Catalytic activity for synthesis of isomerized products from benzene over platinum-supported sulfated zirconia

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Abstract

The catalytic activity of $Pt/SO_4{}^{2-}/ZrO_2$ in the benzene hydrogenation and isomerization reaction at 250°C is superior to that of other Pt/conventional solid acid catalysts such as Pt/HY-zeolite and Pt/H-mordenite. The catalytic activity of $SO_4{}^{2-}/ZrO_2$ for cyclohexane isomerization to methylcyclopentane at 250°C is higher than that of HY-zeolite and H-mordenite. $SO_4{}^{2-}/ZrO_2$ and HM10 have more Brönsted acid sites of the highest strength and show a higher percentage of isomerization conversion. In contrast, ZrO_2, which contains almost no Brönsted acid sites, and HY5.6, which contains almost no Brönsted acid sites of the highest strength, show a lower conversion percentage. Consequently, Brönsted acid sites of the highest strength are active sites responsible for cyclohexane isomerization. However, the isomerization conversion percentage does not completely correlate with the number of highest-strength Brönsted acid sites, suggesting that not all of these sites contribute to the reaction nor do only Brönsted acid sites influence cyclohexane isomerization. Neither the total number nor the number of highest-strength Lewis acid sites correlates with the isomerization conversion rate, indicating that Lewis acid sites are not responsible for cyclohexane isomerization. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Benzene, a valuable common solvent used in the chemical industry, has been recognized as an important component in gasoline because of its relatively high octane number compared with some of the other hydrocarbons normally used. However, many countries are contemplating, or have already enacted, leg-islation to restrict the benzene concentration allowed in motor fuel because serious toxic effects following prolonged exposure have been reported [1]. Therefore, the maximum benzene concentration allowed in motor fuel in some countries will be reduced in the near future. Recently, the removal of benzene from gasoline created an imbalance between supply and demand, and, because of oversupply, the price of benzene dropped dramatically by nearly 50% (USA, FOB), from US$ $0.40 1^{-1}$ (1990) to approximately US$ $0.21 1^{-1}$ (1998) [2]. Benzene hydrogenation to cyclohexane is a first step in reducing the use of benzene. However, because the low octane number (83) [3,4] of the cyclohexane produced lowers the quality of motor fuel, isomerization of the cyclohexane to

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methylcyclopentane (octane number, 91) is necessary to maintain a sufficiently high octane number. Benzene hydrogenation and isomerization is of importance not only as regards environmental quality but also as a process for converting surplus benzene while satisfying the high-octane-number requirement of modern engines.

Lawson and Okla of the Phillips Petroleum Company reported a two-step process: high naphthenic and benzene feed stocks were hydrogenated with a catalyst at approximately 204°C under a hydrogen pressure of 3.6 MPa; the hydrogenated product was then isomerized with a platinum-on-alumina catalyst (Penex catalyst) at 400°C under a hydrogen pressure of 3.6 MPa to produce methylcyclopentane [5]. UOP has developed a process for benzene reduction in reformer feed and for the isomerization of light paraffins (C4 to C6) with less attention focused on the isomerization of the cycloalkanes and alkylcycloalkanes that result from the hydrogenation of benzene and other aromatics [6]. IFP has developed a two-step process consisting of the hydrogenation of a high-benzene feed (light reformate) with Pt/Al_2O_3 under a hydrogen pressure of 3.0 MPa (180–250°C) as the first step and isomerization of the produced naphthenic with Pt/zeolite under a pressure of 3.0 MPa (240–270°C) as the second step [7]. In this IFP process, the octane of the product is improved by recycling non-converted n-paraffins and cycloalkanes to the isomerization step. These processes are mostly two-step, and the recycling mode in the isomerization step is necessary to achieve a sufficiently high octane number. Fujimoto's group reported that cyclohexane isomerization to methylcyclopentane can be achieved using a physical mixture composed of the catalysts Pt/SiO_2 and H-ZSM-5 at 290°C under a hydrogen pressure of 0.1 MPa [8,9]. A high-benzene feed is treated with a group V–X metal supported on Al_2O_3 and sulfated zirconia (SO_4^{2-}/ZrO_2) to produce a methylcyclopentane-rich product [10,11].

SO_4^{2-}/ZrO_2 is a highly active catalyst in the isomerization and alkylation of alkanes at comparatively low temperatures, although when these reactions were first studied, the origin of the unusually high catalytic activity of SO_4^{2-}/ZrO_2 was uncertain and controversial [12–18]. Pt-supported sulfated zirconia ($Pt/SO_4^{2-}/ZrO_2$) was studied as a highly acidic solid catalyst for n-alkane isomerization [19], but few

studied the sulfate radical zirconia as a bifunctional catalyst for hydrocarbon conversion. Figueras et al. reported that $Pt/SO_4^{2-}/ZrO_2$ is able to isomerize methylcyclohexane into an alkylcyclopentane [20]. Methylcyclopentane can be isomerized to cyclohexane at 65°C with SO_4^{2-}/ZrO_2, which exhibits catalytic activity higher than that of $AlCl_3$ [21–23]. Recently, Parvulescu et al. reported that C6 hydrocarbons such as hexane, cyclohexane, and methylcyclopentane are isomerized and degraded over a gallium-, indium-, or thallium-promoted sulfated zirconia catalyst [24]. The catalytic activity of SO_4^{2-}/ZrO_2 for the isomerization of a cycloalkane depends on the solvent [25].

In the present study, the catalytic activity of $Pt/SO_4^{2-}/ZrO_2$ for benzene hydrogenation and isomerization was examined under milder reaction conditions using the model-compound mixture of benzene and isopentane. The isomerization activity of each catalyst was considered in relation to the number of Brönsted and Lewis acid sites and the distribution of the acid strengths of these sites on ZrO_2, SO_4^{2-}/ZrO_2, HY-zeolite, and H-mordenite.

2. Experimental

2.1. Catalyst preparation

Zirconium hydroxide was prepared by the hydrolysis of zirconium oxide chloride ($ZrOCl_2·H_2O$, Wako Chemical Inc.; purity >99%) with aqueous ammonia (25%, Wako Chemical Inc.). Aqueous ammonia was added slowly to an aqueous solution of zirconium oxide with vigorous stirring (600 rpm) at 70°C, until the pH reached 3.95, after which the pH was increased to 7.90 by the dropwise addition of aqueous ammonia with stirring (600 rpm). After the solution had been stirred at 70°C for 3 h, it was left standing for 12 h at the same temperature. The precipitated gel (zirconium hydroxide) was washed thoroughly with deionized water by decantation and filtration, dried at 110°C for 12 h, and crushed to particles having a diameter of less than 150 μm. The zirconium hydroxide was soaked with excess 1N sulfuric acid solution (15 ml g^{-1} of zirconium hydroxide) with stirring for 2 h at room temperature, filtered, and then dried at 110°C for 36 h. The H_2SO_4-impregnated zirconium hydroxide was heated in air at a rate of 1°C min^{-1} to 200°C and held at this temperature for 1 h. The sample was then

calcined at 550°C for 3 h in air, having been heated to this temperature at the rate of $1°C\,min^{-1}$.

HY-zeolite (JRC-Z-HY5.6), H-mordenite (JRC-Z-HM10), and SiO_2/Al_2O_3 (JRC-SAL-2) were also used for the cyclohexane isomerization reaction. Pt/HY-zeolite (Pt/HY5.6) and Pt/H-mordenite (Pt/HM10) were prepared by ion exchange of the ammonium-form zeolites NH_4-HY5.6 and NH_4-HM10, respectively, with a $0.01\,mol\,l^{-1}$ $[Pt(NH_3)_4]Cl_2$ solution ($[Pt(NH_3)_4]^{2+}$). The ammonium-form zeolites were prepared by the following method: 0.1N aqueous ammonia, which is three to four times the molar ratio of the acid sites in each zeolite, was added dropwise to the zeolites at room temperature with stirring for 48 h; the product was then dried at room temperature. The Pt/HY5.6 and Pt/HM10 were pretreated with an H_2 stream (4% in Ar, $60\,ml\,min^{-1}$) at 400°C for 4 h before the reaction.

2.2. Characterization

The surface area was determined by the BET method; the adsorption isotherm of nitrogen at 196°C was measured by means of a BELSORP28SA. Prior to the adsorption measurements, all samples were degassed at 350°C for 20 min. The adsorption isotherms were determined over the pressure-ratio range $P/P_0=0.1$ to 0.99. The sulfur content of the catalysts was measured by a flask-combustion method, in which the sample was combusted in oxygen and hydrogen peroxide at 1097°C, followed by determination of the SO_4 content by ion chromatography. The Pt concentration was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a SHIMADZU ICP-8000 after decomposing the catalyst with $HF/HClO_4/HCl/HNO_3$. The properties of the various solid acid catalysts and the Pt/solid acid catalysts are summarized in Table 1.

2.3. Reaction procedures

The hydroisomerization of benzene or isomerization of cyclohexane (Wako Chemical Inc.; >99%) to methylcyclopentane was carried out in a stainless-steel autoclave (150 ml) at 250°C in the presence of isopentane under a hydrogen pressure of 5.5 MPa. The isopentane was >99% pure. These reagents were dried with molecular sieves 3 Å 1/8 (Wako Chemical Inc.) before use. The sulfated zirconia (diameter: 355–600 μm; surface area: $157\,m^2\,g^{-1}$) was pretreated at 350°C for 20 min under vacuum before the reaction. Pretreated sulfated zirconia (1.0 g) in reagent (3.0 g), together with isopentane (11.0 g), was placed in a cooled autoclave. The reaction mixture under a hydrogen pressure of 3.6 MPa was heated at $3.5–4.0°C\,min^{-1}$ to 250°C and held at this temperature under autogenous pressure. This reaction temperature was maintained for 60 min. After the reaction, the contents of the autoclave were separated from the solid catalyst by pressure through a filter (pore size 0.2 μm). The products were analyzed with a GC (HP 5890).

2.4. Acid-strength distribution of Brönsted and Lewis acid sites

The number of Brönsted and Lewis acid sites and their acid-strength distributions on the catalyst

Table 1
Physicochemical properties of various catalysts

Catalyst	Pt content (wt.%)	S content (wt.%)	Si/Al ratio	Surface area ($m^2\,g^{-1}$)
ZrO_2	–	–	–	54
2%Pt/ZrO_2	2.1	–	–	62
SO_4/ZrO_2	–	3.7	–	155
2%Pt/SO_4^{2-}/ZrO_2	2.0	3.9	–	157
H-mordenite (HM10)	–	–	10	358
2%Pt/mordenite (2%Pt/HM10)	1.4	–	–	354
H-Y zeolite (HY5.6)	–	–	5.6	519
2%Pt/H-Yzeolite (2%Pt/HY5.6)	2.7	–	–	511
SiO_2/Al_2O_3	–	–	4.8	506
2%Pt SiO_2/Al_2O_3	2.1	–	–	435

surface were calculated using the integrated absorbances from the pyridinium-ion band at $1540\,cm^{-1}$ (due to pyridine chemisorbed on Brönsted acid sites) and the coordinately bonded-pyridine band at $1440\,cm^{-1}$ (due to pyridine chemisorbed on Lewis acid sites), respectively. Pyridine was purified by passage through 4 Å molecular sieves, dried, and subjected to repeated freeze-pump-thaw degassing cycles. A self-supported wafer (diameter: 20 mm; weight: 30–50 mg), placed in an in situ IR cell equipped with CaF_2 windows, was pretreated by outgassing at $400°C$ for 1 h. The pretreated catalyst, after FT-IR spectrum measurement at room temperature, was exposed to 0.015 Torr of pyridine at $150°C$ for 3–5 min and then to a vacuum at the same temperature. After the catalyst had cooled to room temperature, its FT-IR spectrum was measured. This process was repeated using 0.03, 0.06, 0.10, 0.20, 0.30, 0.40, and 0.50 Torr of pyridine after the pyridine from the previous exposure had been completely adsorbed on the catalyst. Molar absorption coefficient (ε)×length (l) was calculated for each catalyst wafer from the slope of the calibration curve for the Brönsted or Lewis acid sites using the following formulas:

$$A = \varepsilon C_T l \tag{1}$$

$$\varepsilon l = \frac{A}{C_T} \tag{2}$$

where A is the peak area of adsorbed pyridine on Brönsted (A_B) or Lewis (A_L) acid sites, C_T the adsorbed pyridine (μmol), l the length of catalyst wafer (cm) and ε is the molar absorption coefficient (cm μmol^{-1}).

The calibration curve relating the total adsorbed pyridine (approximately 0.015, 0.03, 0.06, 0.10, 0.20, 0.30, 0.40, and 0.50 Torr) and the total peak area is required for calculating the ratio of adsorbed pyridine on the Brönsted acid sites to that on the Lewis acid sites.

$$A_T = A_B + \left(\frac{\varepsilon_B l}{\varepsilon_L l}\right) A_L \tag{3}$$

where A_T is the total peak area, A_B the peak area of Brönsted acid sites, A_L the peak area of Lewis acid sites, $\varepsilon_B l$ the slope of calibration curve for adsorbed pyridine on Brönsted acid sites and $\varepsilon_L l$ is the slope of calibration curve for adsorbed pyridine on Lewis acid sites.

The catalyst was exposed to excess pyridine (5 Torr) and then to a vacuum at $150°C$ for 30 min. IR spectra were measured at room temperature after heating the sample stepwise to 150, 200, 250, 300, 350, and $400°C$. The catalyst was held at each temperature for 30 min under evacuation. All spectra were measured at room temperature with an infrared spectrometer (NICOLET AVATAR 360) equipped with a DTGS detector. The FT-IR instrument was operated at a scan speed of $0.1\,cm^{-1}\,s^{-1}$ and with a resolution of $1\,cm^{-1}$, accumulating 150 scans per spectrum.

The amount of adsorbed pyridine at the Brönsted or Lewis acid sites at each temperature (150, 200, 250, 300, 350, and $400°C$) was calculated using the following formulas:

$$C_B = C_T \left(\frac{A_B}{A_T}\right) C \tag{4}$$

$$C_L = C_T - C_B \tag{5}$$

where C_T is the total adsorbed pyridine (μmol), C_B the adsorbed pyridine on Brönsted acid sites (μmol) and C_L is the adsorbed pyridine on Lewis acid sites (μmol).

The calculation of the number of acid sites (μmol) was normalized by the amount of catalyst (30–50 mg).

3. Results

3.1. Catalytic activity in benzene hydrogenation and isomerization over a Pt/solid acid catalyst

The distribution of product in the benzene hydrogenation and isomerization reaction with various Pt-supported solid acid catalysts at $250°C$ is shown in Fig. 1. Benzene was almost completely hydrogenated for all Pt-supported acid catalysts under this reaction condition, although the reactions without any catalyst and with only sulfated zirconia resulted in very little hydrogenation. No isomerization to methylcyclopentane was observed in the reaction catalyzed with Pt/ZrO_2. In contrast, the 47% isomerization conversion observed using Pt/SO_4^{2-}/ZrO_2 was much higher than that observed for the reactions using Pt/SiO_2–Al_2O_3, Pt/HY5.6, and Pt/HM10 catalysts.
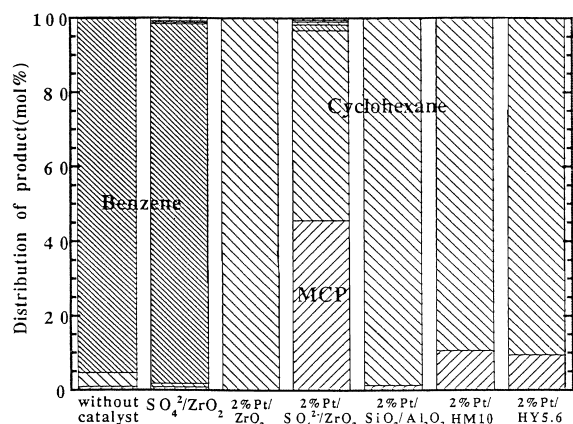
Fig. 1. Distribution of product in the benzene hydrogenation and isomerization reaction using various Pt-supported solid acid catalysts at 250°C.

3.2. Catalytic activity of various solid acid catalysts in cyclohexane isomerization

The distribution of product in the cyclohexane isomerization reaction using various solid acid catalysts at 250°C is shown in Fig. 2. Isomerization to methylcyclopentane did not occur using ZrO_2, as was also the case for the reaction using Pt/ZrO_2 (see Fig. 1). HY5.6 showed only 2% conversion, and HM10 showed approximately 30%. In contrast, SO_4^{2-}/ZrO_2 catalyzed
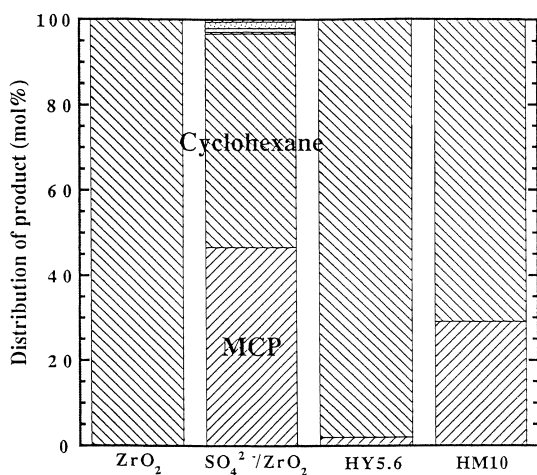
a significantly increased isomerization percentage of 46.2%.

3.3. Brönsted acid strength distribution

Acid-strength distributions of Brönsted acid sites on the surface of a solid acid catalyst, and the relationship between the Brönsted acidity of each solid catalyst and the percentage of isomerization conversion are shown in Fig. 3. Each pattern shows the number of Brönsted acid sites that desorb pyridine with evacuation temperature increasing in steps of 50°C. In this study, temperature was increased in six steps from 150, to 200, 250, 300, 350 and 400°C. An acid site that can keep linking pyridine even at higher temperatures is recognized as an acid site of higher strength. Consequently, pyridinium ions, even at 350 or 400°C, are defined as pyridine linked with a Brönsted acid site of higher strength. In contrast, pyridinium ions observed at 150 or 200°C are defined as pyridine linked with a Brönsted acid site of lower strength. Zirconium oxide had few Brönsted acid sites, and these were mostly weaker sites (150°C). However, the number of Brönsted acid sites was greatly increased by the introduction of sulfated groups up to 115 $\mu mol\, g^{-1}$ of catalyst. Brönsted acid sites of the highest strength, which could keep linking pyridine at 400°C, were also observed in SO_4^{2-}/ZrO_2. The HY5.6 resulted in the formation of the largest number of Brönsted acid sites, but no sites of the highest strength (400°C) were observed, and

Fig. 2. Distribution of product in the cyclohexane isomerization reaction using various solid acid catalysts at 250°C.
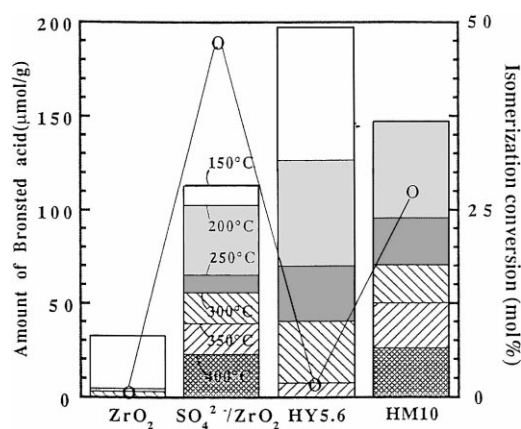

Fig. 3. Relationship between Brönsted acidity of each solid catalyst and percentage of isomerization conversion.

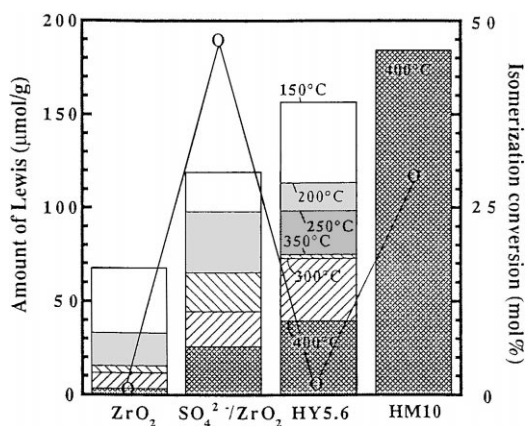Fig. 4. Relationship between Lewis acidity of each solid catalyst and percentage of isomerization conversion.
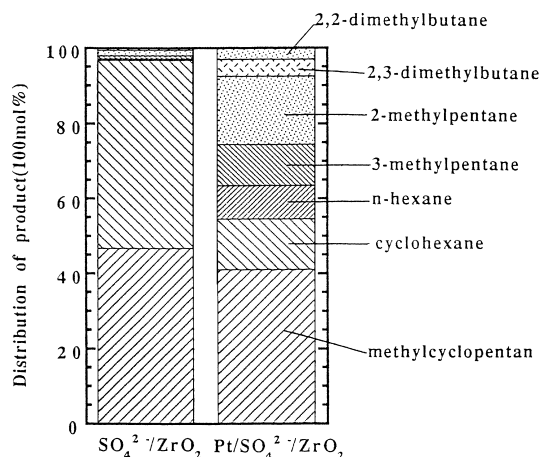

Fig. 5. Distribution of product in the cyclohexane isomerization reaction using sulfated zirconia and Pt-supported sulfated zirconia catalysts at 250°C.

sites of weaker strength (150 and 200°C) were most prevalent. Although the total number of Brönsted acid sites for HM10 was lower than for HY5.6, HM10 had more sites of higher strength; it had almost the same number of high-strength sites as SO_4^{2-}/ZrO_2 did.

3.4. Lewis acid strength distribution

Acid-strength distributions of Lewis acid sites on the surface of various solid acid catalysts and the relationship between the Lewis acidity of each solid catalyst and the percentage of isomerization conversion are shown in Fig. 4. The Lewis acidity also depended on the catalyst. ZrO_2 had 68 μmol Lewis acid sites per gram, and these consisted mostly of weaker sites (150 and 200°C). Pyridine adsorbed on Lewis acid sites in HM10 could not be desorbed at 400°C by evacuation, indicating that HM10 had many high-strength sites. The number of Lewis acid sites and the strength of these sites in both HY5.6 and HM10 were higher than the corresponding quantities in SO_4^{2-}/ZrO_2.

3.5. Catalytic activity in cyclohexane isomerization with various solid acid catalysts

The distribution of product in the cyclohexane isomerization reaction using sulfated zirconia and Pt-supported sulfated-zirconia catalysts at 250°C is shown in Fig. 5. Cyclohexane, which is probably the primary product resulting from benzene hydro-

genation, must be isomerized to methylcyclopentane. SO_4^{2-}/ZrO_2 showed approximately 47% conversion to methylcyclopentane along with small amounts of other products; the isomerization selectivity for methylcyclopentane was very high. In contrast, 2% Pt-supported SO_4^{2-}/ZrO_2 provided a considerable amount of C_6H_{14} product resulting from a ring-opening reaction. It is apparent that Pt on sulfated zirconia can open the ring and produce C6 alkanes and isoalkanes.

4. Discussion

The catalytic activity of $Pt/SO_4^{2-}/ZrO_2$ in benzene hydrogenation and isomerization at 250°C is superior to that of Pt/HY-zeolite and Pt/H-mordenite. The catalytic activity of SO_4^{2-}/ZrO_2 for cyclohexane isomerization to methylcyclopentane at 250°C is higher than that of HY-zeolite and H-mordenite. Sulfated groups on ZrO_2 are required for cyclohexane isomerization, indicating that the sulfated groups probably contain the active site or cause an active site to form.

The total number of Brönsted acid sites and their strength distribution vary among the catalysts. The relative order by the total number of Brönsted acid sites is

$$HY5.6 > HM10 > SO_4^{2-}/ZrO_2 > ZrO_2$$

However, their relative order by the number of Brönsted acid sites of highest strength, which can keep linking pyridine at 400°C, is

$$HM10 \simeq SO_4{}^{2-}/ZrO_2 > ZY5.6 \simeq ZrO_2$$

$SO_4{}^{2-}/ZrO_2$ and HM10 have more Brönsted acid sites of the highest strength and show a higher percentage of conversion (see Fig. 2). In contrast, ZrO_2 contains almost no Brönsted acid sites, and HY5.6 contains almost no sites of the highest strength, Consequently, these catalysts show a lower conversion percentage

$$SO_4{}^{2-}/ZrO_2 > HM10 > HY5.6 > ZrO_2$$

These results indicate that Brönsted acid sites of the highest strength are responsible for cyclohexane isomerization. Consequently, Brönsted acid sites of the highest strength (400°C) contribute the most to the isomerization reaction; conversely, sites of lower and medium strength probably do not contribute significantly. However, the percentage of conversion does not completely correlate with the number of Brönsted acid sites of highest strength, suggesting that not all of these sites contribute to the reaction, nor do only sites of the highest strength influence cyclohexane isomerization.

The relative number of Lewis acid sites of the highest strength as well as the total number of sites can be described as follows:

$$HM10 > HY5.6 > SO_4{}^{2-}/ZrO_2 > ZrO_2$$

Neither the total number of Lewis acid sites nor the number of these sites of the highest strength are correlated with the percentage of isomerization conversion, indicating that Lewis acid sites are not responsible for cyclohexane isomerization.

The determination of heats of desorption from ammonia and pyridine TPD plots is probably the most familiar method to date for characterizing acidity in solid acid catalysts, although measurement of heats of adsorption on solid surfaces cannot differentiate between a Brönsted acid site and a Lewis acid site [26,27]. Fogash et al. found that saturation ammonia coverage was approximately $230\,\mu mol\,g^{-1}$ on a $SO_4{}^{2-}/ZrO_2$ catalyst (MEl sample) [26]. Jin et al. reported coverage of 210 and $260\,\mu mol\,g^{-1}$, based on pyridine and ammonia adsorbed, respectively, on a $SO_4{}^{2-}/ZrO_2$ catalyst [27]. Their results are approximately equal to the total number ($234\,\mu mol\,g^{-1}$) of Brönsted and Lewis acid sites on $SO_4{}^{2-}/ZrO_2$ found in this study, although their preparation method was different. The Brönsted acidity in H-mordenite is higher than in HY-zeolite as reported in a ^{13}C NMR study of acetone adsorption in a solid acid catalyst [28], suggesting that H-mordenite has higher Brönsted acidity than does HY-zeolite. The results from this study of the quantitative analyses of Brönsted and Lewis acid sites by IR-spectroscopic monitoring of adsorbed pyridine are consistent with those already reported.

It has recently been claimed that the strength of acid sites in $SO_4{}^{2-}/ZrO_2$ is lower than the strength in 100% H_2SO_4, H-ZSM-5, HX- and HY-zeolite [29–31]. In this study, the number of Brönsted acid sites of higher and highest strength in HM10 (H-mordenite) is almost the same as in $SO_4{}^{2-}/ZrO_2$, and the Brönsted acidity of HY5.6 (HY-zeolite) is lower than that of $SO_4{}^{2-}/ZrO_2$ although the Lewis acidity of HY5.6 is higher than that of $SO_4{}^{2-}/ZrO_2$. These results indicate that the acidity of $SO_4{}^{2-}/ZrO_2$ is neither higher nor lower than the acidity of a conventional solid acid catalyst.

$Pt/SO_4{}^{2-}/ZrO_2$ can open the ring and produce C_6H_{14} alkanes and isoalkanes, as in the case of the cyclohexane isomerization reaction (Fig. 5). $Pt/SO_4{}^{2-}/ZrO_2$ can participate in the ring-opening reaction in benzene hydrogenation and isomerization under severe reaction conditions such as a longer reaction time or a higher reaction temperature. However, the main products obtained under these conditions were 2-methylpentane (73), 3-methylpentane (75), and n-hexane (25), which have lower octane numbers than do methylcyclopentane (91) and cyclopentane (83). The octane numbers of 2,2-dimethylbutane (92) and 2,3-dimethylbutane (103) are almost equal to or higher than the methylcyclopentane octane number, but the yields of these compounds are lower. These C6 alkanes and isoalkanes are in equilibrium, as indicated by their distribution at 250°C. The following equilibrium is predicted: n-hexane 15%, 2-methylpentane 30%, 3-methylpentane 15%, 2,2-dimethylbutane 29%, and 2,3-dimethylbutane 11% [32], indicating that components of lower octane number are thermodynamically favored at 250°C, although the molar ratio of components having higher octane numbers is high at reaction temperatures between room temperature and 150°C. Consequently, ring-opening at 250°C is

an undesirable side reaction from the standpoint of octane number and fuel quality.

5. Conclusion

The catalytic activity of $Pt/SO_4^{2-}/ZrO_2$ in benzene hydrogenation and isomerization at $250°C$ is superior to that of Pt/HY-zeolite and Pt/H-mordenite. The catalytic activity of SO_4^{2-}/ZrO_2 for cyclohexane isomerization to methylcyclopentane at $250°C$ is also higher than that of HY-zeolite and H-mordenite. Sulfated groups on ZrO_2 are required for cyclohexane isomerization, indicating that the sulfated group is probably the active site or causes the active site to form.

SO_4^{2-}/ZrO_2 and HM10 have more Brönsted acid sites of higher and highest strength, and they show a higher isomerization conversion percentage. In contrast, ZrO_2 and HY5.6 contain almost no Brönsted acid sites (ZrO_2) or no sites of highest strength (HY5.6), and they show a low conversion percentage. Consequently, Brönsted acid sites of highest strength are responsible for most of the cyclohexane isomerization. However, the percentage of conversion does not completely correlate with the number of Brönsted acid sites of highest strength, suggesting that not all of these sites contribute to the reaction, nor do only the sites of highest strength influence cyclohexane isomerization.

Neither the total number of Lewis acid sites nor the number of high-strength Lewis acid sites are correlated with the isomerization conversion percentage, suggesting that Lewis acid sites are not responsible for cyclohexane isomerization.

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