Effect of fluorination of alumina support on activity of platinum catalysts for complete oxidation of benzene

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Platinum supported on fluorinated alumina is more active for the total oxidation of benzene than is the catalyst with the same Pt loading supported on hydrophilic unfluorinated alumina. The Pt–F/alumina catalyst contains well-dispersed small Pt particles, in contrast to Pt/alumina. The high dispersion is a consequence of a strong metal–support interaction.

Keywords: fluorination, alumina, platinum catalysts, oxidation, oxidation of benzene

1. Introduction

Industrial waste gases from chemical or petroleum plants contain volatile organic compounds (VOC) at low concentration and high humidity. Several VOCs are toxic and carcinogenic. One of the techniques available for destructive removal of such compounds is catalytic oxidation. However, the commercial catalysts are mainly noble metals supported on alumina, and this support is highly hydrophilic. The humidity present in the industrial waste gas streams causes rapid deactivation and shortens catalyst lifetime to an unacceptable level. Therefore, for a conventional catalyst to be both effective for the removal of VOC and long-lived, water must be continuously removed from the catalyst surface. Consequently, a process using a conventional catalyst is operated at high temperature. However, fluorination of silica and alumina is known to render the surfaces of the materials hydrophobic [1]. In this paper we will describe the use of such a modified catalyst for a low-temperature process which we have developed. We will show that Pt supported on fluorinated alumina is more hydrophobic and has higher catalytic activity than the unfluorinated system.

It is known that several groups of volatile organic compounds can be destroyed using air and hydrophobic catalyst systems [2,3]. Aldehydes, alcohols and benzene can be destroyed up to 100% by catalytic oxidation at or below 403 K, even in the presence of humidity. Thus the hydrophobic catalysts are effective at temperatures below 473 K, which is lower than those needed for the current commercial catalysts. Operation of this new low temperature process offers strong potential for significant energy and cost saving for commercial applications. The large improvements in reactivity of the hydrophobic catalysts compared to the hydrophilic counterparts have been attributed to changes to both the support and the active noble metal catalyst. The objectives of the present investigation of wet-proofing the support are to determine the effects on both the support surface properties and the electronic state of the supported platinum catalyst, and to determine the effect of the changes on the activation and total oxidation of benzene. Catalysts have been prepared using both untreated alumina (hydrophilic) and fluoridated (wet-proofed) alumina as supports. In each case the active catalytic component was 0.1% Pt. The oxidation of benzene to CO_2 and water has been used as the probe reaction to examine and compare the catalytic activity of the two catalysts.

The methodology which we have selected to examine and compare the natures of the catalyst surfaces is infrared spectroscopy (IR) using CO as a probe molecule, a technique which has been shown to provide valuable information on the surface features [4–6]. Vibrational spectra of CO adsorbed on dispersed metal catalysts give valuable information on: (i) dispersion and morphology of the particles; (ii) the oxidation state of the noble metal; (iii) the presence of co-adsorbed species; (iv) interactions between adsorbate molecules, and (v) metal–support interactions. Thus, the CO molecule serves as a sensitive probe for the changes in the electronic state of the metal, the state of the metal surface, and the distribution of the metal particles arising from changes in the nature of the support for sample treatment. Further, the interaction of CO with available Lewis acid sites of the surface of the support provides information on the concentration, nature and properties of such sites.

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2. Experimental

2.1. Catalyst preparation

(a) A 0.1% Pt/alumina catalyst was prepared by impregnating alumina spheres (La Roche, surface area 320 m^2/g) with an aqueous solution containing a desired amount of ammonia platinum nitrate (Johnson Matthey). The wetted alumina was then dried by evaporation at 60 to 80°C for 6 h and further dried at 105°C in air for 16 h, followed by reduction in H$_2$ and calcination in air at 350°C.

(b) A hydrophobic catalyst was prepared by first treating the alumina support with an aqueous solution of HF. After drying, the fluorine-containing alumina was calcined at 500°C for 4 h. The fluorinated alumina was impregnated with a solution of the same platinum salt, and the Pt–F/alumina catalyst was then reduced and calcined following procedures similar to those for the Pt/alumina catalyst.

2.2. FTIR measurements

A Nicolet 740 instrument was used to obtain IR spectra. A Kiselev-type IR cell was connected to a vacuum line ($P = 10^{-7}$ kPa), which allowed in situ treatment and monitoring of a sample during thermal treatment and adsorption–desorption experiments.

Typically, a sample was sequentially heated to 773 K under vacuum for 4–12 h, cooled to room temperature, and then exposed to 0.1–100 Torr CO. The spectra for the adsorped CO were determined, after subtraction of the background spectra for the catalyst pellet and any residual CO in the gas phase.

2.3. Catalytic activity testing

Evaluation of catalytic activity was carried out in a fixed-bed U-shaped reactor (i.d. 15 mm). The reactor was packed with 2.5 g of a catalyst, placed into an oven, and operated at atmospheric pressure. The reaction temperature was monitored using two thermocouples mounted at the bottom and the top of the catalyst bed. Benzene vapor was introduced by passing sampling air through a saturator which was maintained at ambient temperature. The flow rates of the air streams were controlled by mass flow controllers. To analyze the feed gas on the effluent gas the appropriate stream was directed to an on-line gas chromatograph (Hewlett Packard model 5890 series II) equipped with both flame ionization (FID) and TCD detectors. A 6 ft×1/8 in stainless steel column packed with Porapak Q was employed for the separation and analysis of each stream. The quantitative determination of VOC concentration was performed by calibration using a gas mixture of known composition.

3. Results and discussion

3.1. Catalytic activity

Both the Pt/alumina and Pt–F/alumina catalysts are active for the oxidation of benzene to carbon dioxide and water. The activities of the catalysts have been determined over the temperature range 130–300°C, at a standard space velocity of 20,000 h^{-1} (figure 1). The activity of the catalyst on the fluorinated support was significantly greater than that of the catalyst on the unfluorinated support, especially at lower temperatures.

For both catalysts the effect of humidifying the feed was to reduce the benzene conversion (figure 1). However, the effect on the Pt–F/alumina catalyst, although significant, was less than that for the Pt/alumina catalyst, at all temperatures. At the lower temperatures the effect is most dramatic: at 175°C the conversion using the Pt–F/alumina catalyst drops from 83.5% for dry feed to 62.7% for humidified feed. In contrast, the conversion using the Pt/alumina catalyst drops from 70.5 to 26.1%. At temperatures above 250°C the effect is less dramatic because the conversion is higher in each case, but Pt/alumina again shows a greater loss of activity than does Pt–F/alumina.

It is noteworthy that even in the presence of high humidity the activity of the Pt–F/alumina catalyst is similar to or exceeds the best attainable activity of the Pt/alumina catalyst. It had been shown previously that Pt/FCC (FCC is hydrophobic fluorinated carbon) was more effective than Pt/Al$_2$O$_3$, even under humid conditions [3]. The results herein show that the improvement in activity is directly attributable to the hydrophobic

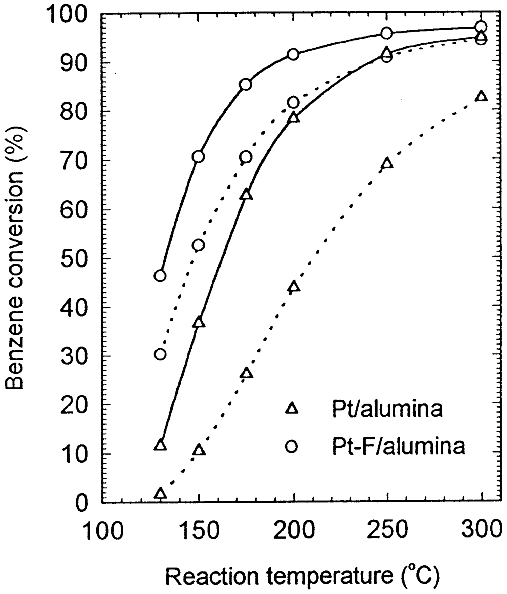

Figure 1. Benzene conversion as a function of reaction temperature, in dry feed (—) and humid feed (- - -), on 0.1% Pt/alumina and 0.1% Pt–5.0% F/alumina catalysts.

character of the catalyst support resulting from fluorination.

3.2. Spectroscopic investigation

Hydroxyl groups. The hydroxyl groups present on the surface of alumina give rise to a series of IR absorption bands, the position of which is characteristic of the different sites and acidities for each type of hydroxyl present [7]. Catalysts comprising noble metals supported on alumina usually display similar IR bands [7,8].

When alumina is treated with HF, the intensity of hydroxyl IR bands diminishes to much lower values, showing that virtually all surface hydroxyls can be replaced by fluoride [9]. Samples of Pt–F/alumina exhibit essentially no hydroxyl absorption bands in the IR spectrum (figure 2), in contrast to the spectrum of Pt/alumina. Thus there were negligibly few hydroxyl groups remaining on the surface of Pt–F/alumina.

Carbon monoxide as a probe molecule. Samples of Pt–F/alumina were exposed to CO. The IR spectra of exposed samples exhibited two bands assigned to coordinated CO, one in the range 2216–2230 cm^{-1} and the second in the range 2086–2091 cm^{-1}. The precise positions and relative intensities of these two bands were dependent upon the surface coverage of CO (figures 3 and 4). The peak at 2216–2230 cm^{-1} is attributed to CO coordinated at coordinately unsaturated (cus) Al^{3+} sites. The values are within the range expected for coordination at highly active tetrahedral Al^{3+} sites, rather than the less active octahedral cus Al^{3+} sites [3,10]. In contrast, no significant absorption band was detected in the range 2200–2230 cm^{-1} for Pt/alumina exposed to CO (figure 5). Therefore, there are relatively few available cus Al^{3+} sites on unfluoridated alumina upon which platinum has been deposited [11]. The treatment of the Pt/Al$_2$O$_3$ catalyst with HF not only renders the surface hydrophobic, but also increases the number and Lewis acidity of surface cus Al^{3+} sites. These observations are consistent with the effects of replacement of surface hydroxyls with fluoride ions [12,13].

The band at 2086–2091 cm^{-1} arises from CO coordinated to Pt. Adsorption of CO on supported Pt particles containing several atoms usually gives rise to linear, bridged and multiply coordinated CO species. The CO ligands which are coordinated in a linear manner are characterized by IR bands close to 2050 cm^{-1}, the exact frequency of which depends upon the size of the Pt particles, surface coverage, and electronic properties of the Pt. The bands due to bridged CO are usually close to 1850 cm^{-1}, and CO ligands bonded to more than two Pt centers give rise to bands at lower frequencies. The IR spectrum of CO on well dispersed Pt characteristically exhibits only linear CO bands, while large crystallites coordinate CO in both linear and bridged mode. No bands associated with bridged or multi-bonded CO were detected in the IR spectra of Pt–F/alumina exposed to CO (figure 4). The only Pt–CO IR band detected was close to 2087 cm^{-1}, and in each spectrum the peak was intense and its contour was symmetrical. The occurrence of a single Pt–CO IR band in this region shows that all CO bonded to Pt was coordinated in a linear manner. The intensity of the band, and the absence of any IR band characteristic of bridged CO bonded to large Pt particles, showed that the Pt was highly dispersed on the surface of the alumina. The highly symmetrical shape of

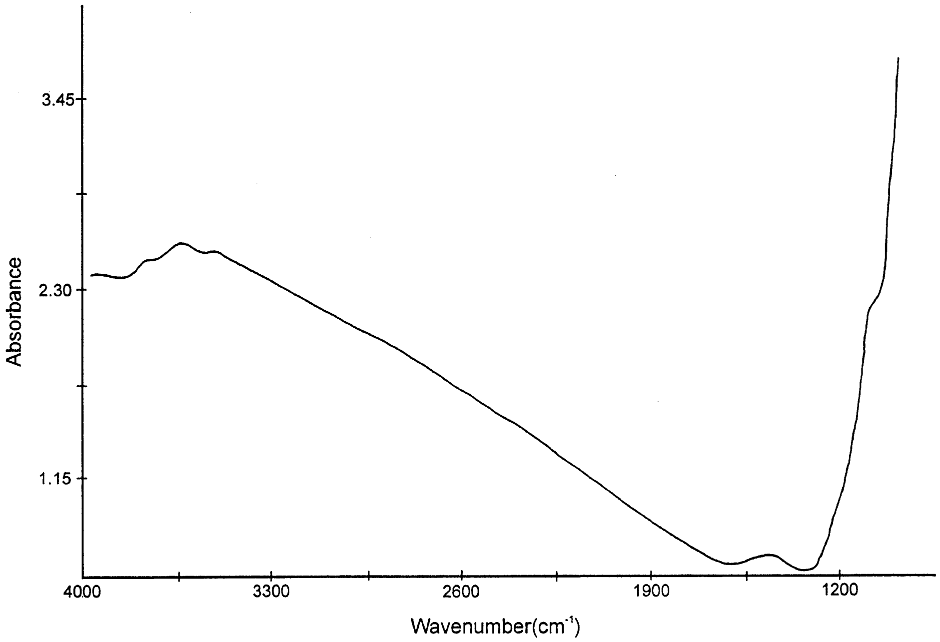

Figure 2. FTIR spectrum of Pt–F/alumina after treatment under vacuum at 773 K for 12 h.

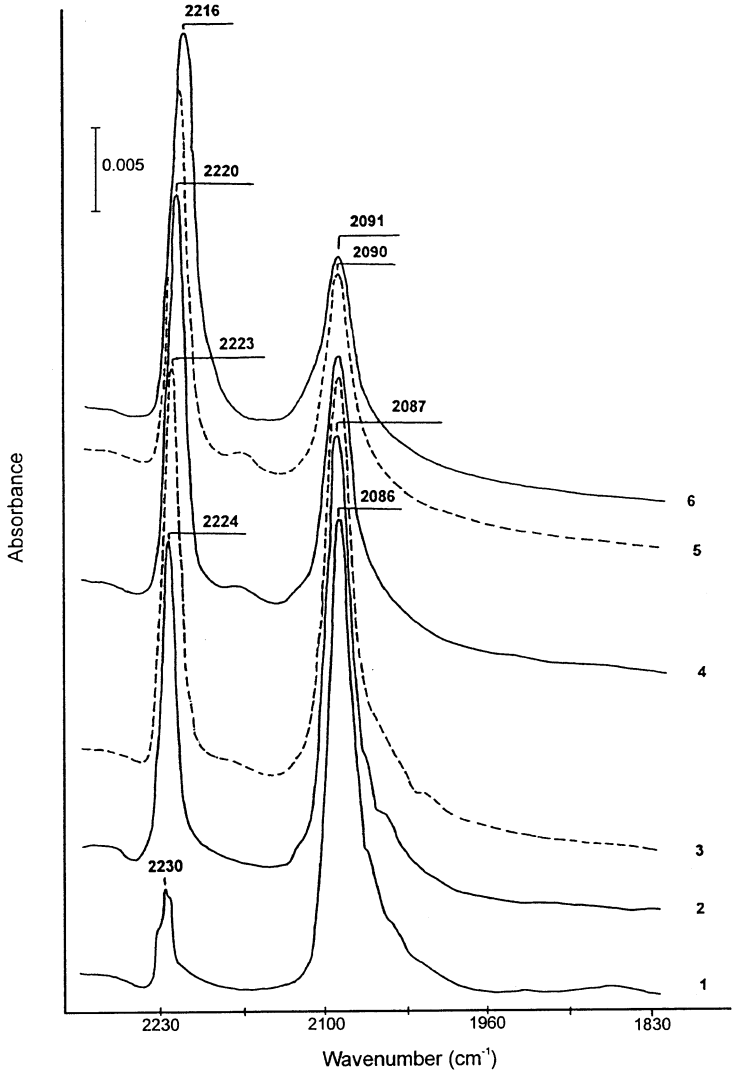

Figure 3. FTIR spectra of CO absorbed on Pt–F/alumina as a function of CO pressure: (1) 0.44 kPa; (2) 0.84 kPa; (3) 1.47 kPa; (4) 5.0 kPa; (5) 10.0 kPa; (6) 50.0 kPa.

the band showed that the dispersion on the surface was uniform [4,5]. The size of the Pt particles was below that which can be determined using X-ray microscopic techniques [14]. Further, there is intense interaction between fluorine and platinum which greatly reduces adsorption of hydrogen on platinum [3]. As a result, the use of hydrogen adsorption measurements does not give reliable data for the metal surface area on fluorinated supports.

Surprisingly, for Pt–F/alumina the position of νCO in linear carbonyls did not depend strongly on the degree of coverage of the metal surface by CO in the range 10^{-5} to 10^{-3} Pa, and very little up to 5.0 Pa (figures 2 and 3). The absorption band is shifted to 2090 cm^{-1} only when the pressure is increased to at least 50 kPa. This effect is consistent with the explanation that small clusters of Pt are stabilized on the strong electron acceptor sites of the support, and that the effect of these sites on the metal is stronger than the effect of the metal particle sizes. The same effects are usually observed for highly dispersed metals which are also under a strong influence by the support, for example in zeolites [4,11].

For CO adsorbed on large metal clusters the position of the absorption band for linear carbonyl is shifted by approximately 30 cm^{-1} from that of free CO, the precise value depending on the surface coverage. The relatively high position of the absorption M–CO band in the spectrum for supported metal particles is due entirely to the surface coverage effect. For such systems the linear Pt^0–CO complexes with low coverage exhibit one band at about 2050 cm^{-1}.

In contrast to these results, for CO adsorption sites on small clusters, or well-distributed metal, the complex which is formed exhibits νCO at 2087–2085 cm^{-1}. This assignment is confirmed by the observation that the absorption band at 2087 cm^{-1} is not shifted on (for example) vacuum treatment (figure 4), whereas with coarsely dispersed metals νCO decreases with decreas-

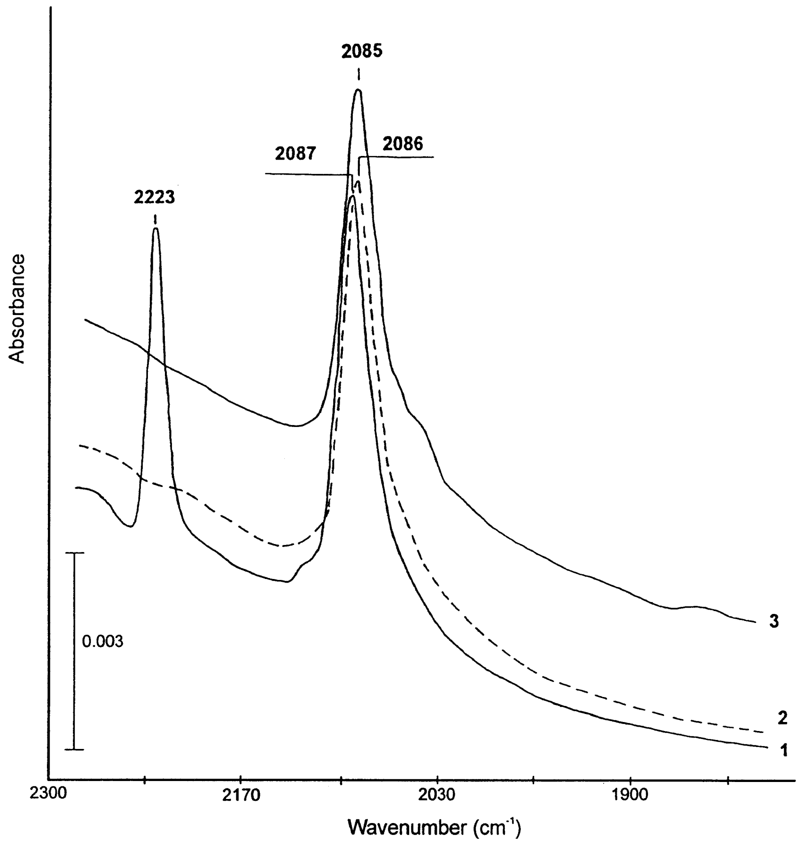

Figure 4. FTIR spectra of CO absorbed on Pt–F/alumina after desorption as a function of desorption pressure: (1) 1.1 kPa; (2) 10^{-2} kPa; (3) 10^{-5} kPa.

ing coverage. The effects of coverage on νCO are usually considered to be determined by the integral electronic properties of a metal. The absence of such effects in the IR spectra for the systems described herein therefore confirms the essentially local and uniform character of the interaction of CO with adsorption sites, which is possible only with very small metal clusters or atoms.

Thus the high value for νCO for Pt–F/alumina is characteristic of the structure for that material. Such high values are usually observed for CO on highly dispersed metal which strongly interacts with the support. Thus the particular electronic properties of the metal in Pt–F/alumina as demonstrated in the above IR data show that the metal particles are small and electron deficient because of the strong interaction with the Lewis acid centers of the fluorinated support.

It was difficult to obtain well-defined spectra for samples of Pt/alumina, as there was only weak IR transmission. The spectra (figure 5) were obtained using at least 1000 scans. The absorption bands which were detected at 2082, 1990, and 1954 cm^{-1} were each weak. Bands in each of these regions have been observed for CO adsorbed on Pt, but the intensities of the bands for CO on Pt/alumina were lower than in previous reports. Nevertheless, the positions of the bands observed are consistent with the presence of both linear and bridged CO, based on the arguments presented above. The high frequency found for νCO in the linear carbonyl region in this case, even at low coverage, is a consequence of the large size of the metal clusters. The low intensities of the adsorption bands for adsorbed CO show that on Pt/alumina there are not a large number of Pt sites at which CO can adsorb. Therefore, the metal is shown to have low dispersion in this sample, in contrast with Pt–F/alumina which has the same metal content. The two bands which are observed at 1990 and 1954 cm^{-1} in the spectrum of the Pt/alumina are assigned to bridging carbonyls, and are also characteristic for low dispersion of metal in the sample. As the coverage by CO changes, the adsorption band at ~2082 cm^{-1} is shifted to 2095 cm^{-1}. Therefore, there is no strong influence of the support on the electronic properties of the metal clusters, and the properties of the supported metal particles on Pt/alumina are dominated by the character of the metal more than for Pt–F/alumina.

Thus, our investigation has shown that, in the case of the catalysts prepared by depositing the metal on hydrophobic fluorinated alumina, the metal is distributed as small particles, and that these small metal clusters are strongly influenced by the support as a consequence of forming strong electron acceptor sites through the fluorination treatment. The spectra of samples exposed to CO show that the metal clusters in these materials are electron deficient.

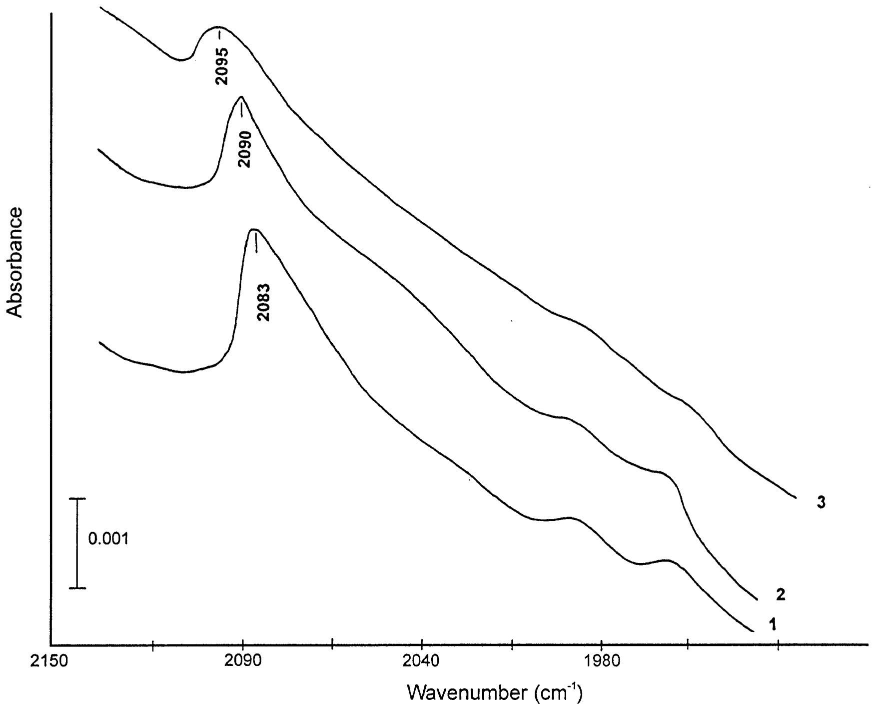

Figure 5. FTIR spectra of CO absorbed on Pt/alumina as a function of CO pressure: (1) 0.44 kPa; (2) 1.2 kPa; (3) 5.0 kPa.

3.3. *Correlation of catalyst activity with spectroscopic data*

The characteristics of the supported platinum catalysts evidenced from the spectroscopic data correlate with the activities of the catalysts for benzene oxidation (table 1). The table shows the influence of both temperature of reaction and wet-proofing on the activity of the catalysts. The hydrophobic catalyst (Pt–F/alumina) is more active than hydrophilic Pt/alumina at any given temperature, and can be used at lower temperatures than the hydrophilic catalyst.

The nature of the initial interaction of benzene (or other unsaturated hydrocarbons) with supported metal particles has been described [14,16]. Coordination of benzene to a metal center of a cluster occurs through donation of the benzene π-electrons to the coordinately unsaturated metal atom ("π-complex"). The donation of the benzene π-electrons is accompanied by a reduction in the C$\underline{---}$C bond order, and strength, when compared with uncoordinated benzene, as evidenced by a reduction in the frequency of the corresponding IR band from 1600 to 1390 cm^{-1} for benzene adsorbed on Pt/SiO_2 [16].

The influence of the fluorinated support makes the platinum catalytic sites more electron deficient when compared with standard catalysts. The electron deficiency at the metal sites in turn effects a greater degree of electron transfer from the benzene ring to the metal, thereby causing weakening of the C$\underline{---}$C and, consequently, C–H bonds also [4]. Thus the fluorinated catalysts are more effective than standard catalysts at activating benzene, and therefore are more active catalysts for oxidation of benzene.

Fluorination of alumina changes the nature of the platinum in three ways: the catalyst becomes hydrophobic, and hence is not deactivated by humidity; the platinum becomes more highly dispersed; and the electronic properties of the support affect the electronic structure of the metal sites, as shown by the characteristics of

Table 1
The data of catalytic measurements for different samples of the catalyst

Catalyst	Benzene conversion (%)					
	403 K	423 K	443 K	473 K	523 K	573 K
0.1% Pt/alumina	30.3	52.6	70.5	81.5	90.9	94.3
0.1% Pt–1% F/alumina	44.6	69.8	81.4	88.1	94.5	96.9
0.1% Pt–5% F/alumina	46.4	70.6	85.3	91.4	95.6	–
0.1% Pt–7% F/alumina	45.8	70.8	85.5	91.3	95.5	98.1

adsorbed CO. The first two effects are clearly beneficial to the catalytic activity of the platinum oxidation catalysts, but the impact of the third effect has not yet been elucidated.

4. Conclusions

The activity of a hydrophobic Pt–F/alumina catalyst for the oxidation of benzene is higher than that of a hydrophilic catalyst Pt/alumina with the same Pt loading. Further, the activity of the hydrophobic catalyst is affected less by humidity in the feed gases than is the activity of the hydrophilic catalyst.

Small, well-dispersed particles of Pt are present on the surface of Pt–F/alumina, in contrast to the larger particles of Pt on unfluorinated alumina. The high dispersion is a consequence of a strong interaction of the metal particles with strong electron-acceptor sites formed by fluorination of alumina.

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