-hexene. It seems the acid or base sites alone are the active center of 1-hexene reactions. However, the benzene yield decreased with increasing the doping amount. This provides additional evidence that the paired acid–base sites of TiO$_2$–ZrO$_2$ catalysts are the active sites of *n*-olefin dehydrocyclization. Table 3 also shows doping with 0.5 wt% K$_2$O and 0.5 wt% B$_2$O$_3$ on TiO$_2$–ZrO$_2$ decreases the C$_1$–C$_5$ cracking products. Further increase of the doping amount (2.0 wt%) of K$_2$O and B$_2$O$_3$ increased the yield of cracking products. It means some strong acid and base sites poisoned by 0.5 wt% K$_2$O and B$_2$O$_3$ are the active center of 1-hexene cracking.

Increasing the amount of K$_2$O increased the yield of 2-hexene and 3-hexene, and decreased the yield of *i*-hexene. On the other hand, the *i*-hexene yield increased with increasing B$_2$O$_3$ doping content. It seems K$_2$O can enhance the double-bond migration reactions, but suppresses the molecular isomerization reactions. But doping with B$_2$O$_3$ showed the opposite effect. Figure 4 shows the yield of (2-hexene + 3-hexene) and *i*-hexene as a function of relative acid/base ratio of catalysts. The yield of 2-hexene and 3-hexene decreased with increasing relative acid/base ratio of the catalysts, while the yield of *i*-hexene increased. The data demonstrates that the acid sites of catalysts enhance the molecular isomerization reaction of 1-hexene, and the base sites of catalysts enhance the double bond migration reaction of 1-hexene.

Based on the above results, we postulate the reaction pathway of 1-hexene over an acid–base bifunctional catalyst, as shown in Fig. 5. (I) The 1-hexene is adsorbed on strong acid/base sites of catalysts, and proceeds through a cracking reaction to C$_1$–C$_5$ products. (II) The 1-hexene is adsorbed on acid sites, and the primary carbenium ion formation follows proton addition. The carbenium ion rearranges following the stability of carbenium ion which is $3^0 > 2^0 > 1^0 > CH_3^+$. Then, the *i*-hexene formation follows proton abstraction. (III) The 1-hexene is adsorbed on base sites of catalysts, and the formation of carbanion after abstraction of one proton on the base sites. The carbanion generated is a resonance hybrid. Thus, 1-hexene undergoes a reversible double-bond migration in the presence of basic sites. (IV) The 1-hexene adsorbed on paired acid–base sites of catalysts proceeds through dehydrogenation and 1–6 ring cyclization reactions to cyclohexene. The cyclohexene is adsorbed on paired acid–base sites without desorption and proceeds through further dehydrogenation to benzene.
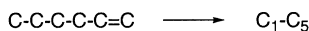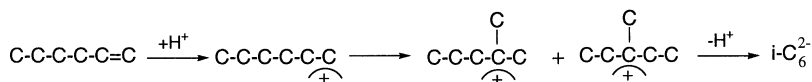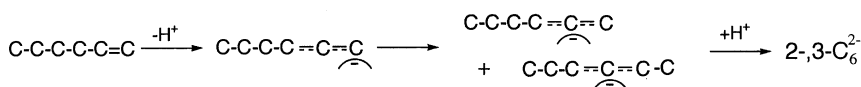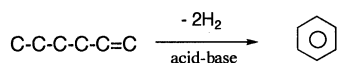

FIG. 5. The proposed reaction pathway of 1-hexene over an acid–base bifunctional catalyst.

Dehydrocyclization of n-Hexane

It is well known that the dehydrocyclization of *n*-hexane to benzene proceeds through the intremediates cyclohexane and 1-hexene. Above results show the active sites of cyclohexane dehydrogenation and 1-hexene cyclization are the paired acid–base sites. It is further proved that the dehydrocyclization of hexane proceeds on the paired acid–base sites on the catalyst surface. Table 4 shows the total conversion and product yield of *n*-hexane dehydrocyclization over acid–base bifunctional catalysts. The total conversion of *n*-hexane decreased with increasing K_2O and B_2O_3 doping content. It seems that K_2O and B_2O_3 poison the active sites of *n*-hexane reactions, and both acid and base sites alone cannot increase the conversion of *n*-hexane.

In general, the first dehydrogenation step of *n*-hexane is a rate determining step in dehydrocyclization of *n*-hexane. Table 4 shows that the yield of dehydrogenation products (hexenes) decreases with increasing the doping amount of K_2O and B_2O_3. It illustrates that both acid and base sites are involved in the dehydrogenation reaction. The benzene yield also decreases significantly with increasing the doping amount of K_2O and B_2O_3. Figure 6 gives the relationship between the relative acid/base ratio of catalysts and the yield of hexenes and benzene of *n*-hexane dehydrocyclization. A volcano-shaped curve was obtained, and the maximum yield was obtained at a relative ratio near unity. It demonstrates that the paired acid–base sites are the active sites for *n*-hexane dehydrogenation and dehydrocyclization reactions. Table 4 also shows that the yield of cracking products decreases via doping with 0.5 wt% K_2O or B_2O_3 on TiO_2–ZrO_2. The strong acid and strong base sites poisoned by small amount of K_2O and B_2O_3 are the active sites for cracking reactions of *n*-hexane.

Based on the results in *n*-hexane reactions, we postulate the reaction pathway of *n*-hexane over an acid–base bifunctional catalyst, as shown in Fig. 7, which is similar to the previous paper (7) about the mechanism of dehydrocyclization over acid–base catalysts. (I) The *n*-hexane is
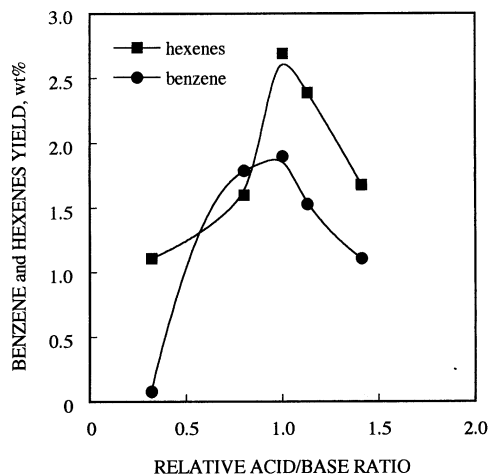

FIG. 6. The hexenes and benzene yields of *n*-hexane dehydrocyclization as a function of relative acid/base ratio. Reaction conditions as in Table 4.

adsorbed on strong acid or strong base sites and proceeds cracking reactions. (II) The *n*-hexane is adsorbed on the paired acid–base sites of catalysts. The first dehydrogenation step is completely through one H^- ions abstracted by acid sites on catalysts followed by one proton abstracted by base sites on catalysts. The, *n*-hexane is dehydrogenated into 1-hexene. (III) The *n*-hexane is adsorbed on the paired acid–base sites of catalysts and is dehydrogenated into cyclohexane through a direct six-membered ring closure. The adsorbed cyclohexane then directly proceeds via dehydrogenation to benzene on paired acid–base sites of catalysts.

Relationship between Aromatization Rate and the Double-Bond Position of Hexenes

Hoog *et al.* (15) found the aromatization rate of 1-hexene was two times that of 2-hexene over Cr_2O_3/Al_2O_3 catalysts. On the other hand, 1-heptene and 2-heptene had the same aromatization rate, but the cyclization rate of 3-heptene was much lower. Hoog *et al.* concluded that the

TABLE 4

Dehydrocyclization of *n*-Hexane over Acid–Base Bifunctional Catalysts[a]

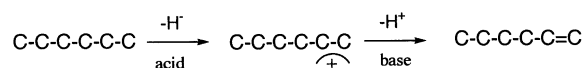| Catalyst	Conversion[b] (wt%)	Product yield (wt%)			
		C_1–C_5	1-, 2-, 3-C_6^{2-}	i-C_6^{2-}	Benzene
TiO_2–ZrO_2	6.18	1.59	1.41	1.28	1.90
0.5% K_2O/TiO_2–ZrO_2	4.62	1.23	0.64	0.96	1.79
2.0% K_2O/TiO_2–ZrO_2	2.42	1.23	0.18	0.93	0.08
0.5% B_2O_3/TiO_2–ZrO_2	4.92	1.00	1.00	1.39	1.53
2.0% B_2O_3/TiO_2–ZrO_2	3.92	1.13	0.56	1.12	1.11

[a] Reaction conditions: $P_{n\text{-}C_6} = 6.66$ KPa; $P_{N_2} = 94.57$ KPa; $T = 793$ K; GHSV $= 6000$ h^{-1}.
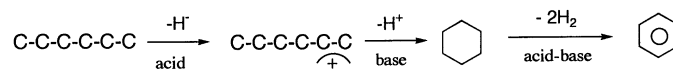[b] Time on stream: 5 h.

FIG. 7. The proposed reaction pathway of *n*-hexane over an acid–base bifunctional catalyst.
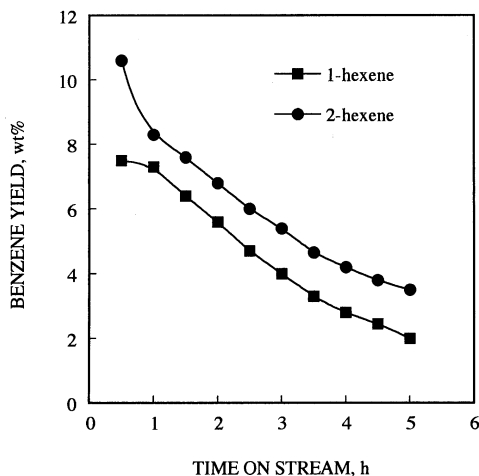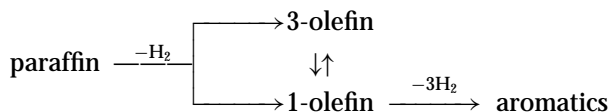
FIG. 8. The benzene yield of 1-hexene and 2-hexene dehydrocyclization over TiO$_2$–ZrO$_2$ as a function of reaction time. Reaction conditions: $P_{C_6} = 6.66$ KPa; $P_{N_2} = 94.57$ KPa; $T = 793$ K; GHSV = 24,000 h^{-1}.

aromatization rate of olefin was dependent on the double bond position of olefin. Olefins with a terminal double bond had higher aromatization rates than those with centrally located double bond. The reaction path is as follows:

$$\text{paraffin} \xrightarrow{-H_2} \begin{array}{c} \longrightarrow \text{3-olefin} \\ \downarrow\uparrow \\ \longrightarrow \text{1-olefin} \xrightarrow{-3H_2} \text{aromatics} \end{array}$$

For example, the 3-heptene or 2-hexene molecules must migrate their double-bond position to be 1-heptene, 2-heptene or 1-hexene which can proceed through a six-ring cyclization reaction to aromatics. It is interesting to know whether the acid–base bifunctional catalysts follow a similar reaction pathway. In this experiment, the dehydrocyclization of 1-hexene and 2-hexene over TiO$_2$–ZrO$_2$ and R-62 catalysts was studied.

Figure 8 is the benzene yield of 1-hexene and 2-hexene dehydrocyclization over TiO$_2$–ZrO$_2$ catalysts as a function of reaction time. 2-Hexene gave a consistently higher benzene yield than 1-hexene on stream over TiO$_2$–ZrO$_2$ catalysts. It showed that 2-hexene had a higher aromatization rate than 1-hexene over TiO$_2$–ZrO$_2$ catalysts. This result was the opposite of that of Cr$_2$O$_3$/Al$_2$O$_3$ catalysts (15) on which 1-hexene had a higher aromatization rate than 2-hexene. Table 5 shows the conversion and the product distribution of 1-hexene and 2-hexene dehydrocyclization over TiO$_2$–ZrO$_2$ catalysts. 2-Hexene had a much lower total conversion, but gave a lower cracking yield, a higher i-hexene and benzene yield than 1-hexene. The results showed that 2-hexene is more stable on TiO$_2$–ZrO$_2$ surfaces than 1-hexene, and it is easily cyclized to benzene. Therefore, 2-hexene gave a lower conversion and a higher benzene yield than 1-hexene. It is also found the dehydrocyclization of n-octane (7) gave a much high yield of o-xylene over TiO$_2$–ZrO$_2$ catalysts. Because 2-octene from n-octane dehydrogenation is more stable than 1-octene on the catalytic surface and it proceeds aromatization through a direct six-membered ring closure to o-xylene. It can be suggested that olefins with terminal double bond had lower aromatization rates than those with centrally located double bond over acid–base bifunctional catalysts.

Figure 9 shows the benzene yield of 1-hexene and 2-hexene dehydrocyclization as a function of reaction time over R-62 catalysts. Both 1-hexene and 2-hexene had the same benzene yield on stream. It showed the aromatization rates of 1-hexene and 2-hexene were the same and independent of their double bond position over R-62 catalysts. Table 5 also shows the conversion and the product distribution of 1-hexene and 2-hexene dehydrocyclization over R-62 catalysts. 1-Hexene had a much lower cracking yield and a lower i-hexene yield than 2-hexene. However, both 1-hexene and 2-hexene had the same benzene yield over R-62 catalysts.

TABLE 5

Dehydrocyclization of 1-Hexene and 2-Hexene over TiO$_2$–ZrO$_2$ and R-62 Catalysts

Catalyst	Reactant	Conversion (wt%)	Product distribution^c (wt%)					
			C$_1$–C$_5$	1-C$_6^{2-}$	2-C$_6^{2-}$	3-C$_6^{2-}$	i-C$_6^{2-}$	Benzene
TiO$_2$–ZrO$_2^a$	1-C$_6^{2-}$	51.66	6.17	48.34	31.07	7.51	3.96	2.95
	2-C$_6^{2-}$	37.58	4.72	7.64	62.42	10.04	9.10	6.08
R-62^b	1-C$_6^{2-}$	78.96	8.78	21.04	40.38	13.08	10.50	6.22
	2-C$_6^{2-}$	72.98	18.20	9.29	27.02	14.43	25.01	6.05

^{a} Catalysts were pretreated by air at temperature 813 K for 2 h.
  Reaction conditions: $P_{C_6} = 6.66$ KPa; $P_{N_2} = 94.57$ KPa; $T = 793$ K; GHSV = 6000 h^{-1}.
^{b} Catalysts were pretreated by hydrogen at temperature 773 K for 2 h.
  Reaction conditions: $P_{C_6} = 6.66$ KPa; $P_{H_2} = 20.00$ KPa; $P_{N_2} = 74.57$ KPa; $T = 793$ K; GHSV = 6000 h^{-1}.
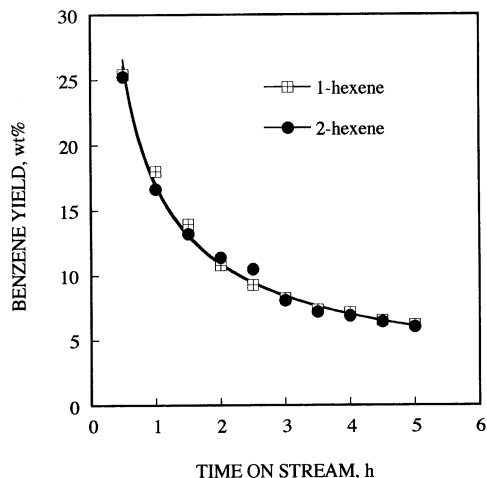^{c} Reaction time 5 h.

FIG. 9. The benzene yield of 1-hexene and 2-hexene dehydrocyclization over R-62 as a function of reaction time. Catalysts were pretreated by hydrogen at temperature 773 K for 2 h. Reaction conditions: $P_{C_6} = 6.66$ KPa; $P_{H_2} = 20.00$ KPa; $P_{N_2} = 74.57$ KPa; $T = 793$ K; GHSV = 6000 h^{-1}.

The results of hexenes dehydrocyclization show that the acid–base bifunctional catalysts TiO$_2$–ZrO$_2$ follow indeed a dehydrocyclization mechanism which is different from Pt–Re/γ-Al$_2$O$_3$ (R-62) catalysts. Here, we discuss again the difference between TiO$_2$–ZrO$_2$ and R-62 catalysts. (1) TiO$_2$–ZrO$_2$ acts as an acid–base bifunctional catalyst. Firstly, the hexene is adsorbed directly on an acid–base bifunctional catalyst with its double-bond position. It is proposed that the adsorbed 2-hexene is more stable and has a higher two-point adsorption rate than the adsorbed 1-hexene. The results also showed TiO$_2$–ZrO$_2$ catalysts had a lower isomerization rate of hexenes than R-62 catalysts. Therefore, 2-hexene does not need to migrate its double-bond position to 1-hexene and proceeds directly through a 1–6 ring cyclization to benzene. Although 2-hexene has a lower conversion, it can give a higher benzene yield than 1-hexene. However, for Cr$_2$O$_3$/Al$_2$O$_3$ catalysts (15), the 2-hexene will migrate its double bond position to 1-hexene and proceeds through a 1–6 ring cyclization reaction. So 2-hexene gives a lower benzene yield than 1-hexene. (2) R-62 acts as a metal-acid bifunctional catalysts. The hexene is adsorbed on the surface of the catalysts and proceeds through five-ring cyclization to benzene. 1-Hexene proceeds through a C$_1$–C$_5$ five-ring closure to cyclize, and 2-hexene proceeds through a C$_2$–C$_6$ five-ring closure to cyclize. Therefore, 1-hexene and 2-hexene both have the same aromatization rate. At the same time, 1-hexene may easily proceed through double bond migration to 2-hexene and then follows other reactions. The reactions can be written as follows:

$$1\text{-Hexene} \rightarrow 2\text{-Hexene} \rightarrow C_1\text{–}C_5 + i\text{-Hexene}$$

Therefore, the yield of cracking and isomerization products of 2-hexene is higher than that of 1-hexene.

CONCLUSION

From the above discussion we conclude that the cyclohexane and *n*-hexane proceeded dehydrogenation on the paired acid–base sites which also played the primary role in the cyclization of *n*-hexane and 1-hexene over an acid–base bifunctional catalyst, TiO$_2$–ZrO$_2$. Doping with 0.5 wt% K$_2$O or B$_2$O$_3$ on TiO$_2$–ZrO$_2$ could decrease the cracking product of *n*-hexane, 1-hexene, and cyclohexane. But the cracking product would not decrease with further increase of doping amount. It is also proven that the acid sites of catalysts can enhance the molecular isomerization of 1-hexene, and the base sites of catalysts can enhance the double-bond migration of 1-hexene. Finally, it showed that the aromatization rate of hexenes is dependent on its double-bond position when using TiO$_2$–ZrO$_2$ catalysts. Therefore, 2-hexene gave a higher benzene yield than 1-hexene.

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