Studies on chlorided Pt/Al_2O_3 catalysts: preparation, characterization and *n*-butane isomerization activity

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A series of chlorided Pt/Al_2O_3 (both γ and η) catalysts were prepared and characterized for various physicochemical properties. The chloride content of the catalysts was found to increase with chloride treatment time up to a certain level and then decrease owing to prolonged exposure at high temperature. The surface area and pore volume of the catalysts were decreased by chloride treatment. The activity of the prepared catalysts were tested in *n*-butane isomerization. The platinum content of the catalysts was found to have no effect on catalytic activity up to 0.2 wt% whereas the chloride content of the catalyst strongly influenced the activity and a >20-fold increase in activity was observed on chloriding Pt/Al_2O_3 catalysts. The catalyst activity was found to be directly related to its acidity.

KEY WORDS: chloriding; Pt/Al_2O_3; ammonia chemisorption; ammonia TPD; Brønsted acidity; butane; isomerization.

1. Introduction

In many important catalytic reactions, such as isomerization, cracking, alkylation, polymerization, etc., acid sites on the catalyst surface play an important role in the transformations. The acid sites are instrumental in the formation of carbonium ions and subsequent transformations of carbon skeletons [1].

Isomerization of straight-chain hydrocarbons to branched hydrocarbons is an important process for the production of clean-burning fuel in the petroleum refining industry [2,3]. The process is applied for the improvement of octane numbers of light naphtha and also for some individual straight-chain hydrocarbons mostly in the range C_4–C_7. Among individual hydrocarbons, isomerization of *n*-butane to isobutane is of particular interest as it can be alkylated with isobutene (which can also be obtained from *n*-butane by dehydroisomerization) to give the most-desired fuel component, isooctane (2,2,4-trimethylpentane). Isobutene, from isobutane, is also a key component for the manufacture of methyl *tert*-butyl ether (MTBE).

As a reaction of high commercial importance, isomerization of *n*-butane has been studied extensively over a wide variety of catalysts. It is generally accepted that isomerization reactions should be carried out on a bifunctional catalyst, consisting of a protonating acid function and a hydrogenating/dehydrogenating metal function.

The effect of platinum loading on the isomerization of *n*-butane over small crystals of H-beta has been studied [4]. Pt–H-beta catalyst demonstrates higher conversion and selectivity to isobutane than H-beta. Based on the product distribution, a mechanism has been proposed for the isomerization reaction which includes hydrogenolysis and dehydrogenation over Pt, and cracking, isomerization and disproportionation over acid sites.

Dehydroisomerization of *n*-butane to isobutene has been studied over Pd/SAPO catalysts [5,6]. The activity and selectivity for isobutene have been reported to change with pore size and the highest values are obtained with Pd/SAPO-11 having a 10-membered ring opening [6]. Dehydroisomerization of *n*-butane has also been studied over Pt-promoted Ga-substituted silicoaluminophosphates and the possible formation of Pt–Ga alloy and/or the formation of discrete Pt particles decorated by metallic Ga are invoked to explain the higher dehydrogenation and lower hydrogenolysis activity shown by Pt–Ga–SAPO-11 catalyst [7].

Sulfated zirconia catalysts have also been extensively studied for their activity in isomerizing linear alkanes [8–13]. The pretreatment of persulfated zirconia in air has been found to enhance its initial activity toward *n*-butane isomerization [14]. The *n*-butane isomerization activity of sulfated zirconia supported on MCM-41 has been improved significantly by the addition of an appropriate amount of gallium as a promoter [15]. The addition of platinum to this catalyst has been shown to exhibit higher steady-state conversion compared with the Pt-free form. Platinum supported on chlorinated alumina and H-mordenite has also been extensively studied for the production of isobutene from *n*-butane [16–21]. However, the acidity of chlorided Pt/Al_2O_3 catalyst has not been extensively correlated with the isomerization activity. The present work is concerned

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with the isomerization of *n*-butane over various chlorided Pt/Al_2O_3 catalysts. The effect of catalyst acidity on isomerization was studied with *n*-butane as the normal alkane and Pt supported on two different alumina (γ-Al_2O_3 and η-Al_2O_3) as the catalysts. The acidity of the catalysts was varied by chloriding the catalysts under different conditions. The catalysts were also suitably characterized using various techniques.

2. Experimental

2.1. Materials

γ-Alumina (Catapal SB) was obtained from CONOCO (New Jersey) and η-Al_2O_3 was obtained from Davison Chemical (Baltimore). Reagent-grade chloroplatinic acid was procured from Alfa Products (Danvers) and carbon tetrachloride (AR grade) from BDH Chemicals (Toronto). *n*-Butane (99.9%) was supplied by Matheson (Edmonton, Alberta).

2.2. Catalyst preparation

A series of Pt-loaded catalysts were prepared using γ- and η-alumina. In the Pt-loading process, 300 g of powdered (0.147 mm) alumina (γ- or η-) were impregnated with 195 ml of an aqueous solution of chloroplatinic acid (6×10^{-3} g Pt/ml water) to incipient wetness. The mixture was mixed thoroughly and air dried in an oven at 110 °C with occasional stirring. After 24 h of drying, the catalyst was crushed to granular form (average size 1 mm) and finally calcined at 500 °C for 6 h in a muffle furnace. The catalyst was then transferred into an airtight container and stored in a desiccator.

The Pt-loaded catalysts were chlorided by treatment with CCl_4 vapor. The chloride treatment parameters, *i.e.*, temperature and time, were varied to obtain catalysts of varying surface acidities. After the chloride treatment, the catalysts were purged with nitrogen at 350 °C for 1 h to remove physically adsorbed CCl_4 and then stored in a desiccator.

2.3. Characterization of the catalysts

The prepared catalysts were characterized using various techniques such as ammonia chemisorption, temperature-programmed desorption (TPD) of ammonia, IR spectroscopy and the BET surface area method. The chloride and platinum contents of the catalysts were also estimated by the procedures detailed below.

2.3.1. Ammonia chemisorption

Adsorption of ammonia on the catalyst surfaces was performed to characterize the acidity of various catalysts. The measurements were made at 200 °C, to minimize physisorption of ammonia, and in the pressure range 0–101 kPa. The amount of ammonia chemisorbed was plotted against ammonia pressure to yield the chemisorption isotherms. Quantitative acidity values were extracted from these isotherms and are reported as meq NH_3/g chemisorbed at 101 kPa ammonia pressure.

2.3.2. Temperature-programmed desorption (TPD) of ammonia

Ammonia TPD of the prepared catalysts were performed in a CHEM-BET 3000 instrument (Quantachrome). In a typical experiment, 0.1 g of the catalyst sample was first degassed at 450 °C for 1 h with a nitrogen flow followed by cooling to low temperature (~0 °C). A flow of about 1 mol% ammonia in nitrogen was then passed through the sample for 1 h. The catalyst sample was heated to 100 °C and kept at that temperature until the steady state was attained. The sample was then heated from 100 to 800 °C at a heating rate of 10 °C/min. The desorbed ammonia was detected by a TCD analyzer.

2.3.3. Surface area and pore volume determination

The surface area and pore volume of the prepared catalysts were measured by nitrogen adsorption–desorption studies using a BET surface area analyzer (ASAP 2000, Micromeritics) at liquid nitrogen temperature. The samples were degassed at 200 °C and 0.01 kPa pressure before the adsorption operation.

2.3.4. Chloride content

For the determination of chloride content, about 0.1 g of the catalyst (weighed accurately to ±0.0001 g) was dissolved in 50 ml of 6 M HNO_3. A 2 ml volume of 10% $Fe_2(SO_4)_3$ indicator solution and 5 ml of 0.1 M $AgNO_3$ solutions were added. The contents were then back-titrated with 0.1 M potassium thiocyanide (KSCN) solution and the percentage of Cl^- was determined. The precision of the measurement was within ±3% of the values reported.

2.3.5. Platinum content

The platinum content of the various supported catalysts was determined by comparing the atomic absorption spectra of the catalysts with the calibration curves for standard Pt solutions. The precision of the measurement was within ±2% of the values reported.

2.4. Determination of catalyst activity for n-butane isomerization

The prepared catalysts were tested for their ability to isomerize *n*-butane in a stainless-steel downflow reactor (1.0 cm i.d. and 15 cm long), the temperature of which could be controlled to within ±1 °C. Gaseous samples were collected from the reactor outlet and analyzed by gas chromatography (GC) using a 6 m × 6 mm i.d. column packed with 20 wt% Dow Silicone 703 on Chromosorb P. All catalytic activity measurements were carried out at atmospheric pressure and 110 °C with 1.5 g of catalyst.

3. Results and discussion

3.1. *Physicochemical properties of the catalysts*

Pt/γ- and Pt/η-Al_2O_3 catalysts containing 0.51 wt% platinum were chlorided at two different temperatures and for varying time periods. The platinum content of the catalysts was determined after treatment as shown in table 1. It can be seen from this table that the platinum content of the catalysts decreases with increase in treatment time and the decrease is greater at higher temperatures and with prolonged treatment times.

The effect of the treatment conditions on the chloride content of Pt/γ-Al_2O_3 is shown in figure 1. As can be seen, the chloride content of the catalysts increases with treatment time, reaches a maximum value and then decreases. It is also evident from figure 1 that an increase in treatment temperature increases the chloride content of the catalysts. A similar trend was observed in the case of Pt/η-Al_2O_3, as shown in figure 2. The decrease in chloride content at longer treatment times was attributed to the loss of chlorine as free $AlCl_3$ formed with longer treatment periods. The formation of $AlCl_3$ was visible from its deposition on the reactor wall and was confirmed be the chemical analysis of the deposited material. The formation of $AlCl_3$ under intense treatment conditions was also reported by Globe and Lawrance [22] and Bassett *et al.* [23] with CCl_4 treatment of alumina-supported catalysts.

Table 1
Effect of chloride treatment conditions on platinum content

Support material	Chloride treatment conditions		Platinum content (wt%)
	Temperature (°C)	Time (min)	
γ-Al_2O_3	No treatment		0.51
	300	30	0.50
		60	0.50
		90	0.45
	350	30	0.48
		60	0.41
		90	0.20
η-Al_2O_3	No treatment		0.51
	300	30	0.50
		60	0.50
		120	0.31
	350	30	0.50
		60	0.47
		120	0.24

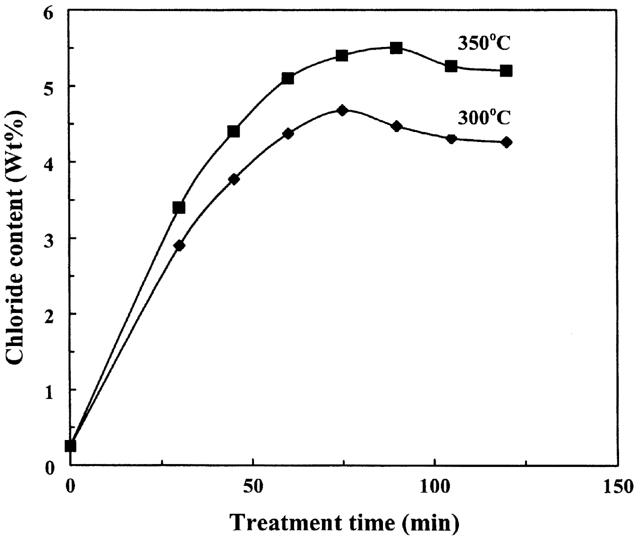

Figure 1. Effect of treatment time on chloride content of Pt/γ-Al_2O_3.

Treatment temperatures >350 °C were not used because CCl_4 tends to crack at such temperatures and deposition of carbonaceous materials takes place on the catalyst surface; >2% carbon deposition was observed on a catalyst treated at 400 °C for 1 h. Supportive evidence of coking of the catalyst surface was also provided by Menon *et al.* [24]. From their pulse injection studies of CCl_4-treated alumina, they discovered that at 400 °C about 2–3% of CCl_4 is converted into coke and deposited on the catalyst surface.

As mentioned earlier, acidity of the catalyst is one of the most important factors in hydrocarbon transformation reactions such as isomerization in the present case. The acidity of the chloride-treated catalysts was therefore determined by ammonia chemisorption. Figure 3 shows the effect of chloride content on catalyst acidity, expressed as milliequivalents (meq) of ammonia

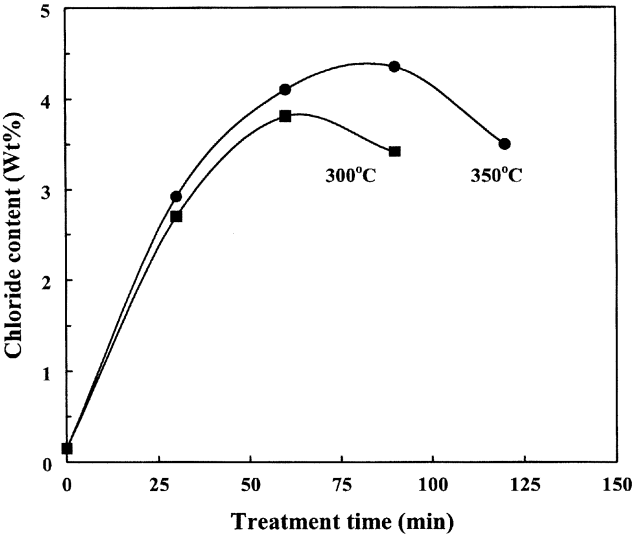

Figure 2. Effect of treatment time on chloride content of Pt/η-Al_2O_3.

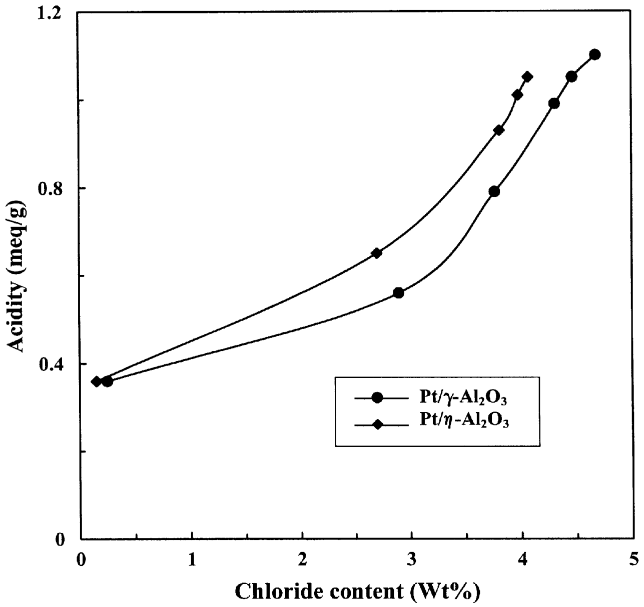

Figure 3. Effect of chloride content on acidity of the catalysts.

absorbed per gram of the catalyst. It is evident that the acidity of the catalyst increases with increase in chloride content for both Pt/γ-Al$_2$O$_3$ and Pt/η-Al$_2$O$_3$ catalysts. Moreover, with the same chloride content, the acidity of Pt/η-Al$_2$O$_3$ is greater than that of Pt/γ-Al$_2$O$_3$. The increase in acidity with chloride treatment is due to the formation of Brønsted acid sites, as explained by Globe and Lawrance [22].

In order to characterize the nature of the acid sites on chlorided catalysts, IR spectra of chemisorbed ammonia on the catalyst surfaces were taken. Only one absorption band was observed in the case of ammonia chemisorbed on chlorided Pt/γ-Al$_2$O$_3$ at a wavenumber of 1425 cm^{-1}, which could be attributed to the H–N–H stretching in NH$_4^+$. This is formed by the protonation of NH$_3$ on the Brønsted acid sites. If Lewis acid sites had been present on the catalyst surface, bands for coordinately bonded ammonia would have been observed in the IR spectra at about 1542 cm^{-1} [25]. In the present case, no bands were observed at such a wavenumber, thus precluding the presence of Lewis acid sites. A similar observation was made by Tanaka and Ogasawara [26] in the IR spectra of ammonia chemisorbed on HCl-promoted alumina.

The absence of Lewis acid sites was also confirmed by an IR spectroscopic study with chemisorbed pyridine on chlorided Pt/γ-Al$_2$O$_3$. The occurrence of a distinct absorption band at 1540 cm^{-1} indicated the presence of pyridinium ions formed on the Brønsted acid sites. No absorption band was found near 1460 cm^{-1} characterizing coordinately bonded pyridine, which could have been formed on Lewis acid sites.

TPD of ammonia was studied with the chlorided catalysts to determine the acid strengths of various sites present in the catalyst. Figure 4 shows the TPD profiles for ammonia from the chlorided Pt catalysts on two different supports, *viz.*, γ- and η-alumina. The desorption of ammonia corresponding to different peaks is

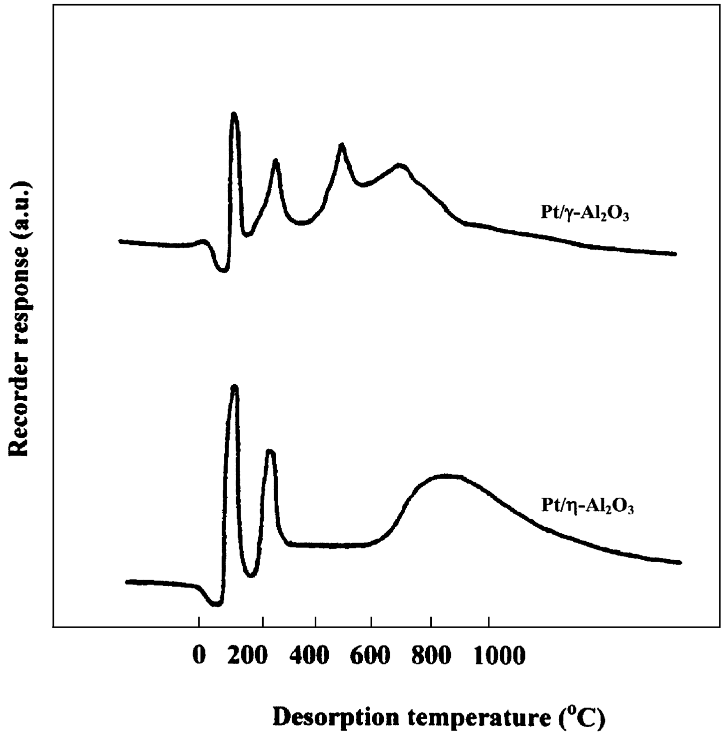

Figure 4. Temperature-programmed desorption profiles for ammonia from chlorided catalysts.

Table 2
Effect of treatment conditions on Hammett acidity of Pt/γ-Al_2O_3 and Pt/η-Al_2O_3 catalysts

Support material	CCl_4 treatment conditions		Hammett acidity (meq/g) at a pK_a of			
	Temperature (°C)	Time (min)	6.8	4.8	3.3	1.5
γ-Al_2O_3	No CCl_4 treatment		0.60	0.40	0.15	0.0
	300	30	1.33	1.00	0.68	0.49
	300	60	1.76	1.36	1.12	0.72
	350	45	1.49	1.34	0.96	0.72
	350	60	1.70	1.52	1.10	0.83
η-Al_2O_3	No CCl_4 treatment		0.63	0.44	0.12	0.0
	300	60	2.22	1.53	0.90	0.34
	300	90	2.32	1.68	0.95	0.33
	350	30	1.08	0.76	0.6	0.0
	350	90	2.14	1.43	1.28	0.39

indicative of the energy levels at which ammonia is bound to the acid sites. The profiles indicate that the catalysts contain acid sites of varying strengths. Moreover, the chlorided η-Al_2O_3 contains relatively larger amounts of stronger acid sites than those present in chlorided γ-Al_2O_3, as both the area and the temperature of the last peak for η-Al_2O_3 are higher than those for γ-Al_2O_3. The TPD profiles of unchlorided Pt/γ-Al_2O_3 and Pt/η-Al_2O_3 showed smaller desorption peaks than the chlorided catalysts, indicating the creation of new acid sites on chloriding. Moreover, no desorption peak was observed at temperatures above 500 °C. This clearly indicates that stronger acid sites are generated by chloride treatment of the platinated alumina.

The presence of acid sites of varying strengths was also further confirmed by the measurement of Hammett acidities at various strengths. The Hammett acidities of various catalysts were determined by the non-aqueous titration method employing a series of Hammett indicators. The titration results are reported in table 2 in terms of meq of n-butylamine required per gram of catalyst to prevent indicators of a given pK_a from assuming the acid color. It is evident from this table that the chloride treatment incorporates acid sites of varying strengths on the catalyst surfaces.

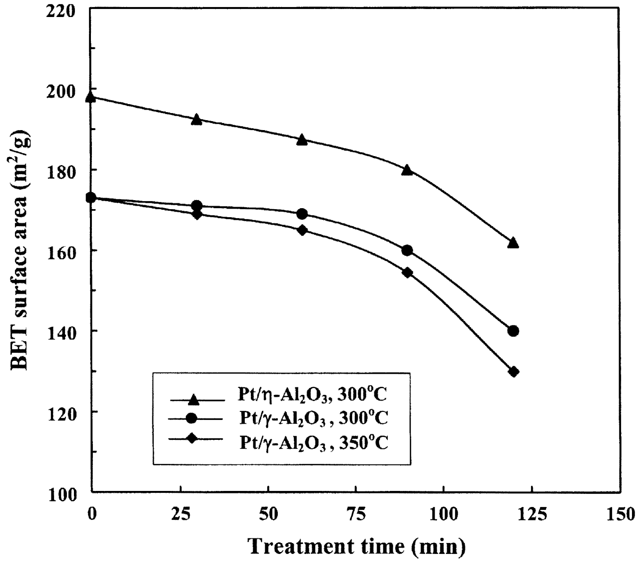

Figure 5. Effect of treatment time on surface area of the catalysts.

The BET surface areas of various catalysts were measured. The variation of the BET surface areas with treatment time is shown in figure 5 for both Pt/γ-Al_2O_3 and Pt/η-Al_2O_3 catalysts. It can be seen that the surface area does not change significantly at moderate treatment conditions. With prolonged treatment, however, a significant decline in surface area takes place. For example, a decrease of 2.3% was observed at a treatment time 60 min compared with a 19% decrease at 120 min and 300 °C with Pt/γ-Al_2O_3. At higher temperature (350 °C), there was a more pronounced decline in surface area, as shown in figure 5 (5% at 60 min and 25% at 120 min). With Pt/η-Al_2O_3, the initial fall in surface area was found to be greater than that with Pt/γ-Al_2O_3 as there was a 5.3% decrease in surface area at 60 min and 300 °C. The decline in surface area under intense treatment conditions may be due to the formation of free $AlCl_3$, which tends to block the alumina pores [22,23].

The pore volumes of the catalysts at various treatment conditions are shown in table 3. Comparing the values of the pore volumes of chloride-treated and untreated catalysts, it may be concluded that the chloride treatment

Table 3
Effect of treatment conditions on pore volumes of chlorided catalysts

Support material	CCl_4 treatment conditions		Pore volume
	Temperature (°C)	Time (min)	
γ-Al_2O_3	No treatment		0.69
	300	75	0.63
	350	90	0.58
η-Al_2O_3	No treatment		0.58
	300	90	0.53
	350	120	0.49

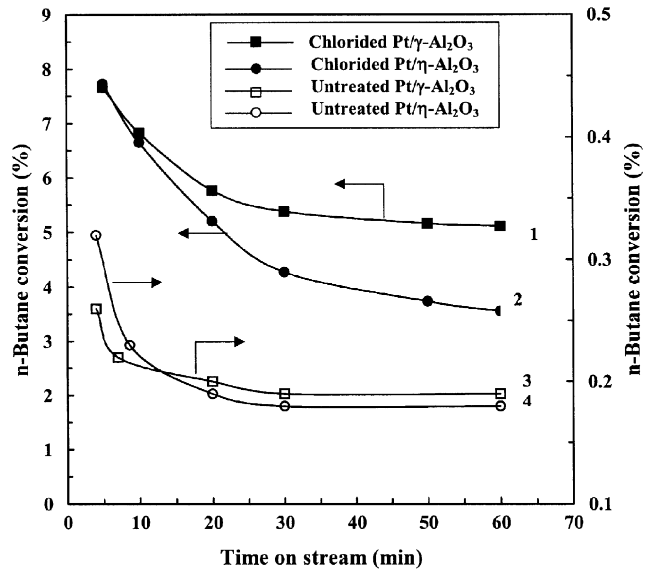

Figure 6. Activity of Pt/Al$_2$O$_3$ catalysts in *n*-butane isomerization.

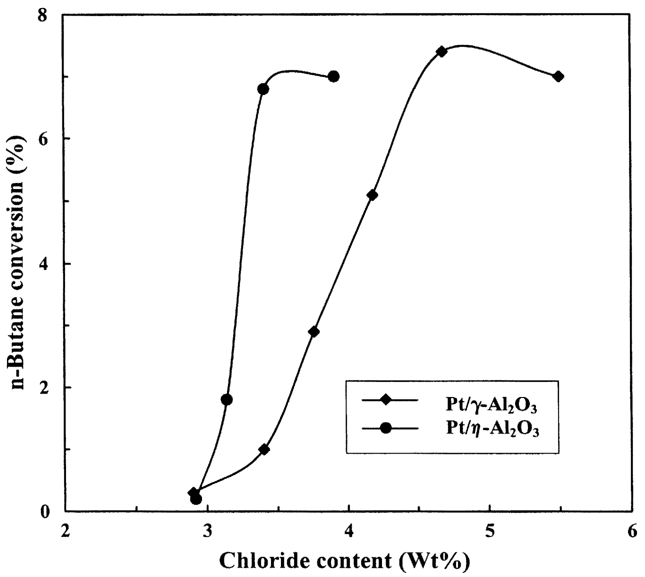

Figure 7. Effect of chloride content on *n*-butane isomerization activity.

decreases the pore volumes significantly under severe treatment conditions compared with a small change under moderate conditions. This is in line with the earlier observation of the variation of surface area with chloride treatment.

3.2. Isomerization activity

The isomerization activity of the prepared catalysts was tested by isomerizing *n*-butane with a space velocity of 13.3 m^3/kg catalyst/h at 110 °C and 1 atm. Figure 6 shows the time-on-stream run for the best performing catalysts of each series. The activity of the catalysts initially decreases rapidly and then remains almost constant for longer times. It is also evident from figure 6 that γ-Al$_2$O$_3$ is a better support than η-Al$_2$O$_3$ as *n*-butane conversion decreases much faster and stabilized at a lower value in the latter case. The initial activity of Pt/η-Al$_2$O$_3$ is, however, greater than that of Pt/γ-Al$_2$O$_3$. As Pt/η-Al$_2$O$_3$ contains more acid sites than Pt/γ-Al$_2$O$_3$, the acidity (or chloride content) of the catalysts would play a major role in determining their activities. The platinum content of the catalysts was found to have no effect on catalyst activity in the concentration range covered in the present study, as reported in table 4 for catalysts A and B. In the isomerization of *n*-heptane over Pt supported on alumina, the Pt content of the catalyst above 0.1% was also reported to have no effect on the activity of the catalyst [27]. As the lowest Pt content of the treated catalysts in the present study is above 0.1 wt%, variation in the amount of Pt >0.1% seems to have no effect on *n*-butane isomerization activity. However, the catalyst acidity has a strong effect on activity as shown in table 4 with catalysts C and D. This is also demonstrated in figure 6 as the initial activities of untreated catalysts are very low (<0.5% conversion) compared with those of treated (chlorided) catalysts (>8% conversions).

Table 4
Effects of Pt content and acidity of the catalysts on isomerization activity

Catalyst[a]	Pt content (wt%)	Acidity (meq/g)	*n*-Butane conversion (%)
A	0.39	1.11	5.8
B	0.14	1.13	5.9
C	0.50	0.48	0.3
D	0.50	1.10	7.4

[a] γ-Al$_2$O$_3$ as catalyst support.

The effect of catalyst acidity (or chloride content) on isomerization activity was further explored by carrying out reactions over a number of catalysts of varying chloride contents. It can be seen from figure 7 that the *n*-butane conversion increases sharply with chloride content for both the series, attains a maximum value and then decreases. As mentioned earlier, the chloride content of the catalysts increases with treatment time (see figures 1 and 2). However, at longer treatment times (higher chloride contents), the surface areas and pore volumes of the catalysts decrease (see figure 5 and table 3). All these lead to a decrease in catalytic activity, after a maximum value, with increase in chloride content. It can also be seen from figure 7 that no noticeable isomerization activity is exhibited until the chloride content (acidity) of the catalyst exceeds a certain value. These limiting chloride contents were found to be 2.35 and 2.74 wt% for Pt/γ-Al$_2$O$_3$ and Pt/η-Al$_2$O$_3$, respectively. The corresponding acidity values as determined from figure 3 are 0.49 meq/g for Pt/γ-Al$_2$O$_3$ and 0.66 meq/g for Pt/η-Al$_2$O$_3$.

Figure 8 shows the effect of Hammett acidity on *n*-butane conversion for both chlorided Pt/γ-Al$_2$O$_3$

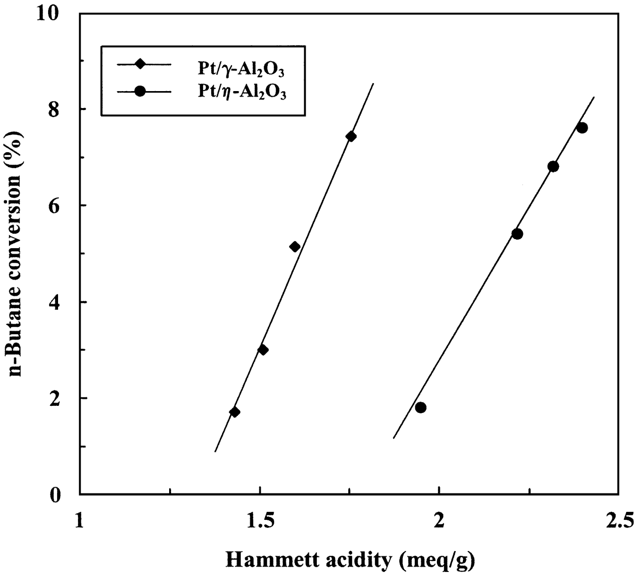

Figure 8. Effect of Hammett acidity on isomerization activity.

and Pt/η-Al_2O_3 catalysts. The isomerization activity increases with increase in acidity, establishing the major role of acid sites in the hydrocarbon rearrangement. The minimum acidity values required for demonstrating isomerization activity were found to be 1.32 and 1.87 meq/g for Pt/γ-Al_2O_3 and Pt/η-Al_2O_3, respectively .

4. Conclusions

Isomerization of *n*-butane was studied with Pt catalysts supported on γ- and η-alumina. A significant improvement in the activity was obtained by chloriding the catalysts with CCl_4 vapor. The chloride content and acidity of the catalysts were found to vary with the treatment conditions. A longer treatment time has detrimental effects on all the catalyst properties such as acidity, surface area and pore volume. By manipulating the treatment conditions, catalysts of optimum activity could be found for isomerization of *n*-butane. γ-Al_2O_3 was found to be a better support material for Pt than η-Al_2O_3 in the isomerization reaction studied.

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