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Gas-phase hydrogenation of benzene to cyclohexane over combustion-synthesized $Ce_{1-x}Pt_xO_{2-\delta}$ ($x = 0.01, 0.02$)

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The gas-phase hydrogenation of benzene to cyclohexane over $Ce_{1-x}Pt_xO_{2-\delta}$ ($x = 0.01, 0.02$) catalyst was investigated in the temperature range 80–200 °C. A 42% conversion of benzene to cyclohexane with 100% specificity was observed at 100 °C over $Ce_{0.98}Pt_{0.02}O_{2-\delta}$ with a catalyst residence time of 1.22×10^4 g s/mol of benzene. The activity of the catalyst was compared with those of Pt metal, combustion-synthesized Pt/α-Al_2O_3 and Pt/γ-Al_2O_3. The turnover frequency value of $Ce_{0.98}Pt_{0.02}O_{2-\delta}$ is 0.292, which is an order of magnitude higher than those of the other Pt catalysts investigated. The kinetics of reaction and the deactivation behavior of the catalyst were studied and a regeneration methodology was suggested. The deactivation kinetics and structural evidence from XRD, XPS, TGA and H_2 uptake studies suggest that the oxidized Pt in $Ce_{0.98}Pt_{0.02}O_{2-\delta}$ is responsible for the high catalytic activity towards benzene hydrogenation.

KEY WORDS: benzene hydrogenation; combustion synthesis; $Ce_{1-x}Pt_xO_{2-\delta}$ hydrogen uptake; catalyst deactivation

1. Introduction

Benzene hydrogenation is of industrial relevance because its reaction product, cyclohexane, is an important industrial intermediate used in the production of nylon-6 and nylon-66 [1]. It also finds application as a solvent for paints, resins, varnishes and oils and in plasticizers. In addition, increasing environmental awareness has resulted in the need to remove benzene, which is a known carcinogen, to aid in the production of aromatic-free solvents and transportation fuels [2].

Unlike double bonds in alkenes, benzene cannot be reduced using the usual catalysts such as platinum or palladium because of the high stability of the aromatic ring. Reduction can be achieved under severe conditions such as several hundred atmospheres of hydrogen with the usual catalysts such as rhodium, platinum on carbon and Raney nickel [3]. Although the hydrogenation of benzene can be carried out in the liquid phase [2,4,5], owing to diffusion limitations and adsorption properties of liquids, reaction in the gas phase is preferred [5–14].

Although several reviews [6,7] have reported that hydrogenation of benzene occurs solely on the metal surfaces, the acidity of the support has been shown to enhance the activity for hydrogenation reactions. Acidic supports such as oxides or zeolites showed significantly higher rates compared with pure metal owing to their Brønsted acid sites [8,9]. Lin and Vannice [10] reported on benzene hydrogenation over Pt dispersed on SiO_2, η-Al_2O_3, SiO_2–Al_2O_3 and TiO_2 and observed higher specific activities for acidic supports. Ceckiewich and Delmon [11] studied the effect of diluent Al_2O_3 on Pt/γ-Al_2O_3 and observed a four-fold increase in the activity with a dilution of 20:1. The high activity and selectivity towards the hydrogenation of benzene by these metal-supported catalysts were attributed to hydrogen spillover, dissociative adsorption of hydrogen on the metal and migration of atomic hydrogen to the surface of the support [12–14]. van Meerten and Coenen [15] observed an optimum in the variation of reaction rate with temperature in hydrogenation on a nickel/silica catalyst. The decrease in benzene conversion at higher temperatures was attributed to a counteractive effect played by increased fractional coverage of active sites by reactants on the catalyst surface. There are reports [3,9,10] on the deactivation of catalysts and it was attributed to the formation of hydrogen-deficient or carbonaceous species on the surface, and self-poisoning due to irreversibly adsorbed benzene residues during hydrogenation of benzene.

In our laboratory, Pt/CeO_2 was synthesized by the solution combustion method and it was shown that Pt is ionically dispersed over nano-sized CeO_2 crystallites [16]. It was shown that 1–2 at% of Pt^{2+} ions are substituted for Ce^{4+} ions forming a $Ce_{1-x}Pt_xO_{2-\delta}$ solid solution. Pt^{2+} ion was shown to be active for CO and hydrocarbon oxidation and NO reduction by CO compared with Pt^0 in Pt/Al_2O_3. Further, $Ce_{1-x}Pt_xO_{2-\delta}$ showed extremely high catalytic activity for the recombination of H_2 and O_2 at room temperature, indicating high dissociation for both H_2 and O_2 [17,18]. Ionically dispersed 1–2 at% Pt/CeO_2 also showed excellent activity for partial oxidation of

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methane without any dissociation of CO and coke formation [19]. Therefore, we considered it is worthwhile to investigate the hydrogenation of benzene to cyclohexane over this $Ce_{1-x}Pt_xO_{2-\delta}$ catalyst. Here we report the catalytic conversion of benzene to cyclohexane at atmospheric hydrogen pressure.

2. Experimental

2.1. Synthesis and characterization

The Pt/CeO_2 catalyst was prepared by the solution combustion method. The combustion mixture for the preparation of 2 at% Pt/CeO_2 contained 2 g of $(NH_5)_2Ce(NO_3)_6$, 0.0386 g of H_2PtCl_6, and 1.035 g of $C_2H_6N_4O_2$ (ODH) dissolved in 30 ml of water in a borosilicate dish. This combustion mixture was introduced into a muffle furnace maintained at 350 °C. The salts dissolved into clear solutions. Then the solution boiled with foaming and frothing and burnt with a flame (~1000 °C). The flame lasted about 1 min and quenched to 350 °C after the flame was extinguished in 1 min, yielding a voluminous solid product. Similarly, 0.5 and 1 at% Pt/CeO_2 were prepared. Details of the synthesis and characterization of these catalysts are presented elsewhere [16]. Pt metal particles of 6–7 nm were prepared by reducing H_2PtCl_6 in ethylene glycol at 170 °C. Pt/γ-Al_2O_3 and Pt/α-Al_2O_3 were also prepared by the combustion method employing ODH and urea as fuels, respectively [20].

Hydrogen uptake measurements on the as-synthesized catalysts were carried out in a 4 mm diameter quartz cell, using a 5% H_2/Ar gas flow of 30 cm^3/min over 0.1 g of catalysis between −80 ° and 750 °C. Hydrogen consumption was measured using a thermal conductivity detector and calibrated with the CuO reduction reaction.

2.2. Benzene hydrogenation

The gas-phase hydrogenation of benzene was carried out in a tubular reactor of 200 mm length and 6 mm diameter. A 0.3 g amount of as-prepared catalyst (−30 to +60 mesh) with 0.2 g of silica as diluent was packed between two quartz-wool plugs. The reactor was heated by a vertical tube furnace to the desired temperature (80–200 °C) and the reaction temperatures were measured with a Cr–Al thermocouple placed inside the catalyst bed. Benzene was pumped using a reciprocating HPLC pump (Eldex, USA) with a flow-rate ranging from 0.1 to 0.89 ml/min and vaporized along the pre-section of the reactor. The flow-rate of hydrogen (30 cm^3/min) was constant and monitored using a flow meter. The product mixture was condensed in the downstream using an ice-bath and the product was collected. The reaction product was analyzed quantitatively by gas chromatography (Mayura Anal. Pvt. Ltd., India) using a fused-silica capillary column (DB 624) (30 m × 0.53 mm i.d.) and a flame ionization detector. Methanol was used as an internal standard for calibration. The conversion of benzene to cyclohexane was determined quantitatively. The conclusive identification of cyclohexane was achieved using ^{1}H NMR spectroscopy. Some experiments were repeated three times and the standard deviation of the conversion obtained was <2%. The experiments were also carried out with polyol-synthesized Pt nano-metal particles, combustion-synthesized Pt/α-Al_2O_3 and Pt/γ-Al_2O_3 and different Pt atomic loadings on CeO_2 for comparison. The kinetics of the hydrogenation of benzene and deactivation of the catalyst were studied.

3. Results and discussion

3.1. Hydrogenation of benzene

As-synthesized 2 at% Pt/CeO_2 catalyst was employed for the hydrogenation of benzene. The product analysis by gas chromatography and ^{1}H NMR spectroscopy proved that benzene was stoichiometrically converted to cyclohexane, without any by-product. Figure 1 shows the effect of the catalyst residence time (W/F_{A0}) on the conversion at various temperatures at 1 atm pressure. The range of catalyst residence times employed was (0.072–1.22) $\times 10^4$ g s/mol benzene. The figure indicates that the conversion increases exponentially with catalyst residence time.

Antonucci *et al.* [13] employed a very wide range of catalyst residence times (2.13×10^6–0.73×10^6 g s/mol) i.e., high catalyst loadings, and observed a maximum conversion of 60% at 150 °C for Pt/γ-Al_2O_3 with the maximum rate being 0.218 μmol/g s. In the current investigation, with a short residence time of 1.22×10^4 g s/mol benzene, 42% conversion was achieved at 100 °C with an absolute rate of 34.4 μmol/g s. This clearly shows that the observed rates are two orders of magnitude higher than the reported rate [13].

To determine the kinetics, the conversion of benzene was limited in such a way that the fraction of hydrogen consumed was <5% where the reactor can be assumed to be differential. Under such a low conversion, mass transfer limitations can be neglected. The arithmetic average of the inlet and outlet concentrations was taken for the kinetic analysis. The reaction rates were calculated at the exit of the reactor, as the difference is negligibly small. The rates were calculated by using the differential expression

$$r_{Af} = \frac{X_{Af} - X_{A0}}{W/F_{A0}},$$

where X_{A0} and X_{Af} are the initial and final conversions and r_{Af} is the rate of the reaction at the final conversion. In the range of operation, benzene was in excess. Hence

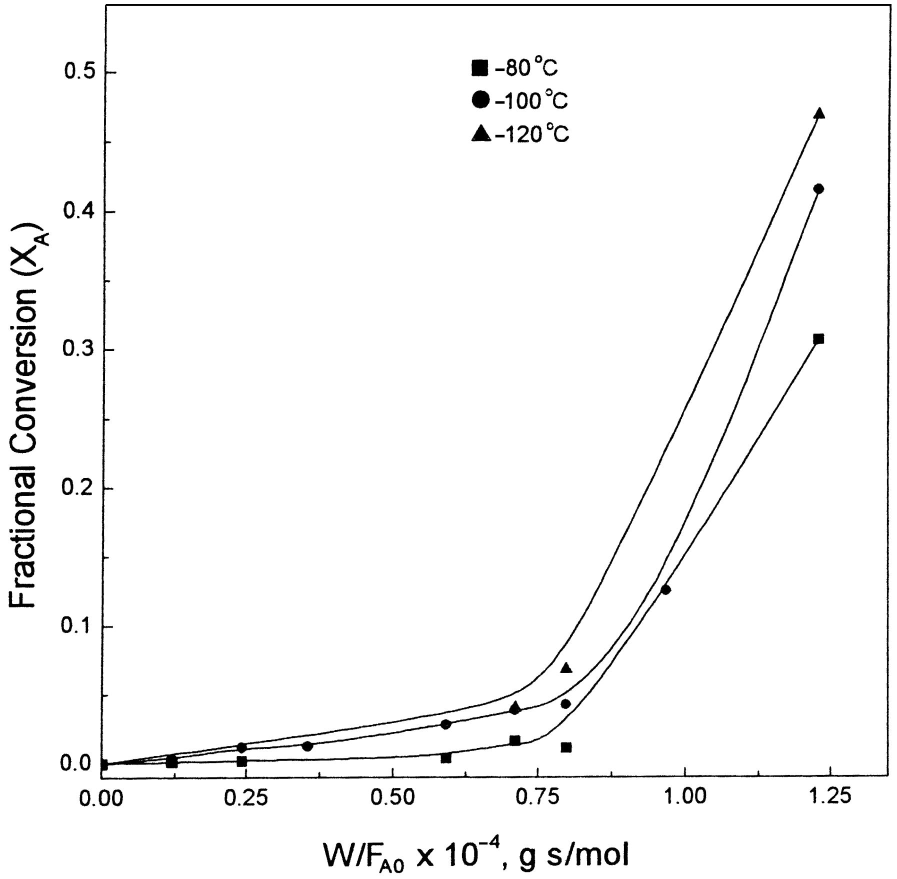

Figure 1. Conversion (X_A) of benzene to cyclohexane over 2 at% Pt/CeO_2 as a function of catalyst residence times (W/F_{A0}) at various temperatures.

the overall order with respect to benzene was taken as zero and is consistent with the literature [13,15,21]. The empirical power law fit, assuming zero order for benzene, was obtained by linearly regressing the experimental data. The rate form is $kC_{H_2}^{0.433}$.

Reactions were carried out over 2 at% Pt/CeO_2 at various temperatures under 1 atm of H_2 and $W/F_{A0} = 1.22 \times 10^4$ g s/mol. The conversions were 33% at 80 °C, 42% at 100 °C, 43% at 120 °C and 46.7% at 200 °C. Since there was no substantial increase in the conversion between 100 and 200 °C, further studies were made at 100 °C. The standard Gibbs free energy change for this reaction is 97.75 kJ/mol with fractional equilibrium conversions of ~1 in the operating range 80–200 °C and thus the thermodynamics may not be limiting. However, not much increase in the conversion is seen at 200 °C, which may be accounted for by hydrogen limitation.

To compare the activity of 2 at% Pt/CeO_2 with those of other combustion-synthesized supported metals (1 at% Pt/α-Al_2O_3, 1 at% Pt/γ-Al_2O_3 and 0.5 and 1 at% Pt/CeO_2) and nano-Pt metal, reactions were conducted at 100 °C and at 1 atm with the same operating conditions. The percentage conversion, amount of catalyst, and amount of Pt in each of the catalysts used are summarized in table 1. It was found that 1 at% Pt/γ-Al_2O_3 gave the lowest conversion of 0.04%, and Pt metal and 1 at% Pt/α-Al_2O_3 gave ~2.5%. Conversion with 1 at% Pt/CeO_2 was 30% whereas with 2 at% Pt/CeO_2 it was 42%. As can be seen from table 1, the amounts of Pt in 2 at% Pt/CeO_2, 1 at% Pt/Al_2O_3, and Pt metal are the same, yet the conversion is much higher over the Pt/CeO_2 catalyst.

In order to compare the catalytic activity of 2 at% Pt/CeO_2 with those of the above-mentioned catalysts, the turnover frequency (TOF = number of moles of products per second/number of moles of Pt) was calculated (table 1). The TOF of 2 at% Pt/CeO_2 is 15 times higher than those of pure Pt nano-metal particles and

Table 1
Percentage conversion of benzene to cyclohexane under 1.0 atm H_2 at 100 °C

Catalyst	Amount (mg)	Amount of Pt (mg)	Conversion (%)	TOF (s^{-1})
Pt metal	6.76	6.76	2.46	0.017
1 at% Pt/α-Al_2O_3	357	6.76	2.11	0.015
1 at% Pt/γ-Al_2O_3	357	6.76	0.04	0.0003
$Ce_{0.995}Pt_{0.005}O_{2-\delta}$	300	1.69	4.95	0.138
$Ce_{0.99}Pt_{0.01}O_{2-\delta}$	300	3.38	30.0	0.422
$Ce_{0.98}Pt_{0.02}O_{2-\delta}$	300	6.76	41.4	0.292

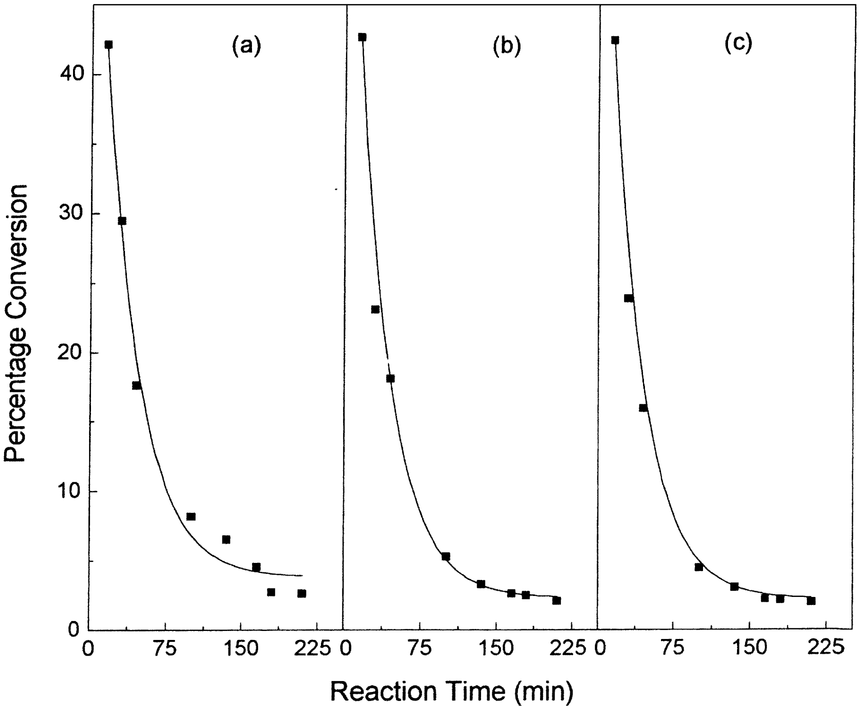

Figure 2. Deactivation study at 100 °C, $W/F_{A0} = 1.22 \times 10^4$ g s/mol: (a) fresh catalyst; (b) first regeneration by O_2 at 200 °C; (c) second regeneration by O_2 at 200 °C.

1 at% Pt/α-Al_2O_3 where the Pt is in the zerovalent state. The TOF of 1 at% Pt/CeO_2 is 1.5 times higher than that of 2 at% Pt/CeO_2. In general, Pt/CeO_2 showed a high TOF.

In the case of 2 at% Pt/CeO_2, up to 25 min, the conversion remained at 40% and thereafter there was deactivation of the catalyst. A plot of percentage conversion versus time up to 240 min over the fresh catalyst is shown in figure 2(a). It should be noted that 2.5–4% conversion was observed even after 240 min, which is close to the conversion over Pt metal. The deactivation constant was determined by assuming first-order decay for the catalyst and is 0.0297 min^{-1}.

Prolonged exposure of Pt/CeO_2 to hydrogen and benzene may result in a decrease in catalytic activity. The regeneration ability of catalyst was investigated by passing water to the extent of 1.5% of benzene through the reaction column to see if Pt/CeO_2 can dissociate H_2O to keep the catalyst oxidized. The catalyst deactivated to the same extent as without H_2O. Then, 1–5% O_2 with respect to H_2 was passed over the catalyst along with benzene to see if the catalyst can be regenerated *in situ*, and this too did not yield any improvement in regenerating the catalyst. After reaction for 240 min, the H_2 and benzene flow was stopped and O_2 was passed over the catalyst at 200 °C for 90 min. The catalyst was completely regenerated, as can be seen from figure 2(b). The percentage conversion was restored to 42.6% up to 25 min and the deactivation rate was similar to that of the freshly prepared catalyst. The catalyst was regenerated a second time by heating it at 200 °C in O_2 for 90 min and the benzene conversion was restored to 42.3%, as shown in figure 2(c). These studies indicate that the oxidized Pt/CeO_2 is the active catalyst. To confirm this, as-prepared 2 at% Pt/CeO_2 was reduced in H_2 at 200 °C for 2 h and conversion over this hydrogen-reduced catalyst was only 6%.

3.2. *Structural analysis of the catalyst*

3.2.1. *Thermogravimetric studies*

Initially, the deactivation was suspected to be due to coke formation. Hence thermogravimetric analysis (TGA) of as-prepared and spent catalyst was carried out in air up to 600 °C with a heating rate of 5 K/min. The TGA of the as-synthesized catalyst showed a 0.8% weight loss up to 600 °C, which may be due to moisture. The spent catalyst also showed a weight loss of 0.8% without any weight loss steps. Therefore, deactivation may not be due to coke formation.

3.2.2. *Hydrogen uptake studies*

Figure 3 shows the hydrogen uptake profile of 2 at% Pt/CeO_2 catalyst as a function of temperature in flowing H_2/Ar. H_2 uptake over Pt/CeO_2 occurs between −40 and 80 °C with a main peak at −25 °C in addition to a slow rise in H_2 uptake due to the reduction of CeO_2 beyond 100 °C. The area under the peak at −25 °C corresponds to a volume of hydrogen uptake of 6.66 cm^3 per gram

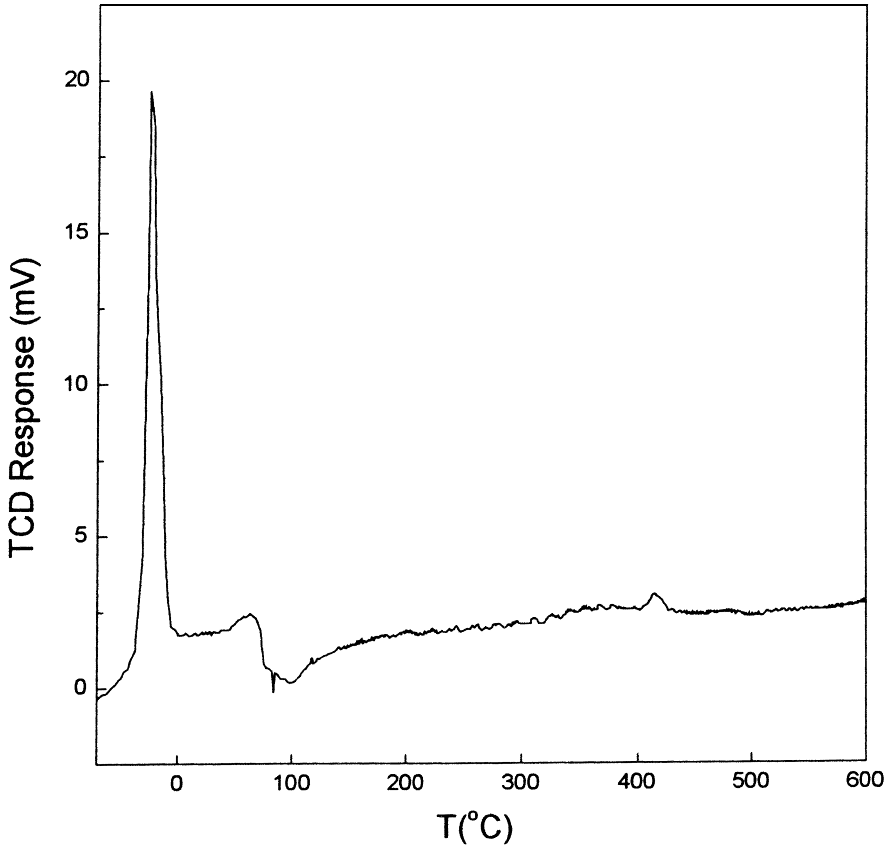

Figure 3. H_2 uptake profile of 2 at% Pt/CeO_2.

of 2 at% Pt/CeO_2. Hydrogen uptake experiments were also conducted with pure Pt metal particles and Pt/Al_2O_3 catalysts. The amount of hydrogen taken up was much less and occurred at higher temperatures (80–150 °C). Hydrogen uptake occurs over Pt metal only to the extent of one hydrogen atom per surface Pt atom. Over Pt/Al_2O_3, adsorption of 2–3 hydrogen atoms per Pt atom is seen. This is attributed to hydrogen spillover [14]. Further, over pure CeO_2 hydrogen uptake occurs above 200 °C and peaks at 450 °C, which can be attributed to the oxygen storage capacity [22]. Therefore, the peak at -25 °C is mainly due to hydrogen uptake over Pt species in Pt/CeO_2.

The Pt/CeO_2 system is certainly different in two ways. First, the number of hydrogen atoms taken up per Pt atom is 5.17, which is much higher than that for pure Pt or Pt/Al_2O_3, and second, it occurs at much lower temperatures. A similar observation has been made recently by Hickey *et al.* [23]. To see if this hydrogen is dissociatively adsorbed, H_2/Ar was passed over Pt/CeO_2 up to 100 °C and then cooled in Ar to room temperature. Then O_2 was passed at room temperature. On repeating the uptake with H_2/Ar from -80 °C, a similar H_2 uptake profile was observed with a peak at -25 °C as in figure 3. The peak intensity and area under the curve remained the same. Therefore, the H_2 adsorbed reacts with O_2 and regenerates the catalyst. Hence H_2 is dissociatively adsorbed. This is in accordance with our earlier study of the $H_2 + O_2$ recombination reaction at room temperature over the same catalyst [17]. In another experiment, H_2/Ar was passed over 2 at% Pt/CeO_2 up to 600 °C and cooled in Ar back to -80 °C. The repeat H_2 uptake experiment showed a small amount of hydrogen adsorption at about 50 °C with an H/Pt ratio of ~ 1. These experiments confirm that only the oxidized Pt/CeO_2 shows high hydrogen uptake. From XPS we find that Pt is present as Pt^0 (14%), Pt^{2+} (77%), Pt^{4+} (9%). The maximum possible H/Pt ratio calculated by considering the ionic state of Pt was <5. Hence this high H/Pt ratio cannot be accounted for by the reduction of ionic state of Pt alone.

3.2.3. *XRD studies*

X-ray diffraction patterns of as-synthesized 2 at% Pt/CeO_2, catalyst after reaction for 240 min, after oxidizing the spent catalyst for 90 min in flowing oxygen at 200 °C (subsequently called the oxidized catalyst), were recorded on a Siemens D5005 instrument with unmonochromatized Cu K_α radiation at 2°/min. The diffraction lines are broad, indicating that the ceria crystallite sizes are small. The ceria crystallite sizes are in the range 30 ± 15 nm, as seen from transmission electron microscopy [16]. As-synthesized 2 at% Pt/CeO_2 does

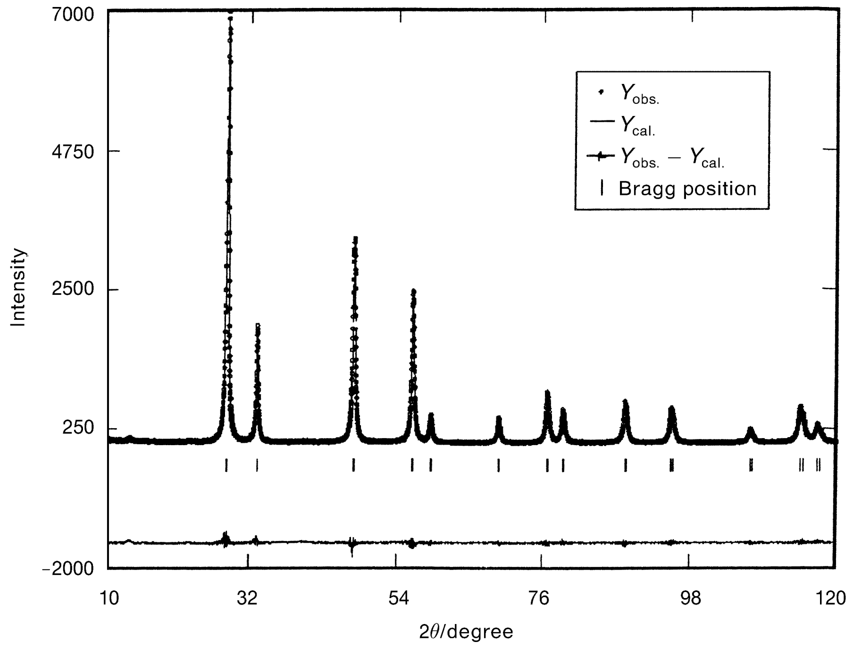

Figure 4. Observed, calculated and difference XRD patterns of as-prepared $Ce_{0.98}Pt_{0.02}O_{2-\delta}$.

not show peaks due to Pt metal or oxides of Pt such as PtO_2 or PtO. The XRD pattern of the catalyst after reaction indeed shows a small peak at ~40° (2θ), indicating the presence of Pt metal (111). However, after oxidation for 90 min at 200 °C, the intensity of the Pt(111) peak decreased. XRD of a physical mixture of 98% of pure CeO_2 prepared by the combustion method and 2 at% of 6–7 nm polyol-prepared Pt metal particles shows a Pt(111) to $CeO_2(111)$ area intensity ratio of 0.08. The surface area is in the range 18–20 m^2/g [19].

A careful XRD study was carried out to see if platinum ions were incorporated into the CeO_2 matrix. XRD data for Rietveld analysis were recorded in a Rigaku-2000 diffractometer with a rotating anode using Cu K_α radiation with a graphite-crystal monochromator to filter Cu K_β lines. Data were obtained at a scan rate of 1°/min with 0.02° range 10–110° and the structure was refined using the FullProf-98 program taking CeO_2 crystallizing in the *Fm*3*m* space group. Observed, calculated and difference XRD patterns of as-prepared 2 at% Pt/CeO_2 are shown in figure 4. For comparison, the pure CeO_2 structure was also refined. The number of parameters refined was 19. The lattice parameter a is 5.4106(3) Å with an oxygen occupancy of 1.92(1) for 2 at% Pt/CeO_2, 5.4105(2) Å for 1 at% Pt/CeO_2 and 5.4113(3) Å for pure CeO_2. The total oxygen in 1% Pt/CeO_2 is 1.883(4) and that in pure CeO_2 is 1.934(4). Accordingly, the R_{Bragg} values were 0.966, 1.31 and 0.91% for 2 at% Pt/CeO_2, 1 at% Pt/CeO_2 and CeO_2, respectively. Therefore, Rietveld analysis shows that Pt^{2+} ions are substituted for Ce^{4+} sites in CeO_2 crystallites. Hence, 1 and 2 at% Pt/CeO_2 prepared by the solution combustion method correspond to $Ce_{1-x}Pt_xO_{2-\delta}$, $x = 0.01, 0.02$ crystallites.

3.2.4. XPS studies

To confirm the electronic state of Pt in $Ce_{1-x}Pt_xO_{2-\delta}$ catalysts, an XPS study was carried out on as-synthesized, spent and oxidized catalysts. The core levels of the catalysts were recorded at a 5 mA emission current and 11 kV in an ESCA-3 Mark II spectrometer (VG Scientific, UK) using Al K_α radiation. The binding energies reported are with reference to C 1s at 285 eV.

The C 1s in these samples seems to be due to a graphitic carbon impurity, generally observed in any sample. Relative intensities of the C 1s to Ce 3d peaks were measured from the areas under the peaks and the values were 0.034 for fresh catalyst and 0.035 for the spent and 0.035 for the oxidized samples. Since there is no significant increase in the C 1s intensities in the spent catalyst, coke formation during the hydrogenation can be ruled out. Similarly, there was no increase in the C 1s to Pt 4f intensity ratio. This is also in agreement with TGA measurements.

The Ce 3d regions of as-synthesized, spent and the oxidized catalyst are shown in figure 5. The Ce 3d peaks along with satellites marked in figure 5 show that Ce is in the +4 state, as expected for CeO_2. There is no indication of CeO_2 being reduced to Ce_2O_3 in the spent catalyst in terms of decrease in the satellite peak intensity at 917.8 eV, which is characteristic of Ce^{4+} in CeO_2 [24].

In figure 6, the Pt 4f spectra of as-synthesized $Ce_{1-x}Pt_xO_{2-\delta}$ ($x = 0.02$), spent catalyst and after its oxidation at 200 °C for 90 min are shown. The Pt 4f

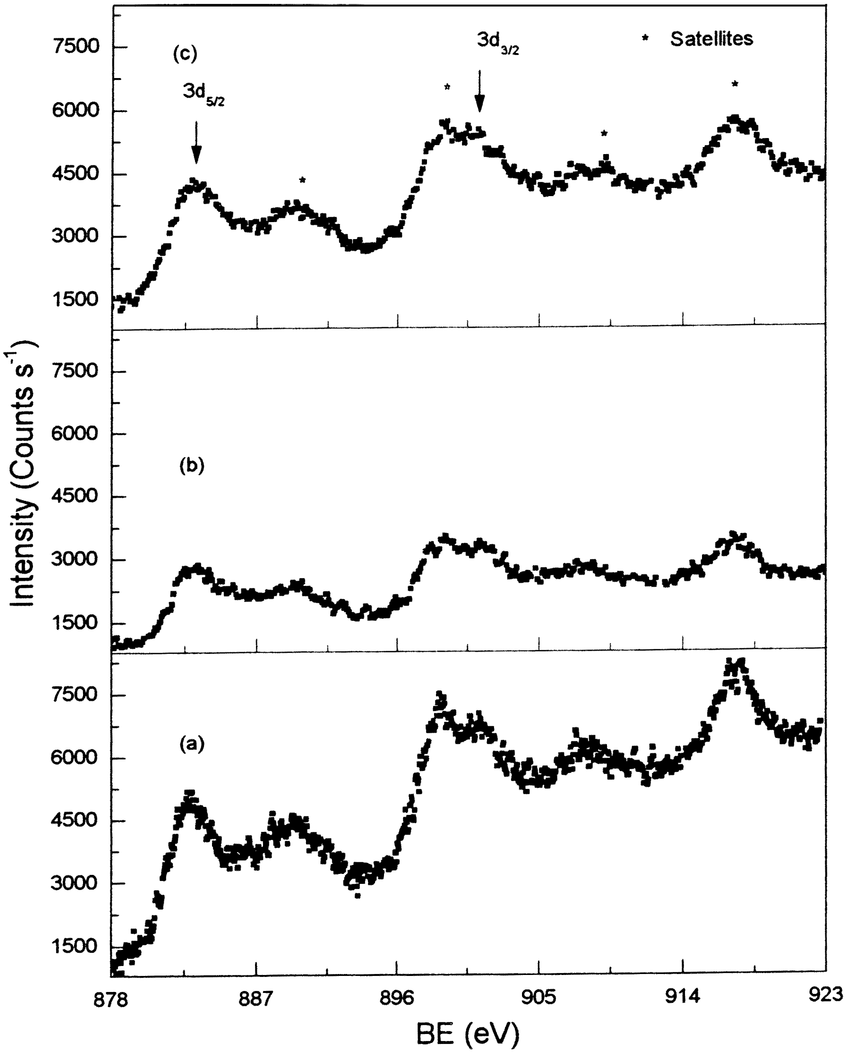

Figure 5. Ce 3d region of (a) as-synthesized, (b) spent, and (c) oxidized catalysts.

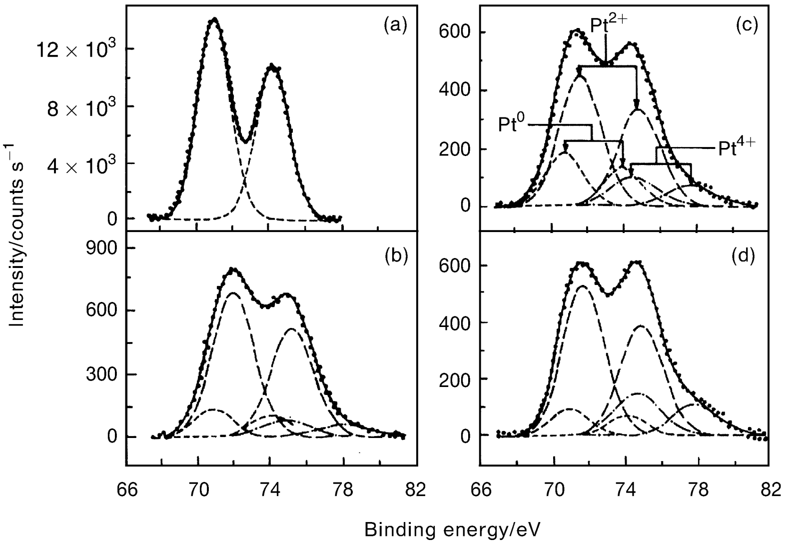

Figure 6. Pt 4f region of (a) Pt metal, (b) as-synthesized, (c) spent, and (d) oxidized catalysts.

spectrum of Pt nano-particles synthesized by the polyol method is also given for comparison. A comparison of the Pt 4f spectra of polyol-prepared Pt metal in figure 6(a) and that of $Ce_{1-x}Pt_xO_{2-\delta}$ in figure 6(b) shows that there are multiple oxidation states of Pt in Pt/CeO_2 catalyst. A similar observation was made by Daniel [25] for $Ce_{1-x}Pt_xO_{2-\delta}$ prepared by the impregnation method. The peaks were resolved into three sets of Pt $4f_{7/2,5/2}$ spin–orbit doublets. The doublets at 71.0, at 74.2, 71.9, at 75.1, 74.2, and at 77.4 eV are attributed to Pt^0, Pt^{2+} and Pt^{4+}, respectively. The relative intensities of Pt^0, Pt^{2+} and Pt^{4+} were 14 : 77 : 9 in the as-prepared $Ce_{1-x}Pt_xO_{2-\delta}$ sample. The Pt 4f spectrum of the spent catalyst showed more Pt^0 and the relative intensities of Pt^0, Pt^{2+} and Pt^{4+} were 23 : 62 : 15. However, on oxidation of the spent catalyst, an increase in the 2+ and 4+ states occurred at the cost of Pt^0. The relative intensities of Pt^0 in the as-synthesized and oxidized catalyst were of similar magnitude. Under no conditions did the Pt 4f structure correspond completely to Pt metal with Pt $4f_{7/2,5/2}$ at 71.0 and 74.2 eV, respectively, as seen in pure polyol-prepared Pt metal. From the XPS results, it can be concluded that Pt is present mostly in +2 and +4 states and there is an increase in the Pt^0 state in the spent catalyst from 14 to 23%.

Although the catalyst is reduced at 100 °C in flowing H_2 + benzene reaction conditions for 240 min, the Pt 4f spectrum in the spent catalyst is not similar to that of Pt metal. Higher binding energy components are still present in the spent catalyst. As-synthesized and re-oxidized catalyst can be represented as $Ce_{1-x}Pt_xO_{2-\delta}$ and the spent catalyst as $Ce_{1-x}Pt_xO_{2-\delta-y}$. This implies that oxygen around Pt is removed, reducing Pt^{2+} and Pt^{4+} to Pt^0, only partially during the catalytic reaction. It may be possible that the spent catalyst represented by $Ce_{1-x}Pt_xO_{2-\delta-y}$ may adsorb O_2 at room temperature since it is exposed to the atmosphere before mounting the sample on the XPS probe. *In situ* hydrogen reduction and oxidation of $Ce_{1-x}Pt_xO_{2-\delta}$ were also studied by XPS. The *in situ* reduced sample showed more Pt^0 along with Pt^{2+} and Pt^{4+}. Oxidized Pt in CeO_2 could not be completely reduced to the Pt^0 state even in *in situ* H_2 experiments. On oxidation at 200 °C, partially reduced Pt ionic species in the spent catalyst ($Ce_{1-x}Pt_xO_{2-\delta-y}$) is restored to oxidized Pt as in the as-prepared catalyst ($Ce_{1-x}Pt_xO_{2-\delta}$). Restoring the catalytic activity to 42.6% over the oxidized sample corroborates the XPS and XRD investigations. Hydrogen uptake also demonstrated that it is the oxidized Pt in $Ce_{1-x}Pt_xO_{2-\delta}$ that is the active species for the uptake of hydrogen.

The structural studies in addition to the hydrogen uptake experiment suggest that the rate of dissociation of H_2 at 100 °C could be high over $Ce_{1-x}Pt_xO_{2-\delta}$. Even at −25 °C, more than 2.5 mol of H_2 per Pt ion are available, mostly in dissociated form, which can readily react with O_2 at room temperature. Therefore, the availability of a higher number of dissociative hydrogen atoms per Pt ion is responsible for the higher rate of benzene hydrogenation over this catalyst. At 100 °C, slow reduction of Pt ions due to the removal of lattice oxygen forming water seems to reduce the hydrogen adsorption/dissociation propensity.

4. Conclusions

The activities for benzene hydrogenation over $Ce_{1-x}Pt_xO_{2-\delta}$ ($x = 0.01, 0.02$) catalysts synthesized by the solution combustion method were investigated at various temperatures (80–200 °C) and atmospheric pressure of hydrogen. A 42% conversion of benzene to cyclohexane with 100% selectivity was observed at 100 °C with $Ce_{1-x}Pt_xO_{2-\delta}$ ($x = 0.02$) catalyst. The turnover frequency of this catalyst was over an order of magnitude higher than those of other Pt based catalysts. Catalyst deactivation occurring due to reduction of $Ce_{1-x}Pt_xO_{2-\delta}$ to $Ce_{1-x}Pt_xO_{2-\delta-y}$ and was activated by oxidation in O_2. The deactivation studies and structural studies suggest that it is the oxidized Pt in $Ce_{1-x}Pt_xO_{2-\delta}$ that is primarily responsible for the catalytic hydrogenation of benzene.

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