

ISOMERISATION OF CYCLOHEXANE TO METHYLCYCLOPENTANE OVER $\text{Pt}/\text{SO}_4^{2-}\text{-ZrO}_2$ CATALYST

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ABSTRACT

Skeletal isomerisation of cyclohexane to methylcyclopentane over $\text{Pt}/\text{SO}_4^{2-}\text{-ZrO}_2$ (PSZ) catalyst was studied in a closed recirculation reactor in the temperature range 413-503 K. In the presence of Pt and hydrogen, the stability and activity of catalyst were enhanced markedly due to generation of protonic acid sites acting as a catalytic site for acid-catalysed reaction and suppression effect in the formation of polymeric material on the surface of catalyst. FTIR study of pyridine adsorbed on PSZ catalyst have been used to monitor the generation of active sites for isomerisation of cyclohexane. The results revealed that the active sites for acid-catalysed reaction were generated from molecular hydrogen molecules on the surface of catalyst. A high stability and steady state activity of PSZ catalyst for cyclohexane isomerisation in the presence of hydrogen were observed for at least 1 h with the estimated apparent activation energy of 20.2 kJ/mol. The activity of catalyst declined continuously due to the formation of polymeric materials and reached to zero level within 2 h. However, the treating used-catalyst in a circulating oxygen at 573 K followed by outgassing at 573 K restored about 80 % of the catalytic activity.

Keywords: Hydrogen Treatment, Isomerisation, Oxygen Treatment, PSZ Catalyst

INTRODUCTION

Skeletal isomerisation of light naphtha becomes an important process in modern refining processes for a gasoline of high quality. In industrial scale, $\text{Pt}/\text{Al}_2\text{O}_3\text{-Cl}$ and $\text{Pt}/\text{zeolite}$ catalysts are used for isomerisation of *n*-butane in the presence of hydrogen, though they also have a lot of disadvantages. $\text{Pt}/\text{Al}_2\text{O}_3\text{-Cl}$ catalyst is highly active but suffered from extreme sensitivity to all kinds of feed contaminants. $\text{Pt}/\text{zeolite}$ needs high temperature to operate satisfactorily.

Recently, sulfate-treated zirconium oxide ($\text{SO}_4^{2-}\text{-ZrO}_2$) catalyst has been explored widely for isomerisation process [1-4]. Arata [5] reported that sulfate-treated zirconium oxide catalyst exhibits extremely strong acidity with 10^4 times stronger than 100% sulphuric acid and is capable to isomerize *n*-butane to isobutane at room temperature in the presence of Pt and hydrogen. Although the effects of precursor catalyst, preparation method, activation method, the nature of Pt and active site, and reaction mechanism are now better understood for straight alkanes isomerisation over PSZ catalyst, the literature related to the isomerisation of aromatic compounds is lacking because of the difficulty on the isomerisation such as the lower selectivity of desired isomer product or the deactivation rate of PSZ catalyst is too high. Aromatic compounds are usually utilised as high-octane additive for gasoline in order to maintain a sufficiently high quality of motor fuel. However, it is desirable to reduce the percentage of aromatic compounds in gasoline since the aromatics are known to be carcinogenic substances. In this regard, the development of new process for conversion of aromatics such as benzene and cyclohexane to environmentally harmless products is required. In particular, only a few papers related to the cyclohexane isomerisation to methylcyclopentane were published, though methylcyclopentane is suitable for additive for gasoline which has a higher Research Octane-Numbers (RON=91) compared to that of cyclohexane (RON=83)

and *n*-hexane (RON=25) [6]. Therefore, in this report study, we focused on the isomerisation of cyclohexane to methylcyclopentane using PSZ catalyst under hydrogen atmosphere. The reaction was carried out in a closed recirculation reactor under mild reaction conditions in order to (1) elucidate the roles of hydrogen, (2) examine the effects of oxygen-treatment in order to restore the catalytic activity of used PSZ catalyst, and (3) study the kinetic of cyclohexane isomerisation.

2. EXPERIMENTAL

2.1. Catalyst Preparation

The $\text{Pt}/\text{SO}_4^{2-}\text{-ZrO}_2$ (PSZ) catalyst was prepared as follows. Zirconium hydroxide was prepared from aqueous solution of $\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}$ by hydrolysis with 2.5 wt% NH_4OH aqueous solution. The final pH was 10. The precipitate was filtered and washed with deionized water. The obtained gel was dried at 383 K to form $\text{Zr}(\text{OH})_4$. The sulfate ion-treated $\text{Zr}(\text{OH})_4$, which is denoted as $\text{SO}_4^{2-}\text{-Zr}(\text{OH})_4$, was prepared by impregnation of the $\text{Zr}(\text{OH})_4$ with 1 N H_2SO_4 aqueous solution followed by filtration and drying at 383 K. $\text{SO}_4^{2-}\text{-ZrO}_2$ (SZ) catalyst was obtained by calcined $\text{SO}_4^{2-}\text{-Zr}(\text{OH})_4$ stepwise from 373 K to 873 K in 100 K increments in air. The PSZ catalyst was prepared by impregnation of SZ catalyst with H_2PtCl_6 aqueous solution followed by drying and calcination as in the case of SZ catalyst. The content of Pt was adjusted to be 0.5 wt %.

2.2. Characterisation

JEOL X-Ray Diffractometer JDX-3500 and Coulter SA 3100 were used to determine the crystalline structure and specific surface area of prepared samples.

Temperature-programmed desorption (TPD) of ammonia was carried out with Bell Multitask MS-TPD as follows. The sample was pretreated with hydrogen flow at 673 K followed by purging with helium flow. Then, the pretreated sample was

exposed to dehydrated-ammonia at 373 K followed by purging with He flow at 373 K. The TPD was run at a heating rate of 10 K/min from room temperature to 950 K, and the desorbed ammonia was detected by mass spectrometry.

FTIR measurement was carried out with a Perkin-Elmer Spectrum One FTIR Spectrometer equipped with a MCT detector. Pyridine used for probe molecule to determine the type of acid sites was purified by repeated freeze-pump-thaw degassing cycles. The sample of self-supported wafer was pretreated in a hydrogen flow at 673 K followed by outgassing at 673 K. For the measurement of pyridine adsorbed on the sample, the sample was exposed to pyridine at 423 K followed by outgassing at 423 K. For the measurement of IR spectra of adsorbed pyridine affected by the presence of hydrogen, the sample was exposed to pyridine at 423 K followed by outgassing at 673 K, then the pyridine pre-adsorbed sample was exposed to 150 Torr of H₂ at 473 K and followed by heated at 573 K. The spectra was recorded at room temperature with a spectral resolution of 4 cm⁻¹ and with 128 scans.

2.3. Hydrogen Adsorption

The hydrogen uptake was measured by automatic gas adsorption apparatus Belsorp 28SA. The sample was pretreated in hydrogen flow at 573 K, followed by outgassing at same temperature, and cool to an adsorption temperature of 523 K. Hydrogen was then introduced to the system, and hydrogen pressure change with time was monitored for 10 h. The hydrogen uptake was calculated from a pressure change.

2.4. Reaction Procedure

Isomerisation of cyclohexane was carried out in a closed recirculation reactor. Cyclohexane was purified by passing it through a silica-alumina column chromatograph and subjecting it to repeated freeze-pump-thaw degassing cycles. The catalyst was pretreated with circulating hydrogen at 573 K followed by outgassing at 573 K. The isomerisation was carried out at 413 – 503 K with the partial pressure ratio of hydrogen/cyclohexane = 0/1 - 6/1. The products were analysed by on-line Shimadzu Gas Chromatograph and a VZ-7 column was used. Restoration the activity of used catalyst was done as follows. Used catalyst was treated with circulating oxygen at 573 K followed by outgassing at 573 K in order to remove the deposition of polymeric materials from the active sites. Prior to the catalytic runs, the catalyst was subjected to the treatment of a fresh catalyst.

3. RESULTS AND DISCUSSION

3.1. Physical Properties of Catalyst

The textural properties of the samples are summarized in Table 1. The zirconia (ZrO₂) support catalyst obtained by calcining amorphous Zr(OH)₄ at 873 K showed a lower specific surface area compared to that of SZ and PSZ catalysts which were prepared by calcining amorphous Zr(OH)₄ after sulfate and Pt were added. However, the change of total pore volume was not observed, though the disappearance of a fraction of large pores has occurred with a concomitant appearance of a fraction of small pores by addition of sulphate and Pt. The maximum of d(volume)/d(diameter) function has been shifted toward smaller pores. Pore size distribution plots of the acid-treated catalysts are shown in Figure 1.

Figure 2 illustrates the XRD pattern for zirconia, SZ and PSZ catalysts. The peak at about 2θ = 30° is assigned to tetragonal

Table 1: Textual properties of prepared samples

	Surface Area m ² /g	Total Pore Vol. ml/g	Ratio of M/T*
ZrO ₂ (Zirconia)	33	0.136	90/10
SO ₄ ²⁻ ZrO ₂ (SZ)	99	0.137	6/94
Pt/SO ₄ ²⁻ -ZrO ₂ (PSZ)	100	0.137	9/91

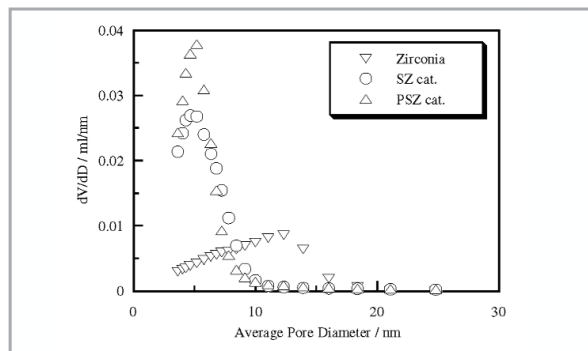


Figure 1: Pore size distribution of prepared samples

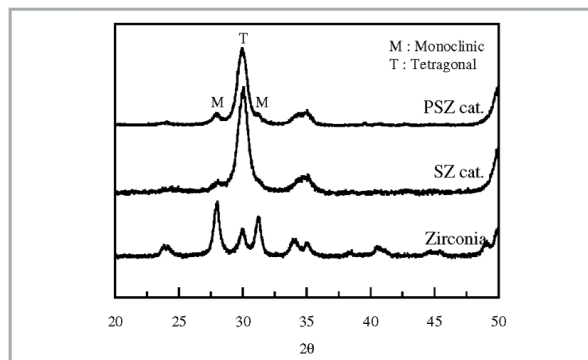


Figure 2: X-ray diffraction spectra of prepared samples

phase of zirconia, and the peaks at about 2θ = 28° and 2θ = 32° are assigned to monoclinic phase of zirconia. Peaks assigned to tetragonal and monoclinic phase of zirconia were observed on the zirconia support catalyst. By adding sulphate and platinum, predominant monoclinic phase of zirconia disappeared and the tetragonal phase of zirconia developed markedly. The similar patterns and almost the same intensity of peaks were obtained for the SZ and PSZ catalysts with the fraction of monoclinic phase of zirconia were less than 10%. Toraya's Equation was used to determine the fraction of tetragonal and monoclinic phase of zirconia [7].

The intense peaks of metallic platinum at 2θ = 40° corresponding to Pt (111) and 2θ = 45° corresponding to Pt (200) were not observed which may show that the amount of Pt was too small for mass analysis or there were too many indistinct lines in the background.

3.2. Intrinsic and Nature of Acidity

Ammonia TPD and FTIR spectra of pyridine adsorbed on sample catalysts had been used to evaluate the acidity and acid strength of catalyst. The acid distribution and strength were characterised by ammonia TPD. Figure 3 illustrates the ammonia TPD plots for zirconia, SZ and PSZ catalysts. The TPD plots consist of three TPD peaks; indicating the existence of weak (a peak appearing at about 450 K), medium (a peak appearing at

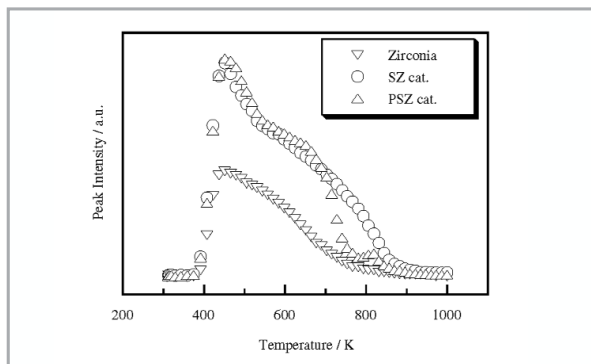


Figure 3: Ammonia TPD plot of prepared samples

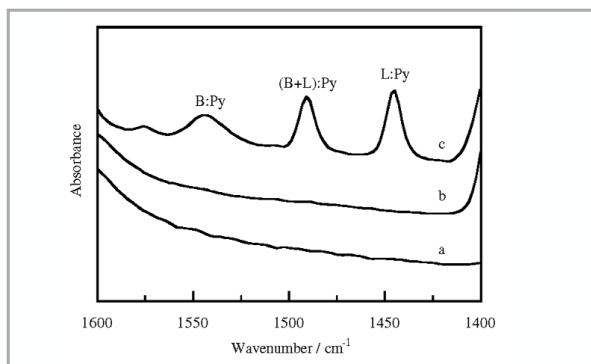
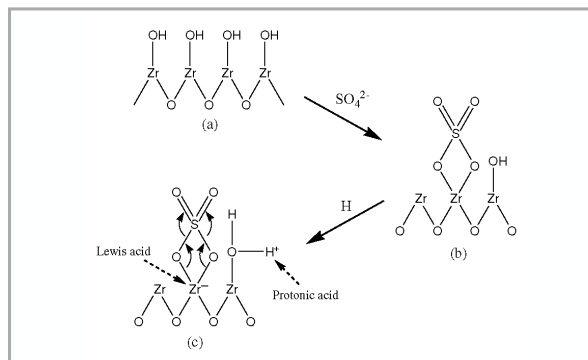


Figure 4: IR spectra of a) fresh, b) reduced at 673K, and c) pyridine preadsorbed PSZ catalyst

about 650 K) and strong (a peak appearing at about 823 K) acid sites. For zirconia support catalyst, low intensity of peak assigned to weak and medium acids were detected and no peak assigned strong acid was detected. The addition of sulfate ion followed by calcination at 873 K increased the intensity of weak and medium acid and developed a new peaks at about 823 K corresponding to the strong acid sites. The further addition of Pt did not much affect the acid strength distribution, even considerably change was observed at about 800 K due to the desorption of hydroxyl group at high temperature which is facilitated by Pt catalyst. Several research groups reported the similar phenomena of desorption ammonia from the PSZ catalyst. Vaudagna *et al.* [8] and Ganapati *et al.* [9] reported that in the absence of Pt, desorption peaks of ammonia were observed below 623 K which are corresponding to the weak and medium acid sites. The peaks have been shifted slightly toward higher desorption temperature and new peak was observed at about 850 K corresponding to the strong acid sites as Pt was introduced on the SZ catalyst.

FTIR spectroscopy of adsorbed pyridine was used to determine the acid-sites types on the PSZ catalyst. The spectra of fresh and treated catalysts were illustrated in Figures 4. The spectrum of adsorbed pyridine on PSZ catalyst is also illustrated in Figure 4. As the PSZ catalyst was pretreated and outgassed at 673 K prior to adsorption of pyridine, the peaks in the spectra showed the pyridine adsorbed only on the strong acid sites. The absorption band at 1450 cm^{-1} is due to pyridine adsorbed on Lewis acid site (L:Py), the absorption band at 1490 cm^{-1} to pyridine adsorbed on Lewis acid site and on protonic acid site ((B+L):Py), and the absorption band at 1540 cm^{-1} to pyridine adsorbed on protonic acid site (B:Py) [10].

In order to understand the role of sulfate ion in the enhancement



Scheme 1: Proposed structure of sulphated-zirconia catalyst

of surface acidity of zirconia, a lot of studies attempted to determine the nature of acid sites in this catalyst. Various model structure of sulfated zirconia were proposed such as a double bond structure with two S=O [11], triple bond structure with single S=O [12] and penta-coordinated model sulfate species [13]. However, based on results from FTIR and Raman spectroscopy, the most probable structure of this species was proposed as model (b) in Scheme 1 [5]. Ebitani *et al.* also pointed out that the strong acidity is generated by the inductive effect of the S=O double bonds, which increase the electron deficient nature of the Zr^{4+} atom attached to the sulfate group as illustrated by arrows in (c) [14].

Clearly, the nature of active sites on the sulfated zirconia catalyst remains controversial. However, their catalytic properties obviously elucidate the strong effect of surface modification of zirconia by sulfate ion.

3.3. Generation of Active Sites From Molecular Hydrogen

The skeletal isomerisation is normally carried out in the presence of hydrogen to enhance the activity of catalysts. We already reported the effects of hydrogen on the catalytic activities of PSZ catalyst for acid-catalysed reactions. Our results suggested that protonic acid sites are generated from molecular hydrogen and act as catalytically active sites for the skeletal isomerisation of alkanes [4,14-16]. We also proposed that surface protons are formed from molecular hydrogen as follows. Hydrogen molecules are dissociatively adsorbed on the Pt sites to form hydrogen atoms which undergo spillover on the surface of SZ catalyst. The spilt-over hydrogen atom migrates over the surface of SZ catalyst to Lewis acid site where the hydrogen atoms release an electron to form a proton. The proton may be stabilised on the O atom nearby the Lewis acid site as illustrated in Scheme 1(c). The Lewis acid site trapping an electron reacts with a second hydrogen atom to adsorb hydrogen in the form of a hydride.

In the present report, we demonstrated the generation of protonic acid sites from molecular hydrogen molecules by an IR study of adsorbed pyridine and hydrogen adsorption isotherm on PSZ catalyst.

The spectra of pyridine adsorbed on PSZ catalyst followed by heating in the presence of hydrogen at 473 K and 573 K are shown in Figures 5, curves b and c respectively, while curve a showed the spectrum of pyridine adsorbed on PSZ after outgassing of the pyridine-covered at 673 K. Heating in the presence of hydrogen resulted in a decrease in the intensity of pyridine adsorbed on Lewis acid sites at 1450 cm^{-1} , concomitant an increase in the intensity of pyridine adsorbed on protonic acid sites at 1540 cm^{-1} . The increasing of the intensity of pyridine adsorbed was also

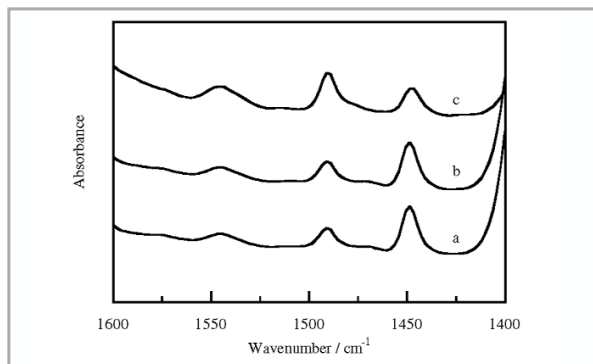
ISOMERISATION OF CYCLOHEXANE TO METHYLCYCLOPENTANE OVER Pt/SO₄²⁻-ZRO₂ CATALYST

Figure 5: IR Spectral changes when pyridine-adsorbed PSZ a) evacuated at 673K, heated at b) 473K and c) 573K in the presence of hydrogen

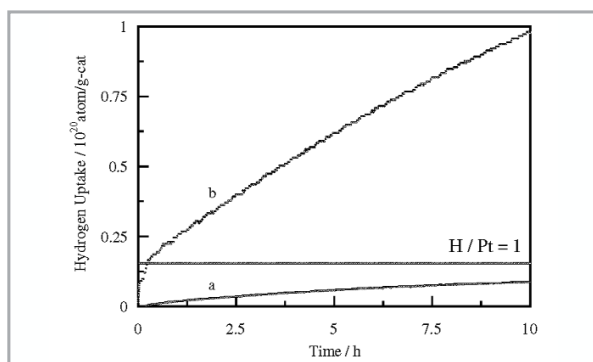


Figure 6: Variations of hydrogen uptake as a function of time at 523K. a) SZ, b) PSZ catalysts

detected at 1490 cm⁻¹ which is assigned to the absorption band containing protonic and Lewis acid sites. The interaction between hydrogen molecules and the PSZ caused the increase in the number of the protonic acid sites on the surface of SZ catalyst. Although it is not shown in the present paper, the evacuation at high temperature caused the decrease in number of protonic acid sites and a restoration of the number of Lewis acid sites to its original. This implies that the acid properties of PSZ catalyst dynamically change with heating in the presence of hydrogen and evacuation. It also suggested that the modification of the acid properties by hydrogen exposure is a reversible process.

Figure 6 illustrates the variations of hydrogen uptake on the SZ and PSZ catalysts as a function of time. At a constant hydrogen pressure, the hydrogen uptake still continued after 10 h when adsorption was carried out at 523 K on PSZ catalyst. The hydrogen uptake reached 9.9×10^{19} H-atom/g-cat corresponds to the number H/Pt ratio of 6.5 which exceed unity. A large number of the H/Pt ratio indicating that the hydrogen adsorption involved hydrogen spillover and surface diffusion. However, in the absence of Pt, the hydrogen uptake was scarcely appreciable. The above results strongly revealed that the active sites for acid-catalysed reaction were generated from molecular hydrogen molecules on the surface of PSZ catalyst through; 1) hydrogen dissociatively adsorbed on the Pt sites to form hydrogen atoms, 2) hydrogen spillover onto the support and 3) surface diffusion of hydrogen spillover.

3.4. Cyclohexane Isomerisation

The effects of Pt and hydrogen on the catalytic activity of SZ catalyst for skeletal isomerisation of cyclohexane are shown in Figures 7 and 8, respectively. Cyclohexane isomerisation was

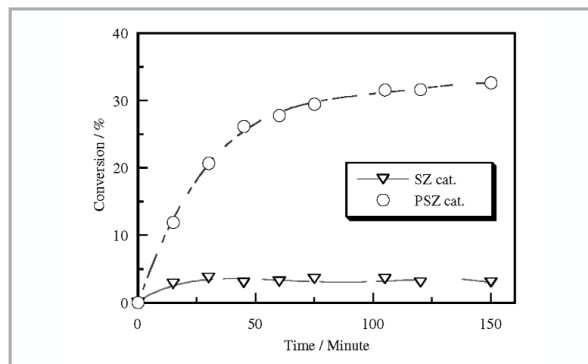


Figure 7: The effect of Pt on the cyclohexane isomerisation, reaction was carried out at 503K with hydrogen/ cyclohexane = 6/1

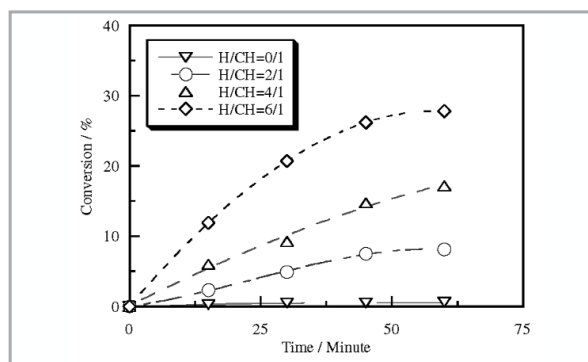


Figure 8: The effect of hydrogen on the cyclohexane isomerisation over PSZ catalyst

carried out at 503 K with the range of hydrogen/cyclohexane partial pressure ratio is 0/1 - 6/1. In this isomerisation, products other than methylcyclopentane were at a much lower level. Therefore, cyclohexane isomerisation was close to methylcyclopentane yield only under these reaction conditions.

As shown in Figure 7, the activity of SZ catalyst was scarcely observed in the initial period of reaction and no further improvement of the catalyst activity was observed, although the reaction was carried out in the presence of hydrogen for more than 2 h. However, in the presence of Pt and hydrogen, SZ catalyst showed a higher catalyst activity in the initial period of reaction compared to that of Pt-free SZ catalyst. The high activity of Pt loaded SZ catalyst was observed for at least 1 h and lost the activity after 2 h. The deactivation of catalyst may be caused by the catalyst poisoning due to the deposition of polymeric materials on the surface of catalyst during reaction. The above results indicated that the addition of SO₄²⁻ is required to generate the strong acid sites over the zirconia support catalyst as shown by ammonia TPD results, but it is still not sufficient to raise the catalytic activity for cyclo-alkane isomerisation. Therefore, the presence of metal catalyst, like Pt, which facilitated the generation of protonic acid sites on the surface of SZ catalyst is necessary for raising and stabilising the initial activity of catalyst and the suppression of activity decay when the isomerisation is carried out in the presence of hydrogen.

Figure 8 illustrates the dependence of cyclohexane conversion to methylcyclopentane on reaction time over PSZ catalyst under different partial pressure ratio hydrogen/cyclohexane. At partial pressure ratio hydrogen/cyclohexane = 0/1, the catalytic activation was observed near zero level from initial period of reaction. The increasing of partial pressure of hydrogen up to

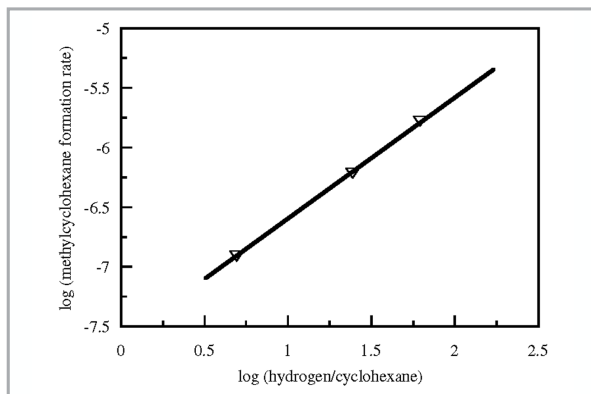


Figure 9: Dependence of catalytic activity of cyclohexane isomerisation on the partial pressure ratio of hydrogen/ cyclohexane

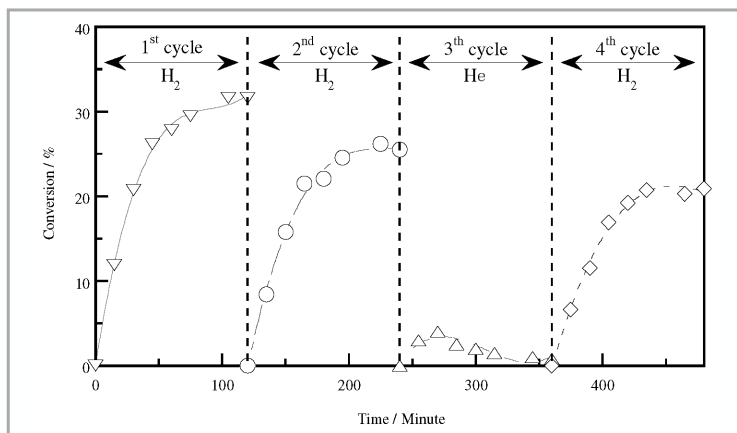


Figure 10: Restoration of PSZ used-catalyst by heating in the presence of oxygen followed by outgassing at 573K

hydrogen/cyclohexane = 6/1 increased the activity of catalysts and it was stable for at least 1 h due to the role of hydrogen to generating protonic acid sites and removing the deposition of polymeric material. Figure 9 illustrates the dependence of catalytic activity of cyclohexane isomerisation on the partial pressure ratio of hydrogen/cyclohexane. It shows that the formation rate of methylcyclopentane increased linearly with the partial pressure ratio of hydrogen/cyclohexane.

The effect of hydrogen was also showed in Figure 10. In the present of hydrogen, the activity is high as shown in Figure 10 region B, however, the activity is very low and declined continuously with reaction time as the carrier gas is switched to helium as shown in region C of Figure 10. As the carrier gas switched back to hydrogen, the activity of catalyst gradually recovered as shown in region D. Prior to the switching of carrier gas, the reaction was terminated and the catalyst was subjected to treatment in a circulation of oxygen followed by outgassing at 573 K. From the above results, it was concluded that hydrogen strongly affected the stability and steady state activity of PSZ catalyst.

The activity of catalyst decreased slowly with the time and reached to zero level-activity within 2 h due to the formation of polymeric materials during reaction as shown in region A, B and D. The phenomena of deactivation PSZ catalyst during reaction was studied widely. Spielbauer *et al.* [17] reported that deactivation of PSZ catalyst is caused by formation of allylic and polyenylic species during *n*-butane isomerisation. Comeli *et al*

[18] and Garin *et al.* [19] suggested that the dehydrogenated carbonaceous species are considered to be a precursor of coke formation at the active sites. Decomposition of sulfate facilitated by the present of metallic-Pt was also reported to be the reason for the deactivation of PSZ catalyst [20,21]. Moreover, Hong *et al.* [22] reported the effect of feed contaminants such as water and olefins species enhanced the deactivation rates of catalyst. Although the nature and mechanism of the deactivation of PSZ catalyst are not clear yet for alkanes isomerisation, we suggested that the formation of polymeric materials can be considered to be the primary reason for the deactivation of catalyst either in the presence or in the absence of hydrogen.

Figure 11 illustrates the time course of cyclohexane isomerisation over PSZ catalyst at 413 – 503 K with the partial pressure ratio hydrogen/cyclohexane = 6/1. The conversion rate of cyclohexane increased in the increasing of reaction temperature, though the high activity and stability of catalysts were observed for about 1 h for all reaction temperatures. As shown in Figure 12, the apparent activation energy estimated from the initial conversion rate of cyclohexane to methylcyclopentane was 20.2 kJ/mol. The apparent activation energy obtained is lower than that of 42 kJ/mol [23] for *n*-butane isomerisation over PSZ catalyst and 114 kJ/mol [24] for cyclohexane isomerisation over platinum loaded hydrogen mordenite (Pt/HMOR) catalyst in a fixed-bed continuous flow reactor. It showed the easiness of cyclohexane conversion over the PSZ catalyst in a closed recirculation reactor compared to the conversion of *n*-butane over PSZ catalyst or cyclohexane conversion over the Pt/HMOR catalyst in a fixed-bed continuous flow reactor.

3.5. Restoration of Catalytic Activity

In the present report, restoration of catalytic activity was studied by heating in oxygen atmosphere. The deposition of polymeric materials on the surface of catalyst which lead to deactivate the catalyst was removed by heating in a circulating oxygen at 573 K followed by outgassing at 573 K. As illustrated in Figures region B and D of Figure 10, the activity of catalyst was restored for about 80 % compared to the previous cycle reactions. The loss of sulphur or the decomposition of the nature of active sites during reaction which may cause the sulphur-poisoning of catalyst and conversion of tetragonal into monoclinic phase of zirconia, probably associated to the incomplete restoration of the catalyst activity.

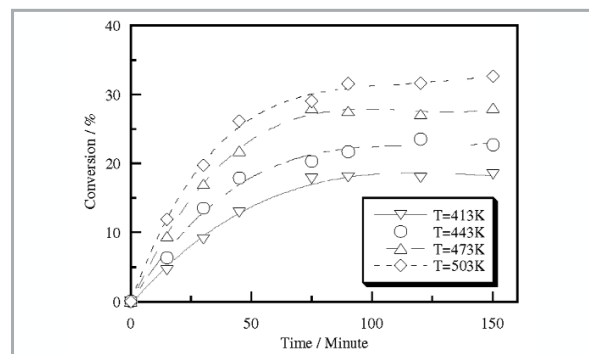


Figure 11: Dependence of cyclohexane isomerisation over PSZ in the different reaction temperature

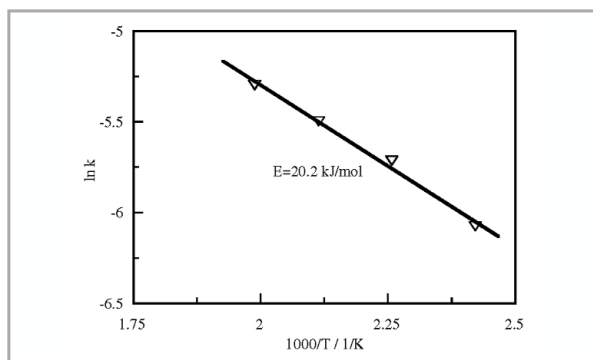


Figure 12: Arrhenius plot of cyclohexane isomerisation over PSZ catalyst

4. CONCLUSION

This study provided information about the role of hydrogen and oxygen and kinetic study of cyclohexane isomerisation over PSZ catalyst. The following conclusion can be drawn from this study;

- In the presence of hydrogen, high stability and steady state activity of PSZ catalyst were observed for at least 1 h with the estimated apparent activation energy of 20.2 kJ/mol. It is suggested that the role of hydrogen is the generation of active for isomerisation.
- The activity of catalyst declined continuously with reaction time due to the formation of polymeric materials on the surface of catalyst and reached to zero level within 2 h. The treating used-catalyst in a circulating oxygen at 573 K followed by outgassing at 573 K restored about 80 % of the catalytic activity. ■

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PROFILES



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