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Probe molecule acid–base characterization of a novel Pt/Al_2O_3 hydrodechlorination catalyst

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Platinum particles (<1.5 nm) have been shown to behave as bases in their interaction with γ-alumina. FTIR spectra of adsorbed pyridine probe molecules showed that the acid strength of the γ-alumina was decreased by the presence of (<1.5 nm) Pt particles. Ammonium chloride treatment converts the primary Pt clusters to $H_xPt_yCl_z$ intermediates that de-anchor from the support. Consequently, agglomeration to ~8 nm Pt particles was observed following treatment in hydrogen at a relatively mild temperature. For the treated catalyst the IR data of absorbed pyridine show a $3\,cm^{-1}$ increase relative to the original Pt/γ-Al_2O_3 catalyst, indicating a strengthening of the acidity. Changes in the Pt particle size were confirmed by FTIR spectroscopy of CO absorbed onto the Pt particles before and after treatment. Consecutive CO and pyridine probe adsorption demonstrated the electronic interplay between the Pt particles and the support. Pyridine adsorption onto the γ-alumina support of a Pt/Al_2O_3 catalyst pre-dosed with CO produces a nearly $40\,cm^{-1}$ lowering of the CO peak position, indicative of CO bond weakening. In the case of CO adsorbed onto a catalyst pre-dosed with pyridine, a shift in the pyridine IR spectrum was only observed from the original highly dispersed catalyst.

KEY WORDS: platinum; hydrodechlorination; clusters; particle size; metal dispersion; alumina; acid; base; pyridine; CO; adsorption; catalyst; chloride; FTIR.

1. Introduction

The acidic nature of solid oxides has been found to have a profound effect on catalytic properties. In the case of cracking or isomerization catalysts, the acid strength is crucial. For oxide supports, the surface acidity can often be an important factor in tailoring catalytic performance. Characterization of support acid site strength has been accomplished by surface spectroscopic [1,2], calorimetric [3] and probe gas adsorption methods [4]. In this report we focus on the use of pyridine and CO probe molecules combined with Fourier transform infrared (FTIR) spectroscopy. Pyridine is used to measure the acid site strength of alumina whereas CO adsorption provides information on the structural and electronic form of the supported Pt particles. An excellent summary of the use of the probe gas approach coupled with FTIR can be found in ref. [4].

Carbon monoxide chemisorption onto noble metals occurs as a result of electronic interactions between the CO and the metal. The exact frequency of the CO stretching mode in the infrared (IR) yields information concerning the electronic state of the noble metal and the metal dispersion on the support. Charge donated into the CO populates the π^* orbital, resulting in a weakening of the CO bond and a consequent lowering of the IR frequency. In the case of an electron-deficient metal particle, electron withdrawal from the CO results in an increase in the observed carbonyl mode frequency. In the present case of Pt/Al_2O_3, CO strongly adsorbs only to the supported Pt at room temperature. The acid–base interaction of CO with alumina is too weak to observe at room temperature and is typically carried out at cryogenic temperatures [5].

Pyridine is a weak base often employed as a probe molecule for the relative determination of Lewis acidity. The strength of the Lewis acid sites is reflected in the position of the observed IR modes of the adsorbed pyridine molecule. For pyridine, the mode of interest is the 8a aromatic mode appearing at $1585\,cm^{-1}$ in the liquid state (4,5). The position of the mode can indicate the relative strength of the acid site and the local geometry of the acid site (coordination geometry of the Lewis acid site), as well as the presence of Brønsted acidity, through the formation of pyridinium ion.

In earlier reports, a robust Pt/Al_2O_3 hydrodechlorination catalyst was demonstrated to have long life (>2000 h), high conversion (80%) and high selectivity (80%) for hydrodechlorination (HDC) of CCl_4 to $CHCl_3$. The novel nature of the HDC catalyst has been ascribed to the morphological form of the Pt particles on the surface of the alumina support in response to treatment with NH_4Cl. As previously demonstrated [6,7], the particle size of the active Pt phase is altered from <1.5 nm on the rapidly deactivated commercial catalyst to 5–8 nm on the treated catalyst. The NH_4Cl treatment results in the formation of acidic $H_xPt_yCl_z$

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mobile intermediates which de-anchor from the alumina support and agglomerate upon elevated temperature in a reductive environment. Chloride has been found to be crucial with regard to the formation of the novel HDC Pt/Al_2O_3 catalyst.

X-ray photoelectron spectroscopy (XPS) analysis of the treated Pt/Al_2O_3 surface detected the presence of residual chloride following NH_4Cl treatment and subsequent hydrogen reduction at 350 °C. The effects of chloride ion on alumina, or alumina-supported catalysts, have been well documented [3,8,9]. Typically an enhancement in the acidic strength of the alumina is observed. Mechanistically the chloride ion increases acid strength by depleting the alumina surface electron density, thereby making the coordinately unsaturated Lewis sites stronger acids. Brønsted acidity is also seen to increase as remaining surface hydroxyl O–H bonds are weakened due to chloride inductive effects.

In the current work we are specifically interested in the acid–base chemistry responsible for the modification mechanism of Pt particles supported on alumina. Platinum is found to exhibit basic character which, as highly dispersed particles, strongly associates with the acid sites of the support. Platinum de-anchoring from the support surface is accomplished by formation of $H_xPt_yCl_z$ mobile intermediates that agglomerate to form the stable catalyst.

2. Experimental

2.1. Catalyst

A single batch of Pt/γ-Al_2O_3 pellet (3.2 mm $(\frac{1}{8}'')$) catalyst with 0.3 wt% Pt loading was obtained from Johnson Matthey (JM-73). Platinum is predominantly distributed at the exterior of the pellets as a thin dark "eggshell" layer. The Pt is highly dispersed on this catalyst with Pt particle sizes of <1.5 nm. Such small particles are known to display unique electronic behavior due to the incomplete population of the metallic band structure. In this report the as-delivered catalyst without NH_4Cl pretreatment is referred to as the "untreated catalyst" or as-received catalyst. All catalysts used in the present study were from the same batch. The reference c-alumina used was also from Johnson Matthey in the form of 3.2 mm $(\frac{1}{8}'')$ pellets. Further discussion in the manuscript will refer to the γ-alumina as alumina.

2.2. Treatment

The as-received commercial catalyst was soaked in a saturated solution of NH_4Cl at ambient temperature for 30 min. During the treatment of the catalyst a distinctive odor of ammonia was noted. Wet litmus paper held above the solution during catalyst treatment rapidly turned blue, confirming the emission of ammonia. The solution was drained and the catalyst was subsequently dried at 100 °C overnight in air. Identical treatment was performed with the alumina to create a chlorided alumina reference sample for comparison of pyridine adsorption behavior relative to the Pt on alumina catalysts.

2.3. In-situ FTIR

FTIR data were collected at room temperature with a Nicolet Magna 760 spectrometer. Spectra were collected at a resolution of 4 cm^{-1} by co-adding 100 scans over the 650–4000 cm^{-1} range. Wavenumber repeatability of this instrument is better than $\pm 0.02\,cm^{-1}$. *In-situ* reduction and probe molecule dosing experiments were performed within a Spectra Tech Collector® diffuse reflectance attachment, equipped with a high-temperature cell. Atmospheric control was maintained in this cell by a ZnSe windowed cover over the sample cup. The heater was incorporated into the ceramic sample cup, where a thermocouple was immersed into the sample for temperature monitoring.

Powdered samples of the catalysts were obtained by scraping the "eggshell" Pt layer from the pellet. The catalyst surface scrapings and the reference alumina pellets were ground to a fine powder with an agate mortar and pestle. The catalyst powder was used neat and placed into the sample cup/heater assembly at the focal point of the diffuse reflectance accessory. Reduction of the catalyst was performed under pure H_2 (~5–10 cm^3/min) at 350 °C for 2 h. Argon gas was used to purge the cell prior to and after reduction. A gas-supply manifold permitting uninterrupted switching between H_2, CO and Ar was attached to the gas inlet of the reaction cell. Pyridine dosings were made at room temperature to saturation during Ar purge by injection through a septum installed on the gas-supply line. Excess pyridine was removed by continuous Ar purge.

3. Results and discussion

3.1. Pyridine adsorption onto the Lewis acid sites of alumina

Pyridine adsorption onto alumina clearly differentiates octahedral ([Py-L]o, 1594 cm^{-1}) and tetrahedral ([Py-L]t, 1615 cm^{-1}) Lewis acid sites, figure 1 [5,10]. The peak position data for pyridine adsorbed onto alumina, chlorided alumina, JM-73 and treated JM-73 samples are summarized in table 1. The presence of the highly dispersed Pt particles on the alumina (JM-73) causes a weakening of the acid site strength as indicated by the lowering of the pyridine IR peak positions (1613 cm^{-1}, 1592 cm^{-1}). Since JM-73 contains residual Cl^- from the chlorinated Pt precursor [6], it would be expected that the acid strength be comparable with

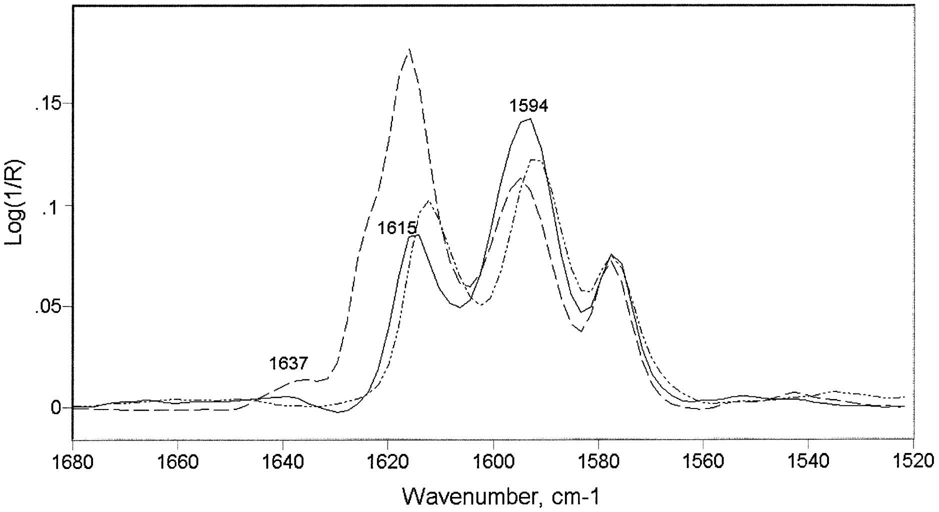

Figure 1. Pyridine adsorbed onto (a) alumina (——), (b) JM-73 (–··–), (c) treated JM-73 (– – –).

chlorinated alumina (1617 cm^{-1}, 1596 cm^{-1}) rather than weaker. From these data it is reasonable to ascribe Lewis basicity (electron donation) to the highly dispersed Pt particles of JM-73.

Treatment of the JM-73 Pt/Al$_2$O$_3$ catalyst with NH$_4$Cl resulted in an increase of the support acid strength as indicated by increases of the pyridine IR absorption frequencies. The residual chloride present on the alumina surface following NH$_4$Cl treatment removes charge and thereby increases the surface acidity similar to that of the chlorided alumina [3,8,9]. Entirely new acid sites are observed at 1623 and 1637 cm^{-1}. The 1623 cm^{-1} peak is due to strong Lewis acid sites, whereas the 1637 cm^{-1} peak is due to Brønsted acidity. Sufficiently strong Brønsted acidity leads to the formation of pyridinium ion, giving rise to the 1637 cm^{-1} peak. The Brønsted acidity has been claimed to arise from the formation of inductively activated surface Al–O–H groups sufficiently acidic to protonate the weak base pyridine [8,11]. Increased support acidity also results from a decrease in Pt particle electron donation to the support. Agglomerated Pt particles of ~8.0 nm are fully metallic in nature [7]. Electron density is therefore more restricted in the Pt band structure, minimizing the neutralizing effect on the support acidity.

Table 1

FTIR peak positions for pyridine adsorbed on Al$_2$O$_3$-supported catalysts

Sample	Peak position (cm^{-1})			
	(Py-H+)	(Py-L)t	(Py-L)o,t	(Py-L)o
Alumina, Al$_2$O$_3$			1615	1594
Chlorided alumina	1637	1623 [a]	1617	1596
JM-73			1613	1592
Treated	1637	1623	1616	1595

[a] Peak difficult to resolve due to the intensity of the 1637 cm^{-1} Brønsted site peak.

3.2. CO adsorption on Pt of the catalysts

Carbon monoxide adsorption onto the Pt of the JM-73 and treated catalyst have been discussed in an earlier paper [7]. In that report the JM-73 demonstrated IR features from adsorbed CO at 2112, 2060 and 1825 cm^{-1} due to positively charged platinum particles, low coordination Pt, and bridging sites respectively. CO on the treated catalyst showed a much lower amount of adsorption, loss of positively charged platinum particles, loss of bridging sites, and an upward (blue) shift of the major CO peak to 2078 and 2067 cm^{-1} due to high coordination surface Pt adsorption sites.

3.3. Sequential adsorption of pyridine and CO

CO adsorption is limited to the surface of the Pt particles at room temperature, whereas pyridine probes the acidic sites on the surface of the alumina support. Sequential adsorption of these probe molecules onto the catalysts in alternating order is instructive with respect to their effects on the metal particles and on the support.

When pyridine is adsorbed onto the alumina support of catalysts pre-dosed with CO, the CO stretching peak position was found to decrease approximately 40 cm^{-1}. The shift of CO is attributed to increased electron density from the Lewis base adsorbed onto the support. Both the highly dispersed Pt of JM-73 and the large particles of the treated catalyst are seen to respond similarly due to the overwhelming amount of pyridine on the alumina support surface relative to the Pt concentration (figure 2). In the case of the treated catalyst there is also a significant decrease in the amount of CO remaining on the Pt particles following pyridine adsorption.

Carbon monoxide adsorption onto the Pt of the treated catalyst, pre-dosed with pyridine, shows no

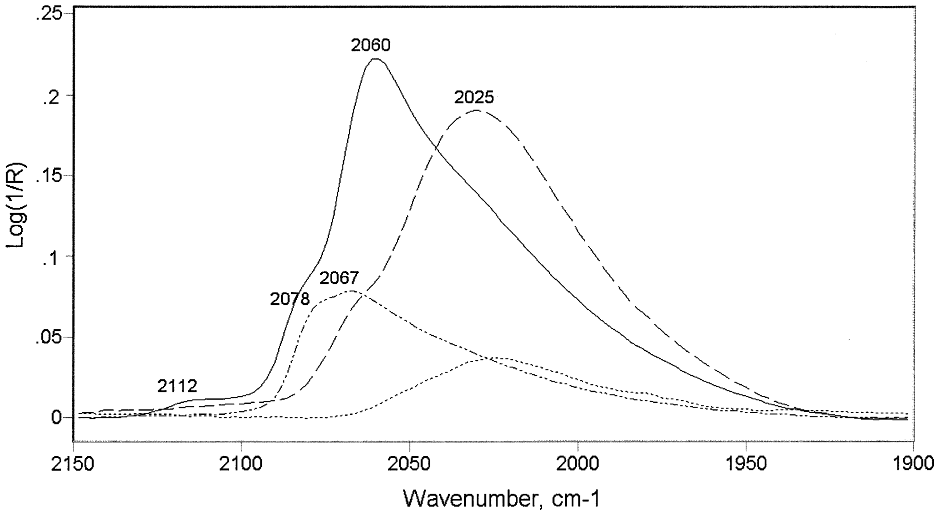

Figure 2. Carbon monoxide adsorbed onto (a) JM-73 (——), (b) JM-73 pyridine dosed (– – –), (c) treated JM-73 (–···–), (d) treated JM-73 pyridine dosed (····).

change in the pyridine spectrum (figure 3). This observation indicates that the interaction of CO with Pt has a negligible effect on the electronic environment of pyridine adsorbed on the alumina.

Carbon monoxide adsorption onto the Pt of the JM-73 catalyst pre-dosed with pyridine shows a reproducible 1.5 cm^{-1} shift of the pyridine spectrum (figure 4). The electron contribution from Pt into the CO upon adsorption is sufficient to increase the apparent acidity of the support, as indicated by the upward shift of the pyridine IR modes. This effect is only observed on the highly dispersed Pt catalyst where there was high CO adsorption. The large particles of the treated catalyst are relatively few and have a lower CO uptake per Pt atom and therefore a reduced effect on the overall charge balance of the system.

4. Discussion

As discussed in the earlier description of the untreated catalyst, the largest observed Pt particles are 1.5 nm [6]. The ability of such Pt particles to decrease the acid strength of the Lewis acid sites on alumina (as indicated by the pyridine adsorption experiment) clearly indicates the basicity of small Pt clusters. The decrease in acid strength of the support is a result of electron donation from the Pt particles into the support. The indication

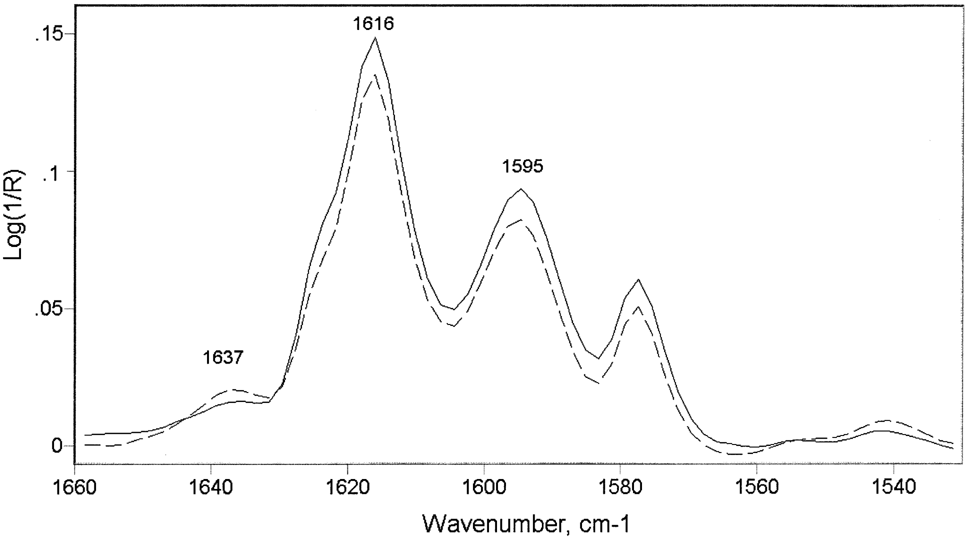

Figure 3. Pyridine adsorbed onto treated JM-73 (——), CO dosed (– – –).

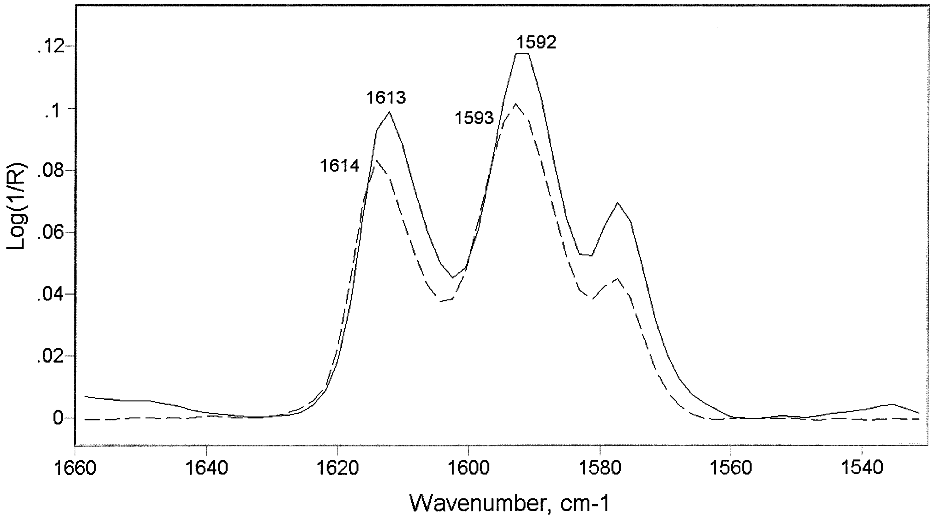

Figure 4. Pyridine adsorbed onto JM-73 (——), CO dosed (- - -).

of positively charged platinum (Pt$^{\delta+}$) by photoelectron spectroscopy and CO adsorption [6,7] supports the pyridine adsorption data presented here, showing the electron-donating ability of the highly dispersed Pt particles. Evolution of ammonia during the treatment of Pt/Al$_2$O$_3$ is a chemical illustration of the basic nature of the highly dispersed Pt particles. The Pt particles displace the ammonia in the formation of the H$_x$Pt$_y$Cl$_z$ cluster intermediate. Recent *ab-initio* thermodynamic calculations [12] show the favorable formation of H$_x$Pt$_y$Cl$_z$ cluster intermediates through the interaction of ammonium chloride and low n (Pt$_n$) atom clusters.

In light of the acid–base point of view, the formation of a chloroplatinic acid-like intermediate H$_x$Pt$_y$Cl$_z$ [7] explains the de-anchoring of Pt particles. This intermediate, no longer tightly bound by acid–base interaction to the acid sites of the support, is free to migrate and agglomerate. Agglomeration is promoted by blocking potential readsorption sites of the growing Pt particles by chloride ion on the alumina surface acid sites. Chloride is critical to the catalyst modification process, as indicated by the ability of LiCl to create active agglomerated Pt/Al$_2$O$_3$ HDC catalysts, whereas NH$_4$OH or NH$_4$NO$_3$ had little beneficial effect.

Treatment of the catalyst with NH$_4$Cl causes alteration of the support acid site strength and concentration. Surface elemental analysis by XPS demonstrated the presence of residual chloride (0.5 at%) following 350 °C, H$_2$ activation of the treated catalyst (6). Bulk chloride concentrations as low as 0.41 wt% (0.22 at%) have been shown to increase the measured acid strength of Al$_2$O$_3$ [3]. Therefore, the increased Lewis acid strength indicated in the IR spectrum of adsorbed pyridine in the presence of residual chloride is consistent with previous observations.

Sequential dosing of CO and pyridine onto the Pt/Al$_2$O$_3$ catalysts demonstrated the effects of acid–base interactions on the local electronic nature of a catalyst particle. These results show that modification of the supported noble metal or support can have effects on the adsorption and electronic properties of the other.

5. Conclusions

Highly dispersed platinum particles have been shown to behave as bases in their interaction with acidic alumina. Probe molecule examination illustrated this point by a decrease in alumina acid strength in response to the presence of <1.5 nm Pt particles. Conversion of the basic Pt clusters to mobile, H$_x$Pt$_y$Cl$_z$ intermediates causes the de-anchoring (loss of acid–base interaction) that leads to Pt particle growth upon reduction. Consecutive CO and pyridine probe adsorption experiments demonstrate the electronic effects on Pt in its acid–base interactions with the support.

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