Comparison of *n*-pentane reforming over Pt supported on amorphous and γ-Al_2O_3

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Received 4 February 2003; accepted 6 June 2003

The *n*-pentane reforming activity of Pt supported on nonhydrolytic amorphous Al_2O_3 (Pt/NH–Al_2O_3), was investigated and compared to the catalytic activity of Pt supported on crystalline γ-Al_2O_3. The Pt was introduced by (a) impregnation with either a solution of H_2PtCl_6 in water or a solution of platinum acetylacetonate (PtAcac) in toluene; (b) *in situ* introduction of a Pt precursor, either $PtBr_4$ or *cis*-bis(benzonitrile)platinum dichloride, before gelation of the NH alumina. The rate-controlling step in the reforming of *n*-pentane for both amorphous and crystalline aluminas was found to be the reaction on the alumina acidic sites. The Pt/γ-Al_2O_3 catalysts exhibit higher conversions of *n*-pentane and higher selectivity to isopentane, than the corresponding amorphous alumina samples. After 1.5 h at 400 °C, the highest conversion of the γ-Al_2O_3-based catalysts was ~47% with 20.3% selectivity to isopentane. The highest conversion of the NH–Al_2O_3-based catalysts under the same conditions was only ~26% with 13.6% selectivity to isopentane. The high intrinsic Cl content (2.6 wt%) of the amorphous alumina was found to have a minor effect on the activity of the alumina, compared to the activity of the more ordered γ-alumina. Catalysts prepared by impregnation of the NH alumina with aqueous chloroplatinic acid, exhibited higher conversions compared to catalysts prepared by impregnation of the NH alumina with a solution of PtAcac in toluene. This result occurred in spite of the lower surface area and lower Pt dispersions of the chloroplatinic acid-impregnated catalysts, and is explained by the formation of microcrystalline surface structures and existence of surface chlorine.

KEY WORDS: amorphous alumina; nonhydrolytic; Pt; catalytic activity; *n*-pentane reforming; impregnation; acidity.

1. Introduction

Porous alumina with large surface area (SA) is one of the most widely used catalytic supports. Most conventional reforming catalysts are based on Pt dispersed on alumina (mainly γ and η) [1], in which the alumina contributes the acidic sites. Over the past decades, many efforts have been made to correlate the structure and catalytic activity of transition aluminas [2–5]. However, since these materials are often highly defected poorly crystalline materials that may exhibit different faces and different defects depending on the preparation method and may be very sensitive to contaminants, the correlation between structure and catalytic activity is very complex and not well understood.

Because of the lack of ordered structure in amorphous alumina, it is expected to possess different surface catalytic sites than the more ordered crystalline transition aluminas. However, in spite of the widespread usage of crystalline alumina supports, utilization of amorphous alumina for catalytic applications is very scarce. Little is published regarding the synthesis of amorphous Al_2O_3 and its catalytic utilization. Amorphous alumina has been used for the dehydration of methanol to dimethylether [6–10]. In [7], it was concluded that the acidic activity of the amorphous alumina is lower than that of crystalline γ-Al_2O_3. In [10], on the other hand, it was concluded that the activities of γ-Al_2O_3 and amorphous Al_2O_3 for the dehydration of methanol are similar. In [4,11–12], the isomerization of 1-butene on amorphous aluminas was studied. According to [4], the amorphous alumina contains smaller amounts of acidic sites and their acidic strength is lower than the acidic sites on crystalline γ-Al_2O_3. Although the Pt/Al_2O_3 catalyst system is studied extensively, we found only one work dealing with Pt supported on amorphous alumina [13]. In that work, the amorphous alumina was impregnated by a methanolic solution of H_2PtCl_6, and the obtained Pt/amorphous-Al_2O_3 catalyst was used to study the spillover of hydrogen and oxygen onto amorphous alumina and was not characterized. However, it was concluded that the disordered surface of the amorphous alumina is more easily activated, by oxygen or hydrogen spillover, than the surface of crystalline alumina.

In the last decade, a new route for the production of transition metal oxides by a nonhydrolytic (NH) sol-gel process was developed [14–21]. The NH route involves the condensation reaction of aluminum halide with ether

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1011-372X/03/0900–0169/0

or aluminum alkoxides in an organic solvent such as CH_2Cl_2, according to either of the following schemes:

$$AlX_3 + Al(OR)_3 \rightarrow Al_2O_3 + 3RX \quad \text{(scheme1)}$$
$$AlX_3 + \tfrac{3}{2}ROR \rightarrow \tfrac{1}{2}Al_2O_3 + 3RX \quad \text{(scheme2)}$$
$$X = Cl,\ Br; \quad R = \text{isopropyl.Sec-butoxide}$$

The NH alumina retains high SA and is in the amorphous state up to 800–850 °C. Additionally, the NH alumina also retains intrinsic 2.6 wt% Cl up to the crystallization temperature. For naphtha reforming, in order to maintain the acidic function of the alumina, Cl is added to the feed, commonly as HCl or CCl_4 [1,22–23]. The intrinsic Cl in the NH amorphous alumina is not easily released from the support at high temperature (upto crystallization at 800 °C), not even after contact with water [24]. As a result, the need to inject Cl in the feed to compensate for the Cl stripping may be eliminated by the utilization of NH alumina because of the strong retention of the intrinsic Cl. However, the intrinsic chlorine in the NH amorphous alumina may be buried within the bulk of the alumina and, therefore, might effect the surface acidity of the alumina differently than the surface chlorine complexes formed by addition of HCl or CCl_4 to the feed.

In this work, we investigated the catalytic activity of Pt/NH-amorphous Al_2O_3 (synthesized in our laboratory [25]), for *n*-pentane reforming, and compare it to the catalytic activity of Pt that was impregnated in our laboratory on commercial γ-Al_2O_3. This reaction is believed to be controlled by the acid function [26–27] contributed by the Al_2O_3 support. The total number of active acidic sites determines the total conversion, whereas the distribution of the acidic site strength determines the selectivity of the reaction towards the reaction products (mainly isomerization and cracking). Therefore, reforming of *n*-pentane emphasizes the difference between the NH amorphous and the crystalline γ-aluminas. The introduction of the Pt into the aluminas included impregnation with (a) an aqueous solution of chloroplatinic acid (CPA) or (b) a platinum acetylacetonate (PtAcac) solution in toluene. In addition, an *in situ* introduction of Pt before the gelation of the NH alumina using PtBr4 or *cis*-bis(benzonitrile)platinum dichloride (BNPtCl) as Pt precursors was also applied. The usage of these various techniques of Pt introduction allowed us to explore the effect of the preparation method on catalytic activity. The catalytic activity of these catalysts is explained, and correlated to their physical and chemical [25] characteristics.

2. Experimental

2.1. Preparation of nonhydrolytic amorphous alumina (NH)

Similar to earlier preparation [25], $AlCl_3$ (Fluka, 99%), Pr^i_2O (Riedel–deHaen, 99%), and CH_2Cl_2 (Carlo Erba, 99.8%) were added under argon into a reactor in a ratio of 1 g/1.6 mL/4.2 mL, respectively. After dissolution, the reactor was immersed in an oil bath at 90 °C for 24 h, for gelation and aging. The average gelation time was 6.5 h with a standard deviation of 0.5 h. After aging, the xerogels were dried at room temperature (RT, 20–25 °C) to a mild vacuum of 0.2–0.3 mm Hg.

The fresh xerogels were calcined in dry air at 650 °C for 5 h to obtain the NH amorphous alumina. The heating rate was 40 °C/h up to 400 °C and then in a rate of 70 °C/h up to 650 °C. The average SA of NH alumina was measured as 274 m^2/g.

2.2. Introduction of Pt

2.2.1. In situ *introduction of Pt into NH alumina*

2.2.1.1. Introduction with BNPtCl. Two hours after the addition of the alumina precursors, as described above (before gelation), the sol was cooled and a solution of 0.02 g/mL of BNPtCl in CH_2Cl_2 was added under argon. The amount of BNPtCl solution added was equivalent to a final product of 1 wt% Pt/Al_2O_3. The reactor was placed again in an oil bath at 90 °C for an additional 22 h for gelation and aging. After aging, the xerogels were dried at RT to a mild vacuum of 0.2–0.3 mm Hg. The catalyst was then calcined at 500 °C for 3 h. For the catalysts prepared by *in situ* introduction of Pt, full uptake of the Pt into the alumina was confirmed by ICP-MS analysis of catalysts dissolved in HNO_3–HCl solution.

2.2.1.2. Introduction with $PtBr_4$. $PtBr_4$ did not dissolve in either Pr^i_2O or CH_2Cl_2, but was found to dissolve in Pr^i_2O/CH_2Cl_2 mixture. However, the time required for the dissolution was several days. Therefore, a stock solution of 0.05 g $PtBr_4$/1 mL, Pr^i_2O/2.5 mL and CH_2Cl_2 was prepared. The procedure used with BNPtCl was followed, except that $PtBr_4$ solution in Pr^i_2O/CH_2Cl_2 was used instead of BNPtCl solution in CH_2Cl_2.

2.2.2. Introduction of Pt by impregnation

For the catalysts prepared by impregnation, the above NH alumina and a commercial γ-Al_2O_3 of Alfa Aesar were utilized. The γ-alumina possess SA of 227 m^2/g. Prior to the impregnation, the aluminas were ground with a mortar to particles of $\sim 50\,\mu$m diameter.

2.2.2.1. Impregnation by CPA solution in water. To each gram of Al_2O_3, 50 mL of a 100 or 200 μg Pt/mL, CPA solution in water was added, to obtain 0.5 or 1 wt% Pt/Al_2O_3 catalysts, respectively. The mixture was stirred for 4 h after which the catalyst was filtered. The catalyst was then dried at 110 °C in vacuum and then calcined at 500 °C for 3 h. Analysis of the liquid phase for Pt traces by a UNICAM UV–Vis spectrometer or with a VARIAN 400 Atomic Absorption instrument, showed

more than 98% uptake of the Pt from the initial solutions onto the aluminas.

2.2.2.2. Impregnation by PtAcac solution in toluene. The aluminas were initially dehydrated under dry air at 500 °C and cooled under the same atmosphere. The alumina was then added to 125 or 250 μg Pt/mL, PtAcac solution in toluene in the ratio of 40 mL/g alumina, to yield a 0.5 or 1 wt% Pt/Al_2O_3 catalysts, respectively. The mixture was stirred for 4 h after which the catalyst was filtered. The catalyst was then dried at 110 °C in vacuum and then calcined at 500 °C for 3 h. The liquid phase was analyzed for Pt traces by a VARIAN 400 Atomic Absorption instrument. In order to avoid interference caused by toluene, the toluene was exchanged to methyl-isobutyl-ketone before the atomic absorption measurement. According to the atomic absorption data, the Pt loading on the NH alumina is complete, whereas the loading on the γ-alumina is only partial.

2.3. Terminology of catalysts

The catalysts are termed by three indices *x*-*y*-*z*, where *x* is the alumina type (NH or γ); *y* is the Pt precursor used (BNPtCl, PtBr4, CPA, PtAcac) and *z* is the actual Pt loading.

2.4. Characterization of the catalysts

Thermal behavior of the xerogels were studied by DTA/TGA measured in a Setaram TG-92 unit, in flowing air, with a heating rate of 5 °C/min, and the composition of the effluent gas was detected using a mass spectrometer (Balzers Thermostar GSD300T). BET specific surface areas were determined by nitrogen desorption using Quantachrome Monosorb. XRD analysis was done using a Siemens 5000 instrument employing Cu Kα radiation. The Cl content of some of the catalysts was measured by ICP-MS (PE-SCIEX ELAN 6000 ICP-MS unit) analysis of samples dissolved in HNO_3. H_2 pulse chemisorption measurements were done with a Zeton Altamira AMI200 instrument. Samples that were reduced by 10% H_2/Ar gas at 400 °C and then saturated by oxygen using 10% O_2/He stream at 35 °C were used. The number of 10% H_2/Ar pulses into Ar, at 35 °C that were consumed by the sample was recorded. The following surface reaction [28]: $Pt–O + 3/2H_2 \rightarrow Pt–H + H_2O$, was assumed to calculate the Pt dispersion.

2.5. Catalytic runs

The catalysts prepared by impregnation are in the form of powder (~50 μm) and in order to avoid internal diffusion limitation were not pelletized. The catalysts prepared by the *in situ* introduction of Pt are in the form of ~12 mm pellets, and therefore, were ground to ~50 μm particles just before the catalytic runs.

0.3 g of the powdered catalyst were mixed with quartz powder of the same size to a volume of 1 mL and placed between quartz wool sheets in plug flow, stainless-steel reactor with a 6.5 mm i.d. In order to get better flow distribution, additional quartz powder was placed on top of the quartz wool. Prior to the reaction, the catalysts were reduced in the reactor at 400 °C by 20.8 mL/min of H_2 flow at atmospheric pressure for 2 h. After the reduction, the flow was switched to a reference reactor containing quartz only, and *n*-pentane in a flow rate of 1.67 mL/h was added (WHSV = 3.5, H_2/HC molar ratio = 3.5) and the pressure was raised to 1.75 atm. After stabilization of the *n*-pentane peak in the gas chromatograph (GC), the flow was switched back to the reactor containing the catalysts. The reaction was run for 1.5 h at 400 °C and then the temperature was raised, at a rate of 5 °C/min to 450 °C. At 450 °C, the reaction was held for another 1.5 h. The analysis of the products was carried out with a Hewlett Packard 5890 series II GC, loaded with a SGE capillary column (30 m, i.d. 0.53 mm with fused silica BP624). Under the above-mentioned reaction conditions, the catalytic activity of the pure NH alumina, and the pure crystalline γ-alumina was found to be negligible.

3. Results

3.1. Physical properties of the catalysts

The characteristic physical properties of the various catalysts are discussed in [25] and summarized in table 1. According to the data in table 1, impregnation of NH alumina with toluene solution of PtAcac results in very well dispersed Pt after calcination at 500 °C (~50%), when the nominal Pt loading (amount of Pt in impregnation solution) is 0.5%. Upon increase in nominal Pt loading to 1%, the Pt dispersion after calcination at 500 °C decreases to ~28%. The number of PtAcac anchoring sites on the crystalline γ-Al_2O_3 is smaller as can be seen that the actual loading of Pt for a nominal loading of 1% is only 0.71%. However, a well-dispersed Pt (39%) is obtained at this loading.

The impregnation of NH alumina with aqueous solution of CPA and calcination in air at 500 °C results in reduction of surface area and in low Pt dispersions of ~20%. However, impregnation of γ-Al_2O_3 with aqueous CPA results in retention of its surface area and well-dispersed Pt (40%). After calcination in air at 500 °C, the γ-Al_2O_3 retains most of the Cl that originates from the anchoring of the CPA. However, for the NH alumina the high intrinsic Cl content of 2.6 wt% masks changes in Cl content upon CPA impregnation. The Cl content of NH–CPA–0.5 and NH–CPA–1.0 catalysts are 3.0 and 2.5%, respectively.

Table 1
SA, Pt uptake and dispersion and Cl content

Catalyst	Surface area (m^2/g)	Nominal Pt loading (wt%)	Actual Pt loading (wt%)	Pt dispersion from pulse chemisorption (%)[a]	Cl content (wt%)
NH–PtAcac–0.46	267	0.5	0.46	49	Not measured
NH–PtAcac–0.96	252	1.0	0.96	28	Not measured
γ-PtAcac–0.45	219	0.5	0.45	43	Not measured
γ-PtAcac–0.71	213	1.0	0.71	39	Not measured
NH–CPA–0.5	177	0.5	0.5	15	3.0
NH–CPA–1.0	173	1.0	1.0	21	2.5
γ-CPA–0.5	227	0.5	0.5	41	0.55
γ-CPA–1.0	213	1.0	1.0	39	0.89
NH–$PtBr_4$–1.0	300	1.0	1.0	32	Not measured
NH–BNPtCl–1.0	370	1.0	1.0	32	Not measured
pure NH-alumina	274	–	–	–	2.6
pure γ-alumina	227	–	–	–	0.0

[a]Based on actual Pt loading.

The catalysts prepared by *in situ* introduction of Pt possess larger SA (300–370 m^2/g) than the NH alumina used for impregnation. This is a result of the lower calcination temperature of the *in situ* prepared catalysts (500 °C), than the calcination temperature of the NH alumina used for impregnations (650 °C). The Pt dispersions obtained in this route are moderate (~30%).

The DTA/TGA patterns of γ-PtAcac–0.45 catalyst, after impregnation and 110 °C vacuum drying and before the 500 °C calcination is shown in figure 1. The main features of these patterns are as follows: (1) A major fall in weight up to ~550 °C. By MS analysis of the effluent gases, it was found that weight loss is due to release of adsorbed water (which originates from the surrounding), and burnout of organic residues. (2) A monotonic decrease of 1.5% in weight in the 550–1100 °C range. (3) During phase transformation to α-Al_2O_3, shown by the exothermic peak at 1140–1220 °C, there is a ~0.5% drop in weight. For the γ-PtAcac–0.71 sample, the drop in weight during the γ to α transition was only 0.14%. No drop in weight during phase transformation to α-Al_2O_3 was observed for either the CPA-impregnated catalysts or the pure γ-alumina nor for any of the NH–Al_2O_3-based catalysts. MS of the effluent gases showed, qualitatively, the release of CO_2 at this temperature range; however, we cannot conclude that the weight loss is due to CO_2 release, because the same level of CO_2 was recorded for samples in which no drop in weight, during the γ to α transition, was observed. The origin of this high-temperature weight loss during the γ to α transition is most likely surface species that are released upon this phase transition, in agreement with Hedvall effect.

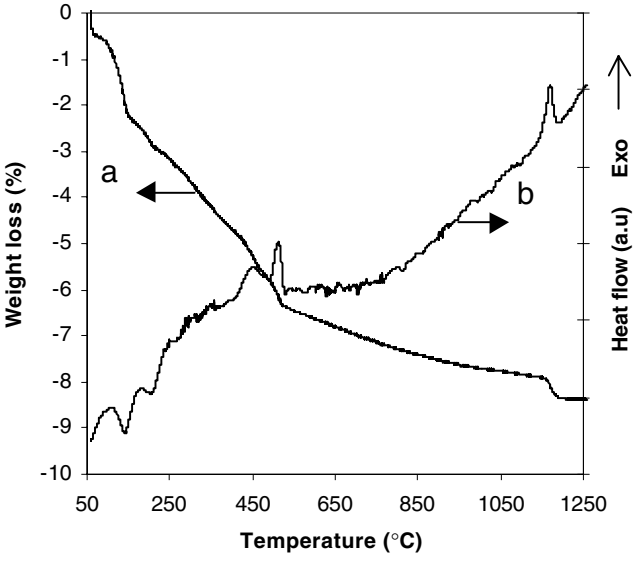

Figure 1. TGA (a) and DTA (b) patterns of γ-PtAcac–0.45. Heating in air at 5 °C/min.

3.2. Catalytic activity measurements

The total catalytic activity (followed as the conversion of *n*-pentane), the molar distribution of the products and selectivity to isopentane after 1.5 h at 400 °C, and after additional 1.5 h at 450 °C are summarized in tables 2 and 3, respectively. The selectivity to i-C_5 was calculated as the molar percentage of *n*-pentane that reacted to form i-C_5. The conversion and selectivity of the various catalysts as a function of time are shown in figures 2–7. All catalysts show deactivation as a function of time, and an increase in activity is observed when the temperature is increased, after 1.5 h on stream, from 400 to 450 °C. The selectivity into i-C_5 either remains constant or increases with time.

3.2.1. PtAcac-impregnated catalysts

The conversion and selectivity to i-C_5 as a function of time, for catalyst impregnated by toluene solution of

Table 2
Catalytic activity and selectivity after 1.5 h at 400 °C

Catalyst	C_1 (mol%)	C_2 (mol%)	C_3 (mol%)	C_4 (mol%)	i-C_5 (mol%)	c-C_5 (mol%)	n-C_5 (mol%)	Conv. (%)	Selec. (%)	C_1/C_4
NH–PtAcac–0.46	5.59	6.68	6.90	5.94	1.26	1.21	72.41	17.31	8.34	0.94
NH–PtAcac–0.96	5.00	5.26	5.62	5.27	1.14	1.53	76.17	14.93	8.53	0.95
γ-PtAcac–0.45	13.58	13.34	14.14	12.50	6.95	0.77	38.71	46.95	20.29	1.09
γ-PtAcac–0.71	13.91	12.57	13.59	13.12	3.08	0.94	42.79	41.60	10.12	1.06
NH–CPA–0.5	5.32	5.32	5.60	5.64	1.23	1.09	75.80	15.00	9.18	0.94
NH–CPA–1.0	6.76	6.67	6.98	6.63	1.33	1.40	70.23	18.78	8.22	1.02
γ-CPA–0.5	9.19	7.66	8.15	9.11	2.29	1.27	62.33	24.88	11.10	1.01
γ-CPA–1.0	14.73	12.13	13.04	13.56	3.10	0.92	42.52	41.76	10.16	1.09
NH–$PtBr_4$–1.0	6.06	6.81	6.94	6.55	2.04	1.39	70.21	19.27	12.15	0.93
NH–BNPtCl–1.0	7.13	8.72	9.61	8.57	2.92	1.07	62.00	25.76	13.55	0.83

PtAcac, are shown in figures 2 and 3 respectively. For the NH alumina increasing the Pt loading from 0.46 to 0.96% does not effect the total conversion significantly. Increasing the Pt loading from 0.46 to 0.96% results in a slight decrease in the conversion at 400 °C, and the conversion at 450 °C is the same for both Pt loading. The conversions after 1.5 h at 400 and 450 °C for the two Pt loadings are in the 14.7–17.3% range. The selectivity to the various products for the two 0.46 and 0.96% Pt loadings are practically the same during all times. The selectivity to i-C_5 for the NH–PtAcac samples remains constant as a function of time at ~8.2% for 400 °C and at ~14.8% for 450 °C.

The crystalline γ-alumina catalysts show higher conversions and higher selectivities to i-C_5 than the amorphous catalysts. Increasing the Pt loading from 0.45 to 0.71% for the two temperatures 400 and 450 °C, results in about 10% decrease in catalytic activity, and a pronounced decrease in selectivity to i-C_5 during all times. All the crystalline γ-alumina samples show increased selectivity to i-C_5 as a function of time. The increase is more pronounced at 450 °C.

3.2.2. CPA-impregnated catalysts

The conversion and selectivity to i-C_5 as a function of time, for catalyst impregnated by aqueous solution of CPA, are shown in figures 4 and 5, respectively. For the NH alumina, increasing the Pt loading from 0.5 to 1% causes moderate increase in activity. After 1.5 h at 400 °C, the conversion increases from 15% for the NH–CPA–0.5 catalyst to 18.8% for the NH–CPA–1.0. The selectivity to isomerization at 400 °C, for both Pt loadings, remains low at ~8.5%, during all times. At 450 °C, the activity is not affected by the Pt loading. However, the selectivity to i-C_5 increases with time up to 31% after 1.5 h for the 0.5% Pt samples, whereas for the 1% Pt sample the selectivity to i-C_5 remains constant with time at ~11.5%. It should be noticed that in spite of the fact that the SA of the samples impregnated with aqueous CPA (175 m^2/g) is significantly lower than the SA of the samples impregnated with toluene solution of PtAcac (260 m^2/g), their activity is not affected dramatically. After 1.5 h at 400 °C, the average conversion for the 0.5% and 1% Pt samples impregnated by PtAcac is 16.1% and the corresponding conversion for the CPA

Table 3
Catalytic activity and selectivity after 1.5 h at 450 °C

Catalyst	C_1 (mol%)	C_2 (mol%)	C_3 (mol%)	C_4 (mol%)	i-C_5 (mol%)	c-C_5 (mol%)	n-C_5 (mol%)	Conv. (%)	Selec. (%)	C_1/C_4
NH–PtAcac–0.46	4.86	4.76	4.62	3.78	2.12	3.28	76.58	15.53	15.08	1.29
NH–PtAcac–0.96	4.92	4.08	4.11	3.76	2.00	3.36	77.77	14.74	14.86	1.31
γ-PtAcac–0.45	15.93	13.47	14.25	10.47	25.81	0.97	19.10	73.25	49.37	1.52
γ-PtAcac–0.71	17.44	14.56	15.49	11.96	16.50	1.22	22.83	66.79	35.96	1.46
NH–CPA–0.5	5.69	5.05	5.15	4.82	5.86	2.83	70.60	21.03	31.17	1.18
NH–CPA–1.0	7.32	5.88	5.89	5.42	1.92	3.09	70.49	19.15	11.50	1.35
γ-CPA–0.5	13.16	10.02	10.50	9.97	12.83	2.12	41.40	46.42	35.76	1.32
γ-CPA–1.0	20.09	15.57	15.69	14.05	12.03	0.93	21.65	66.95	27.42	1.43
NH–$PtBr_4$–1.0	7.56	6.03	5.92	5.68	3.16	3.04	68.60	20.99	17.35	1.33
NH–BNPtCl–1.0	8.98	8.46	8.21	7.84	5.00	2.78	58.74	29.14	20.71	1.14

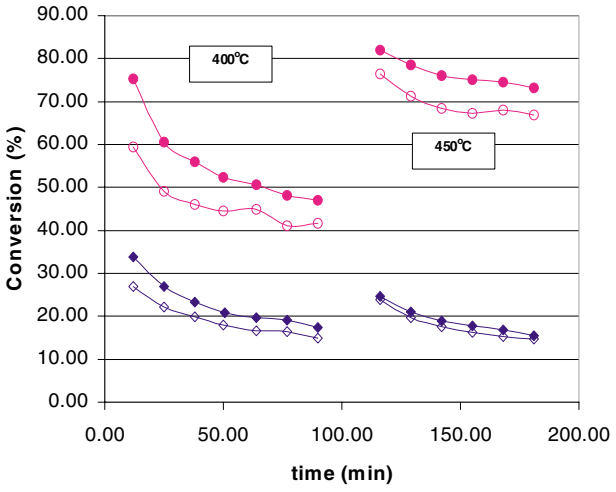

Figure 2. Conversion versus time, PtAcac-impregnated catalysts: (●) γ-PtAcac–0.45; (○) γ-PtAcac–0.71; (◆) NH–PtAcac–0.46; (◇) NH–PtAcac–0.96.

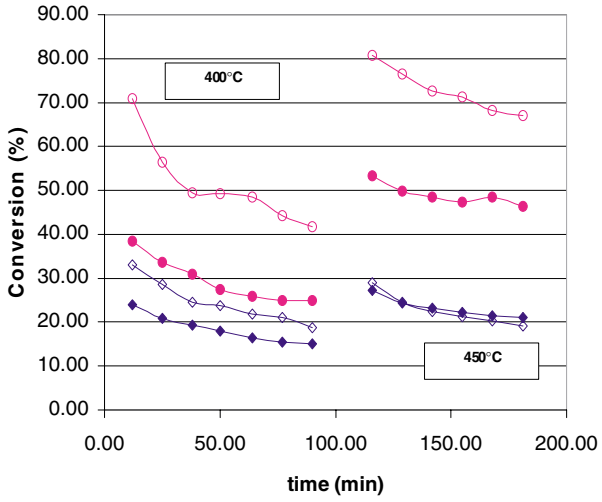

Figure 4. Conversion versus time, CPA-impregnated catalysts: (●) γ-CPA–0.5; (○) γ-CPA–1,0; (◆) NH–CPA–0.5; (◇) NH–CPA–1.0.

samples is 16.9%. After 1.5 h at 450 °C, the average conversion for the 0.5 and 1% PtAcac-impregnated samples is 15.1% and for the CPA samples it is 20.1%. The average total reaction rate of n-C_5 per alumina SA after 1.5 h on stream at 400 and 450 °C is shown in table 4. According to table 4, the reaction rate per alumina surface increases significantly when CPA solution in water is used for the impregnation instead of PtAcac solution in toluene.

As for the PtAcac-impregnated samples, the crystalline γ-alumina catalyst show higher conversions and higher selectivities to i-C_5 than the amorphous catalyst. Increasing the Pt loading from 0.5 to 1% results in a drastic increase in conversion during all times at 400 and 450 °C. After 1.5 h at 400 °C, the conversion increases from 24.9 to 41.8% with the increased Pt content. The corresponding increase in conversion at 450 °C is from 46.4 to 67%. Both 0.5 and 1% Pt crystalline γ-alumina samples show increasing selectivity to i-C_5 with time at 400 and 450 °C with a more pronounced increase at 450 °C. In spite of the fact that sample γ-CPA–0.5 and γ-PtAcac–0.45 contain roughly the same amount of Pt and possess the same SA, the catalytic activity of the latter is much higher (24.9% conversion for the first and 47% for the second after 1.5 h at 400 °C), which is also observed in the lower reaction rates per SA of the CPA-impregnated catalyst (table 4). The total reaction rate of n-C_5 on the γ-CPA–1.0 is similar to the reaction rate on γ-PtAcac–0.45 and γ-PtAcac–0.71.

3.2.3. In situ *Pt-introduced catalysts*

The conversion and selectivity to i-C_5 as a function of time, for the *in situ* $PtBr_4$- and BNPtCl-based catalysts, are shown in figures 6 and 7. The BNPtCl-introduced sample shows higher activity than the $PtBr_4$ analog in

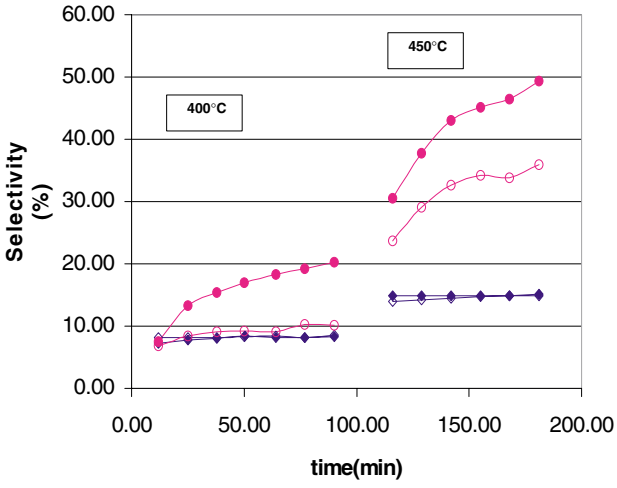

Figure 3. Selectivity to i-C_5 versus time, PtAcac-impregnated catalysts: (●) γ-PtAcac–0.45; (○) γ-PtAcac–0.71; (◆) NH–PtAcac–0.46; (◇) NH–PtAcac–0.96.

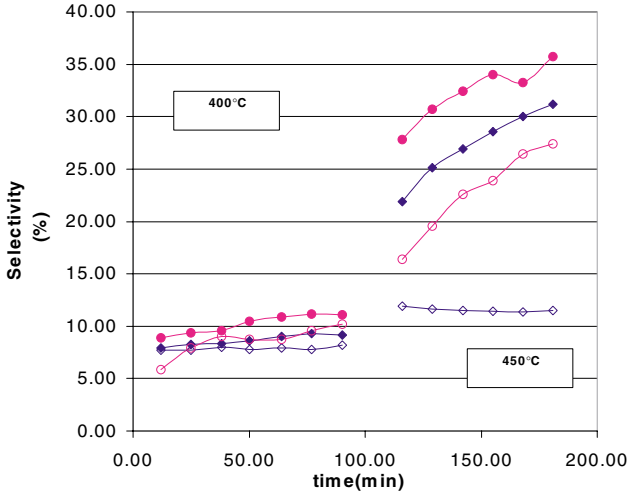

Figure 5. Selectivity to i-C_5 versus time, CPA-impregnated catalysts: (●) γ-CPA–0.5; (○) γ-CPA–1,0; (◆) NH–CPA–0.5; (◇) NH–CPA–1.0.

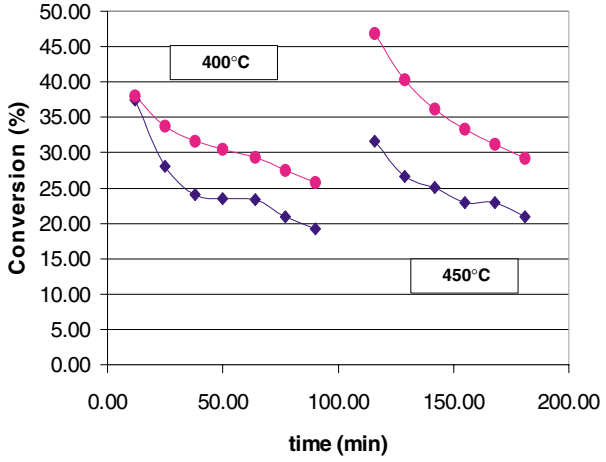

Figure 6. Conversion versus time, *in situ* prepared catalysts: (●) NH–BNPtCl–1.0; (◆) NH–$PtBr_4$–1.0.

Table 4
Reaction rates

Catalyst	Average reaction rate of n-C_5 per SA after 1.5 h, $10^{10} \times$ mol/(m^2s)	
	400 °C	450 °C
NH–PtAcac–0.46	87	78
NH–PtAcac–0.96	80	79
γ-PtAcac–0.45	289	451
γ-PtAcac–0.71	263	423
NH–CPA–0.5	114	160
NH–CPA–1.0	146	149
γ-CPA–0.5	148	276
γ-CPA–1.0	264	424
NH–$PtBr_4$–1.0	87	94
NH–BNPtCl–1.0	94	106

terms of total conversion. However, in terms of reaction rate per SA (table 4), the difference is only 7–12%. The reaction rate per SA of the *in situ* catalysts are slightly higher than that of NH–PtAcac–0.96 catalyst. Similarly, the selectivity of the *in situ* samples to i-C_5 is higher than the analogous selectivity of the NH–PtAcac–0.96 catalyst.

4. Discussion

4.1. Reaction mechanism

The catalytic activity of Pt/Al_2O_3 for alkane reforming is usually explained by the classical bifunctional mechanism [29]. The pentane is first dehydrogenated on the metal function and is then isomerized or cracked on the acidic sites situated on the alumina surface, and finally the isomerized/cracked olefins are hydrogenated on Pt. Under commercial naphtha reforming conditions, equilibrium concentration of olefin, in the gas phase, is formed on the metal function. Therefore, increasing the metal surface area does not increase the reaction rate,

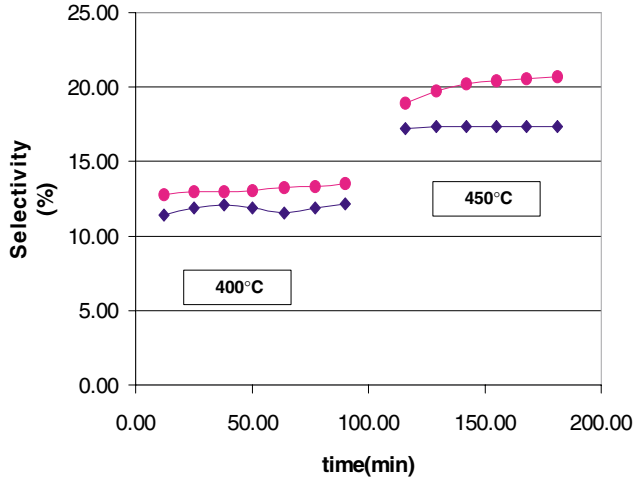

Figure 7. Selectivity to i-C_5 versus time, *in situ* prepared catalysts: (●) NH–BNPtCl–1.0; (◆) NH–$PtBr_4$–1.0.

and the reaction rate is controlled by the activity of the alumina's acid function [26–27], i.e., its acidity. The number of acidic sites determines the total reaction rate, and the distribution of acidic strength determines the selectivity towards the various products.

Increasing the Pt loading for the NH–PtAcac-impregnated catalysts from 0.46 to 0.96% resulted in a catalyst with very similar catalytic activity. This suggests that the Pt does not control the catalytic activity of the Pt–NH catalysts. However, considering the lower Pt dispersion for the 0.96% Pt catalysts (table 1), the increase in Pt surface atoms is only 20%. This may disguise the effect of increased Pt loading. A clear indication that the acid sites on the NH alumina control the catalytic activity of the catalyst is obtained by comparing the catalytic activity of the catalysts obtained by impregnation of NH alumina with toluene solution of PtAcac and with aqueous solution of CPA. If Pt was the rate-controlling function then the low Pt dispersions obtained for the CPA-impregnated catalysts would have resulted in catalysts of very low activity with respect to the PtAcac-impregnated catalysts. In reality, in spite of the lower Pt dispersion of the CPA-impregnated catalysts, they exhibit higher catalytic activity. This is a clear indication that the reactions are controlled by the acid function of the alumina matrix and not by the Pt function. The fact that the catalytic activity does not decline with the decreased SA of the CPA-impregnated catalysts, as will discussed below, is attributed to changes in the surface acidic centers occurring during the impregnation of NH alumina with aqueous CPA.

For the γ-alumina PtAcac-impregnated catalysts, increasing the Pt loading from 0.45 to 0.71%, resulted in net increase of 43% in surface Pt atoms (taking into account the Pt dispersions), and in a slight decrease in n-C_5 conversion. Therefore, similar to the NH alumina samples, the reaction on the Pt is not the rate-controlling step in the reactions, and the acidic centers on the alumina are the rate-controlling functions for the

γ-alumina. The increased n-C_5 conversion of the γ-CPA-1.0 catalyst with respect to γ-CPA-0.5 catalyst is probably a result of the increased Cl content (0.89 and 0.55%, respectively), which is known to increase the acidity of the alumina [1,22–23], and not a result of the increased Pt content.

An insight to the cracking mechanism is obtained by analyzing the product molar distributions in tables 2 and 3. The sum of C1 + C4 is very similar to the sum of C2 + C3, which indicates the same probability of terminal and internal C–C bond cleavage. Indication on the cracking mechanisms is obtained by analyzing the C_1/C_4 ratio. A C_1/C_4 ratio <1 suggests of a bimolecular cracking mechanism [30–31], which is typical of very acidic supports. A C_1/C_4 ratio >1 suggests fast secondary cracking in which large portion of the produced C_4 are further cracked [31]. C_1/C_4 ratio $\sim$1 suggests of monomolecular single cracking. The experimental C_1/C_4 ratios summarized in tables 2 and 3 suggest that at 400 °C the cracking is mainly single monomolecular cracking, whereas at 450 °C fast secondary cracking occurs to a large extent.

4.2. *Effect of support and preparation method on catalytic activity*

The total conversion and selectivity to isomerization or cracking depends on the number of total acid sites and their strength distribution, since the cracking occurs on sites of relatively high acidic strength. In general, the γ-Al_2O_3-based catalysts exhibit higher conversions (figures 2 and 4) and higher reaction rates per SA (table 4) than the corresponding NH–Al_2O_3 catalysts. This means that the density of acidic sites on the crystalline samples is higher. The higher selectivity to isomerization of the γ-Al_2O_3 suggests that the average acid strength of the γ-Al_2O_3 catalysts is lower than the average acidic strength of the NH–Al_2O_3 catalysts.

The γ-CPA–0.5 exhibit lower activity than the corresponding γ-PtAcac–0.45. This is rather surprising, taking into account the surface Cl formed by the contact with CPA of the γ-CPA–0.5 (table 1). This surface chlorine is expected to enhance the acidity [32] and, therefore, its catalytic activity. The Cl content of γ-PtAcac–0.45 was not measured, but is expected to be the same as for the pure γ-alumina, i.e., negligible (there is no contact with a source of Cl during the impregnation). The Cl content of γ-CPA–0.5 (table 1) is 0.55%, which matches the amount expected from the CPA. This chlorine is expected to enhance the acidity of the support, which is expected to result in higher reaction rates. However, the PtAcac-impregnated γ–Al_2O_3 shows a higher activity. Before the impregnation with PtAcac, the alumina was dehydrated at 500 °C. On the other hand, the CPA impregnation is conducted in water. Therefore, we suggest that these pretreatments of the catalysts may result in a higher density of catalytic sites on the PtAcac-impregnated γ-Al_2O_3 than on the CPA-impregnated γ-Al_2O_3, leading to higher catalytic activity of the PtAcac-impregnated sample. The source of the increased activity of the PtAcac samples may also be due to surface species formed on the γ-PtAcac catalysts. The TGA of the γ-PtAcac–0.45 revealed the release of 0.5 wt% of unknown species upon the phase transformation to α-Al_2O_3, probably as a result of the associated SA collapse (consistent with the Hedvall effect). This weight loss was not observed in the TGA of CPA-impregnated catalysts nor from the pure alumina. Therefore, we believe that these surface species are formed as a result of the PtAcac/toluene impregnation of the crystalline γ-alumina (no weight loss was observed during the γ to α transformation of the NH–PtAcac samples). These surface species are probably carbonaceous materials and, therefore, may increase the adsorption of organic reactants on the surface near the catalytic sites, thus increasing the catalytic activity. The increased activity of γ-CPA–1.0 compared to the γ-CPA–0.5 is probably caused by the higher Cl content of the former (0.89, 0.55 wt%, respectively), which increases the alumina's acidity [1,22–23]. The higher selectivity towards cracking (tables 2 and 3) is consistent with higher strength of acidic sites.

For both impregnation methods, the crystalline γ-alumina exhibit much higher conversions than the NH amorphous alumina. This is in spite of the high intrinsic Cl content in the NH alumina. Therefore, we conclude that the Cl in the NH alumina, which is probably held within the alumina matrix (not on the surface), has minor contribution to the catalytic activity compared to the catalytic activity of the ordered crystalline γ-alumina. This conclusion may explain the higher reaction rate per Al_2O_3 SA of the NH–CPA-based catalyst compared to the NH–PtAcac-based catalyst (table 4). According to previous studies [7,24], contact of the NH amorphous alumina with water causes a dissolution re-precipitation process, which reduces the SA with respect to the initial NH alumina and results in the relatively low Pt dispersion [25] of the CPA-impregnated catalysts. Upon subsequent air calcination at $T > 450$ °C, the water-contacted NH alumina undergoes crystallization into γ-alumina. The timescale of the contact with water at RT for significant crystallization upon subsequent heat treatment is days–weeks. In our catalyst preparation procedure, the amorphous alumina is contacted with aqueous phase for only 4 h, and indeed XRD analysis of H_2-reduced NH–CPA–1.0 sample (not shown), did not reveal any crystalline phases. However, we believe that during the 4 h contact with water and the subsequent 500 °C calcination, some of the surface structures (which are too small to be detected by XRD) formed on the amorphous alumina resemble the structures on crystalline γ-alumina. As a result of these surface structures, the CPA-impregnated NH-amor-

phous alumina catalyst exhibit much higher catalytic activity per SA than the NH–PtAcac samples. The γ-CPA catalysts also exhibit higher selectivity towards i-C_5 than the corresponding NH–PtAcac samples. One could therefore expect that if part of the surface structures formed on the NH–CPA catalysts are similar to the structures on the γ-CPA catalyst, they would exhibit higher selectivity to i-C_5 than the corresponding NH–PtAcac catalysts. At 400 °C, the difference in selectivity towards i-C_5 between the NH–PtAcac catalysts (8.3 and 8.5% for the 0.46 and 0.96% Pt catalysts after 1.5 h on stream) and the γ-CPA catalysts (11.1 and 10.2% for the 0.5 and 1% Pt catalysts after 1.5 h on stream) is too small for any significant change to occur. At 450 °C, the NH–CPA–0.5 catalyst exhibit pronounced higher selectivity to i-C_5 (31.2% after 1.5 h on stream), than the NH–PtAcac–0.46 catalyst (15.1% after 1.5 h on stream). However, the NH–CPA–1.0 exhibit a little lower selectivity to i-C_5 than the NH–PtAcac–0.96 catalyst. An additional explanation for the increased reaction rate per SA of the NH–CPA compared to NH–PtAcac catalysts may be the formation of surface chlorine on the NH–CPA catalyst, which may increase the acidity. The origin of this surface chlorine would be chlorine from the CPA and chlorine expelled out of the alumina matrix. Before the contact with water, the NH-amorphous alumina contains 2.6 wt% Cl that is probably buried in the bulk. As mentioned above, upon contact with water followed by 500 °C calcination at air, microcrystalline structures are formed at the surface. These ordered structures could expel the Cl atoms from the bulk to the surface. It should be emphasized that our measurements of the Cl do not distinguish between surface and bulk chlorine.

The *in situ* NH–$PtBr_4$ and the NH–BNPtCl catalysts show a slightly higher total reaction rate per SA (table 4) than the corresponding NH–PtAcac samples, and a higher selectivity to isomerization (tables 2 and 3). The increased conversion of the *in situ* samples is probably due to the larger SA of these catalysts. The difference in total activity per SA and selectivity to isomerization is probably a result of the lower calcination temperature of the *in situ* prepared catalyst (500 °C) than the calcination temperature of the pure NH alumina used for the impregnations (650 °C). The higher calcination temperature of the latter may result in a smaller amount of acidic centers and a stronger average acidic strength.

4.3. Deactivation

All catalysts exhibit pronounced deactivation with time at 400 °C and at 450 °C. However, in the selectivity towards i-C_5 there is marked difference between the behavior with the time of the NH and the γ-alumina-supported catalysts. The NH-supported catalysts (except the NH–CPA–0.5 catalyst) exhibit constant selectivity towards isomerization with time. This means that the catalytic sites responsible for cracking and the catalytic sites responsible for isomerization deactivate at the same relative rate. The γ-supported catalysts, on the other hand, exhibit an increase in selectivity towards isomerization with time. At 450 °C, the yield of i-C_5 for the γ-supported catalysts even increases with time. This indicates that the deactivation of the isomerization sites is compensated by the formation of new isomerization centers. The origin of these new isomerization centers may be: (1) strong acidic centers (cracking sites), which lose acidity and turn into isomerization sites, reducing cracking activity and increasing isomerization activity; (2) the increase of the reaction temperature from 400 to 450 °C may cause some additional dehydration of the support, which may result in the formation of new isomerization sites as the dehydration proceeds.

Summary

The utilization of NH amorphous alumina as a Pt support for *n*-pentane reforming, and the effect of Pt introduction method were studied. The Pt was introduced by impregnation with either CPA solution in water or PtAcac solution in toluene, or by *in situ* introduction during alumina gelation using $PtBr_4$ or BNPtCl as Pt precursors. The performances of the NH-based catalysts were compared with the performances of Pt/γ-Al_2O_3 catalysts prepared by the same impregnation methods. The main findings are as follows:

- For both amorphous and γ-alumina-based catalysts, the rate-controlling step for *n*-pentane reforming is the reaction on the acidic sites of the alumina.
- The *n*-pentane conversion and the selectivity towards isomerization over the Pt/γ-Al_2O_3-based catalysts are higher than on their analogs Pt/NH–amorphous–Al_2O_3.
- The high intrinsic Cl content of the NH amorphous alumina (2.6 wt%) has minor contribution to its catalytic activity compared to the activity of the crystalline γ-Al_2O_3.
- Upon impregnation with aqueous CPA and subsequent calcination, surface crystalline-like structures are formed. These structures cause increased activity per alumina surface compared to catalysts prepared by impregnation of the NH alumina with PtAcac solution in toluene or by introduction of the Pt during gelation of the NH alumina.
- Upon air calcination of Pt/γ-Al_2O_3 samples prepared by impregnation with PtAcac solution in toluene, a 0.14–0.5% drop in weight was observed during the γ to α transition (1140–1220 °C). This is probably due to the release of surface carbonaceous species with the associated SA collapse. The effect of these surface species on catalytic activity is not clear.

In conclusion, the crystalline γ-Al_2O_3 is more active than the NH amorphous Al_2O_3 towards *n*-pentane reforming, albeit the high Cl content of the NH amorphous alumina.

Acknowledgments

The authors would like to thank the Israel Science Foundation, the Technion Grand Water Institute, the Technion Catalysis Project, the Technion Fund for advancement of research and the Center for Adsorption in Science of the Ministry of Immigrant Absorption (under the framework of KAMEA program) for their support. In addition, The authors would like to thank Dr. Michael Reisner for the assistance in X-ray measurements.

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