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Infrared study of benzene hydrogenation on Pt/SiO_2 catalyst by co-adsorption of CO and benzene

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FT-IR spectra of the co-adsorption of benzene and CO have been performed to identify the preferred adsorption sites of hydrogen and benzene on a Pt/SiO_2 catalyst for hydrogenation of benzene. Results of CO adsorbed on atop sites on Pt/SiO_2 includes: an α peak at 2091 cm^{-1}, a β peak at 2080 cm^{-1} and a γ peak at 2067 cm^{-1} indicating three kinds of adsorption sites for dissociative hydrogen on Pt/SiO_2. The site of lowest CO stretching frequency offers stronger adsorbates–metal interaction for benzene and hydrogen. Hydrogen binding on the site of lowest CO stretching frequency before benzene adsorption significantly enhances the reaction rate of benzene hydrogenation.

KEY WORDS: benzene hydrogenation; CO adsorption; FTIR; Pt/SiO_2.

1. Introduction

Hydrogenation of benzene is readily catalyzed by Pt and is assumed to be a very important process in industry, however less attention has been given addressing the relationship between the adsorption sites of benzene and hydrogen on the Pt catalyst surface. Several papers have studied benzene adsorption geometry by co-adsorption of CO and benzene on single crystal Pt surfaces, indicating that the carbon ring of benzene was parallel to the surface and centered over bridge sites [1–3]. Thomas *et al.* have studied temperature programmed desorption of co-adsorption of H_2/C_6H_6 on Pt(110), suggesting that benzene could partially block hydrogen adsorption and that benzene hydrogenation only occurred when hydrogen was adsorbed on top of the benzene adlayer [4]. Moreover, benzene hydrogenation did not occur when benzene was dosed onto a hydrogen covered surface [4]. Nevertheless, these results of studies on well-characterized single crystal surfaces do not seem to entirely reflect the behavior during benzene hydrogenation on Pt catalysts, since many defect sites may exist on the surface of a catalyst system to influence benzene hydrogenation. The main goal of this paper is to understand the relationship between hydrogen and benzene on an actual Pt catalyst system. In the present study, we use CO as a probe molecule to determine preferred adsorption sites of hydrogen and benzene on Pt/SiO_2 catalysts because CO is an ideal probe molecule for vibrational spectroscopy and can usually provide important information about the surface sites of adsorbed species [5]. Experiments have been performed involving co-adsorption of H_2/CO/benzene to obtain information relevant to the surface sites available to H atoms during hydrogenation of benzene on Pt/SiO_2 catalysts.

2. Experimental

A 4.7 wt% Pt/SiO_2 catalyst was prepared by impregnating Cab–O–Sil M-5 SiO_2 with an aqueous solution of H_2PtCl_6. The catalyst was dried at 80 °C and calcined in flowing air at 400 °C for 2 h. Hydrogen (Sun-Fu Gas Co., 99.99% pure) and carbon monoxide (Sun-Fu Gas Co., 99.999% pure) were further purified by being passed through a deoxo purifier. Benzene (Jassen, 99 + % pure) has been degassed with multiple freeze–pump–thaw cycles. The average particle size of the supported Pt after this treatment was estimated by X-ray line broadening method to be c.a. 80 Å.

The infrared (IR) spectra were taken with a Digilab FTS-40 FT-IR spectrometer and were recorded with a resolution of 2 cm^{-1} and 64 scans at 298 K. The IR cell was a standard design, which permitted evacuation and heating of the sample under static condition. A 20 mm diameter sample disk was made of approximately 30 mg catalyst pressed at 5000 psi; the material was oxidized *in situ* in 1 atm O_2 at 673 K for 5 h, reduced in 800 mbar H_2 at 673 K for 5 h and evacuated at 723 K, 4×10^{-5} mbar on a glass vacuum system for 30 min. No IR spectrum of CO/SiO_2 was detected during 30 torr CO adsorption on SiO_2 support. All spectra reported

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here have been corrected by subtraction for absorption of the blank catalyst disk and gas phase background to avoid the perturbation from IR spectra of gas phase molecules. The reduced Pt/SiO$_2$ catalyst was scanned by FT-IR spectrometer and was used to be the blank spectrum for subtraction before CO or benzene adsorption. The catalyst disk mounted on sample holder of the IR cell was paralleled IR beam to obtain the gas phase IR spectra of CO or benzene after CO or benzene adsorption on Pt/SiO$_2$. These gas phase spectra were used as the background during IR scans of CO or benzene adsorption on Pt/SiO$_2$. The measurement of benzene hydrogenation was performed by the flow system equipped with a quadruple mass spectrometer (VG micromass 300D) to immediately monitoring the product of reaction; the system was described in detail elsewhere [6].

3. Results and Discussion

Figure 1 shows IR spectra during co-adsorption of 20 torr benzene and 100 torr hydrogen on the Pt/SiO$_2$ catalyst at 298 K as function of time. Figure1a gives a typical IR spectrum for adsorbed benzene [4]. Benzene hydrogenation occurred readily on the surface at 298 K when 100 torr H$_2$ was added to the Pt/SiO$_2$ catalyst previously exposed to 20 torr benzene. Intensities of the characteristic peaks for benzene rapidly decreased with reaction time. A quadruple mass spectrometer was used to identify the product of hydrogenation of benzene adsorbed on the reduced Pt/SiO$_2$ catalyst at 298 K. Benzene pre-adsorbed on Pt/SiO$_2$ was performed by a helium stream with 100 mL/min at atmosphere carrying saturated vapor of benzene at 298 K to pass through a fixed bed reactor with 0.05 g Pt/SiO$_2$ catalyst for 10 min. Then hydrogen gas flowing at 100 mL/min at atmosphere passed through the benzene covered Pt/SiO$_2$ at 298 K, after helium stream purged the residual gas phase benzene in the reaction system. The only product of benzene hydrogenation on Pt/SiO$_2$ catalyst was cyclohexane (see up-left of figure1). Table 1 compares the IR peaks in this study to those IR spectra of condensed-phase benzene and cyclohexane. The growth of CH stretching bands region at 2935 and 2860 cm^{-1} were assigned to asymmetric and symmetric CH$_2$ vibration of adsorbed cyclohexane, respectively [7]. The band at 1457 cm^{-1} is due to CH$_2$ bending of adsorbed cyclohexane [7]. Figure 2 shows the effect of hydrogen pre-adsorption for benzene hydrogenation on Pt/SiO$_2$ catalyst at 298 K. The Pt/SiO$_2$ catalyst was pretreated by dosing 100 torr hydrogen at 298 K for 1 h, then pumped to a pressure of 0.1 torr of H$_2$ before subsequent adsorption of benzene. When 20 torr benzene was adsorbed to the Pt/SiO$_2$ catalyst covered by 0.1 torr residual hydrogen, a weak hydrogenation reaction of benzene to cyclohexane was found to take place on Pt surface as shown in figures 2a and b. Surprisingly, the addition of hydrogen after benzene adsorption led to more intensive hydrogenation than the reaction given in figure 1, in which adsorbed benzene was completely hydrogenated to cyclohexane within 120 min. Figure 3 gives a plot of the peak intensities for the C–H stretching (2800–3000 cm^{-1}) vibrations of cyclohexane as function of reaction time for the IR spectra of figures 1 and 2. The integrated intensities of C–H stretching of adsorbed

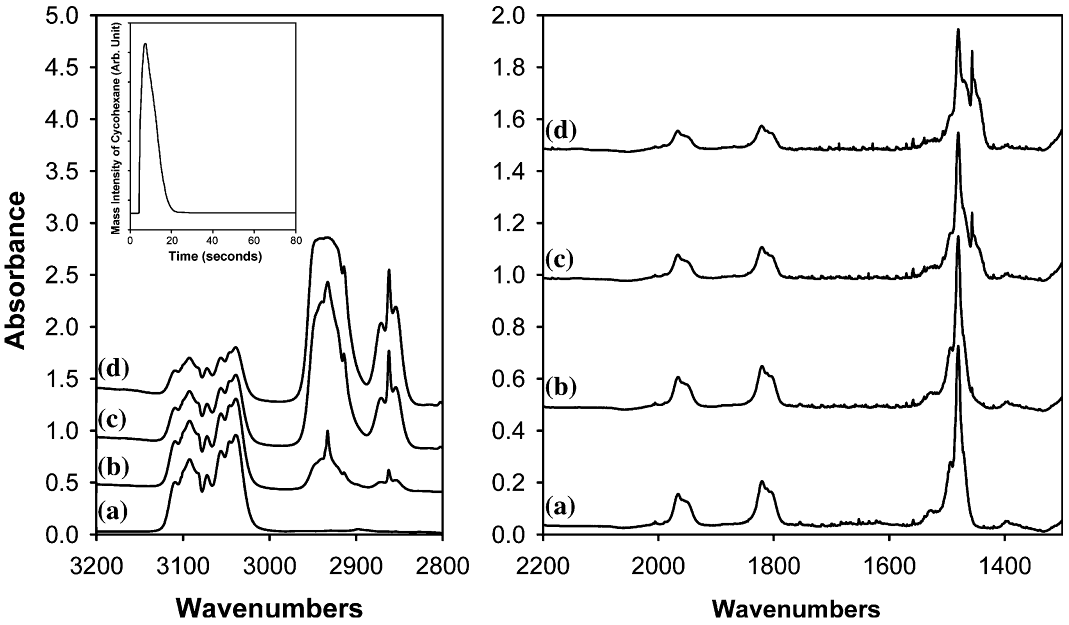

Figure 1. IR spectra for the co-adsorption of benzene and hydrogen on Pt/SiO$_2$ catalyst at 298 K: (a) dosing 20 torr benzene on Pt/SiO$_2$ at 298 K; (b) 100 torr H$_2$ added into the IR cell for 5 min after (a); (c) H$_2$ added for 60 min after (a); (d) H$_2$ added for 120 min after (a).

Table 1
Vibrational mode assignments of benzene and cyclohexane on Pt/SiO_2

Assignment	Liquid benzene	Adsorbed benzene	Liquid cyclohexane	Adsorbed cyclohexane
ν(CH)	3093	3092	2938	2935
	3072	3072	2897	2872
	3047	3037	2860	2860
			2852	2852
Combination	1967	1964		
modes	1820	1816		
ν(CC)	1486	1478		
$\gamma(CH_2)$			1451	1457

cyclohexane were proportional to time for both plots. The residual hydrogen adsorbed on the Pt/SiO_2 catalyst provides higher reaction rates by about a factor of two versus that of the Pt/SiO_2 catalyst without hydrogen pre-adsorption.

Based on the results above, it could be reasonably deduced that the surface sites for dissociative hydrogen adsorption on the Pt catalyst might significantly dominate the benzene hydrogenation reaction. Therefore, CO was used as a probe molecule in this study to determine the adsorption sites of benzene and hydrogen on Pt surface. Figure 4 gives the IR spectra obtained by sequential dosing of benzene, CO and H_2 on the reduced Pt/SiO_2 catalyst at 298 K. The IR band of CO adsorbed on the Pt/SiO_2 surface covered by 20 torr benzene could be assigned to linearly adsorbed CO on atop sites. Apparently, adsorbed benzene could not be hydrogenated by adding H_2 due to a strong CO site blocking effect. Site blocking of H_2/CO may occur through several mechanisms where the sites for dissociative hydrogen adsorption may be occupied by CO or pre-adsorbed CO which modifies the electronic structure of metal surface and increases the barrier for hydrogen adsorption. Figure 5 shows the IR spectra made by sequential exposure of 20 torr benzene, 10 torr CO and 100 torr H_2 on Pt/SiO_2 at 298 K. Low exposures of CO resulted in adsorbed benzene being hydrogenated to cyclohexane by adding H_2. It is noteworthy that the CO peak diminished upon adsorption of large amount of hydrogen. This result implies that adsorbed CO might escape from Pt surface due to increased hydrogen adsorption. Adsorption of CO on Pt single crystal surface has shown that CO molecules preferential adsorb directly onto the atop sites rather than adsorbing on bridge sites [8–11]. Watson *et al.* used *ab initio* calculations to simulate the adsorption energy of hydrogen on atop Pt surface sites, bridge sites and hollow sites indicating that atop sites provided a more favorable adsorption energy than other adsorption sites [12,13]. Therefore, the effect of purely geometric site blocking between H_2 and CO can be proposed to be much higher than that of electronic site blocking.

Figure 6 compares IR spectra of CO adsorbed on the reduced Pt/SiO_2 catalyst with and without exposure of benzene. CO molecules could not adsorb on SiO_2 support evidenced by IR observation of 30 torr CO adsorbed on SiO_2. Brandt *et al.* studied the IR spectra of CO adsorbed on larger Pt particles (ca. 4.2 nm), reporting that three bands at 2067, 2080 and 2090 cm^{-1} were observed during CO adsorption [14]. Raskó also

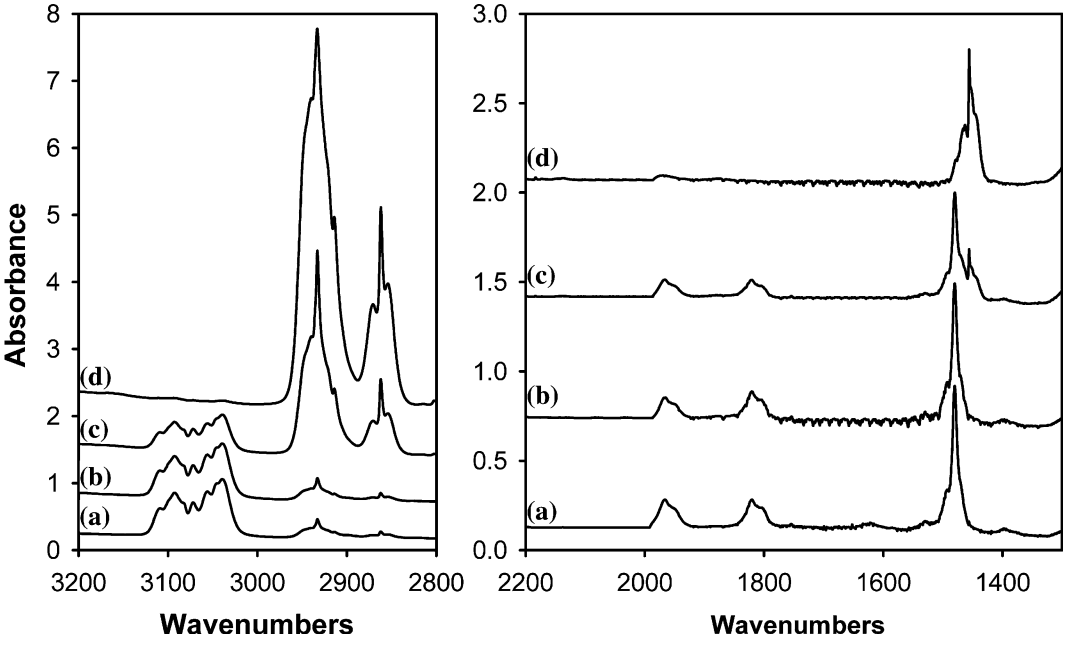

Figure 2. IR spectra for the co-adsorption of benzene and hydrogen on a hydrogen covered Pt/SiO_2 catalyst at 298 K: (a) dosing 20 torr benzene on Pt/SiO_2 covered by 0.1 torr hydrogen at 298 K for 5 min; (b) benzene added for 30 min after (a); (c) 100 torr H_2 added into the IR cell for 30 min after (b); (d) H_2 added for 120 min after (b).

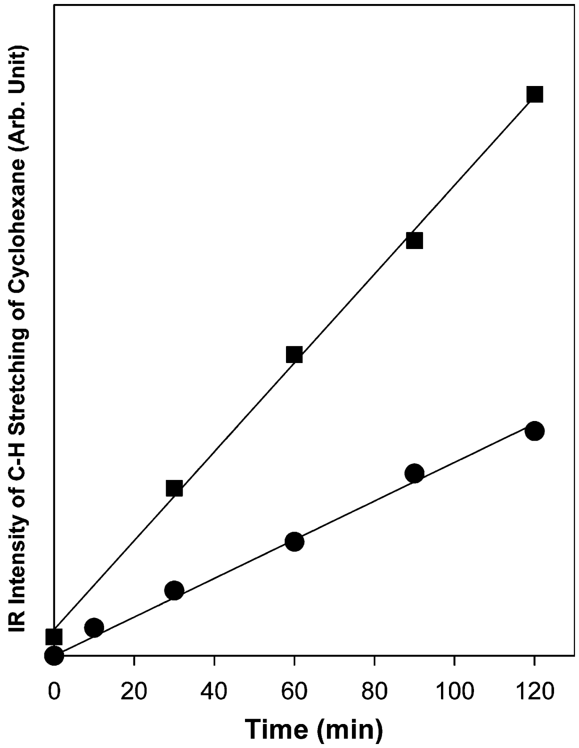

Figure 3. Plot of the peak intensities for the C–H stretching (2800–3000 cm^{-1}) region of adsorbed cyclohexane as function of reaction time for the IR spectra in figures 1 and 2: the circle symbol is for figure 1 and the square symbol is for figure 2.

reported that 0.01 and 0.1 torr adsorbed on reduced 1% Pt/SiO_2 at 300 K appeared three bands at 2107, 2069 and 2045 cm^{-1}, respectively [15]. On the basis of results above, figure 6A (a) shows the IR band of CO adsorbed on clean Pt/SiO_2, which could be reasonably deconvoluted to give bands at 2091 cm^{-1} (α peak), 2080 cm^{-1} (β peak) and 2067 cm^{-1} (γ peak). The deconvolution results are according the literatures reported previously [14,15]. Band assignments have been performed by comparison to Pt single crystal studies [9]. The highest frequency band observed at about 2091 cm^{-1} can be attributed to CO adsorbed on close packed terrace sites. The lower frequency bands of the β peak at 2080 cm^{-1} and the γ peak at 2067 cm^{-1} probably reflects CO located on defect sites, such as edges and kinks. The CO band on the benzene covered Pt surface was observed to be narrower and higher in intensity than the CO band of figure.6A (a), but no appreciable loss in intensity was found after integration of the two CO bands. The intensity of CO peak was independent of benzene adsorption. The α, β and γ peaks of the CO band on a benzene covered Pt surface were shifted to 2079, 2072 and 2060 cm^{-1}, respectively. Pre-adsorbed benzene resulted in a red shift of CO stretching. This phenomenon can be interpreted in term of electronic modification induced by co-adsorption of unsaturated hydrocarbons. Several papers have reported that co-adsorbed benzene, acetylene and ethylene could have the potential to transfer electrons to metals and increase electron density [16–18]. This provides stronger back donation into anti-bonding 2π orbitals of CO resulting in a strengthening of the metal–carbon bond but a weakening the C–O bond.

The integrated intensities of α, β and γ peaks for CO adsorbed on Pt/SiO_2 with and without exposure of benzene are compared in figure 6B. The relative intensities for $\gamma > \beta > \alpha$ exhibited a normal distribution for the

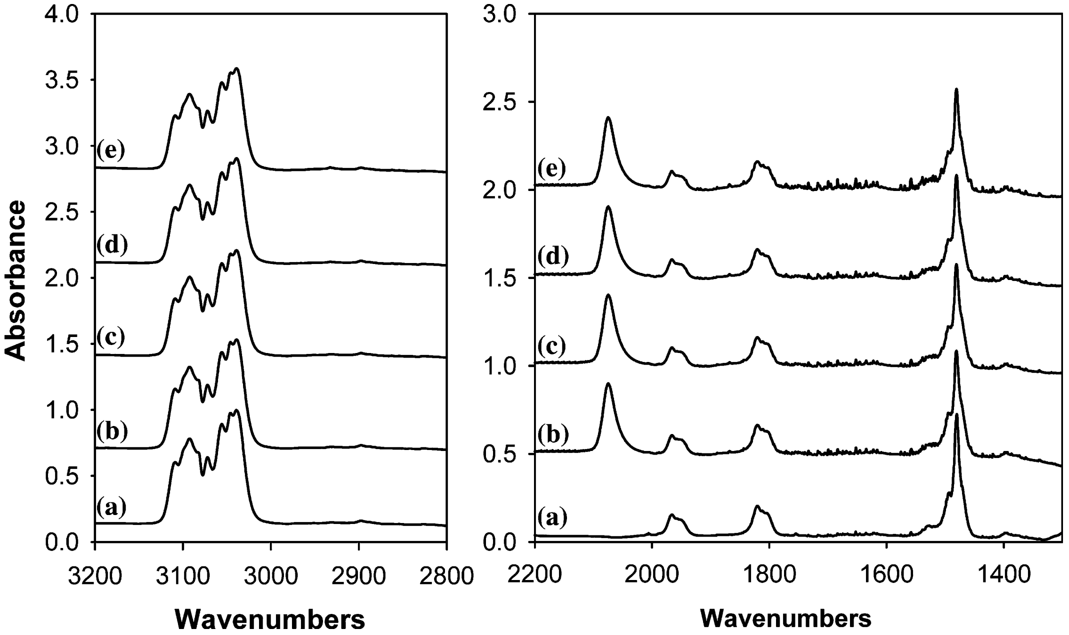

Figure 4. IR spectra from sequential dosing of benzene, CO and H_2 on Pt/SiO_2 catalyst at 298 K: (a) adsorption of 20 torr benzene; (b) 30 torr CO added into the IR cell after (a); (c) 100 torr H_2 added into the IR cell for 5 min after (b); (d) 100 torr H_2 added into the IR cell for 30 min after (b); (e) 100 torr H_2 added into the IR cell for 60 min after (b).

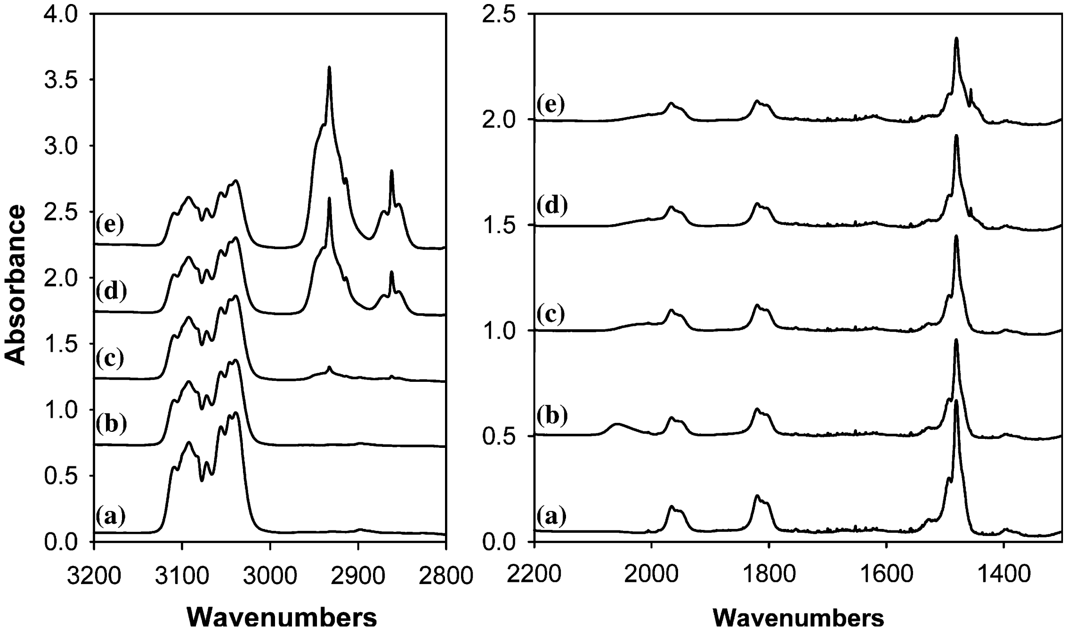

Figure 5. IR spectra from sequential dosing of benzene, CO and H_2 on Pt/SiO_2 catalyst at 298 K: (a) adsorption of 20 torr benzene; (b) 10 torr CO added into the IR cell after (a); (c) 100 torr H_2 added into the IR cell for 5 min after (b); (d) 100 torr H_2 added into the IR cell for 30 min after (b); (e) 100 torr H_2 added into the IR cell for 60 min after (b).

numbers of CO molecules adsorbed on these sites. The sites for lower vibrational energy of CO can result in a stronger CO-metal interaction and thus in the reduction of the CO stretching frequency due to an increased occupation of the antibonding CO 2π orbital [19]. The benzene covered Pt/SiO_2 surface causes a new population for CO adsorption sites on the Pt surface. The intensity of γ peak at lowest frequency was significantly decreased by adsorbed benzene and the intensities of α and β peaks increased when benzene was present on Pt surface. Benzene preferentially bound to the site of the γ peak, but left more α and β sites open for adsorption of CO.

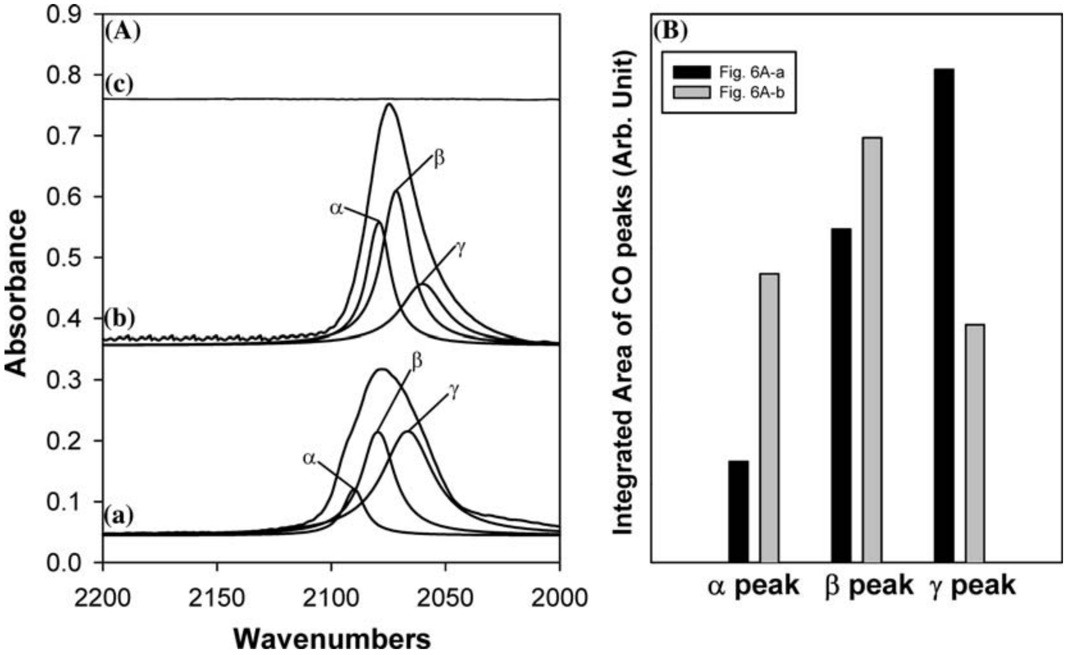

Figure 6. Part (A): Deconvolution of IR spectra from 30 torr CO dosed on Pt/SiO_2 catalyst with and without exposure of 20 torr benzene at 298 K. (a) 30 torr CO dosed on clean Pt/SiO_2; (b) 30 torr CO dosed on benzene covered Pt/SiO_2; (c) 30 torr CO dosed on SiO_2. Part (B): Integrated intensity displayed for results of deconvolution in part (A).

The IR spectra of different exposures of CO on a benzene covered Pt surface further demonstrate the correlation between adsorption of benzene and hydrogen. Figures 4 and 5 show that CO dosed by 30 torr will completely inhibit the hydrogenation of adsorbed benzene on Pt/SiO_2, but low exposure 10 torr of CO will allow progress of the reaction. Undoubtedly, low exposure of CO could not completely occupy the adsorption sites of dissociative hydrogen. The IR spectra of 30 torr and 10 torr CO adsorbed on a benzene covered Pt/SiO_2 surface are compared in figure 7. Low exposure of CO adsorbed on the benzene covered Pt surface gave a weak γ peak. Subtracting figure 7A (a) from figure 7A (b), we obtained the IR spectrum in figure 7B showing that α and β peaks kept almost the same intensities in comparison with the analysis of figure 6.

In figure 4, exposure of 30 torr CO inhibited the adsorption of hydrogen, implying that the intensity of the CO band might be considered to be associated with the numbers of sites allowed for adsorption of hydrogen during hydrogenation of adsorbed benzene. The relative intensity ratio of CO band in figure 7B and the CO band in figure 7A (b) was about 0.76. This result implies that most of the sites for hydrogen adsorption were not shielded when 20 torr benzene and 10 torr CO were exposed to the Pt/SiO_2 surface at 298 K. Nevertheless, the linear curve of the IR peak area for C–H stretching region of cyclohexane versus reaction time during benzene hydrogenation shows that significantly higher reaction rates by a factor of 3.6 without CO adsorption compared to the same reaction with 10 torr CO as shown in figure 8. The adsorption of 10 torr CO binding mainly on γ site markedly reduced the efficient for hydrogenation of adsorbed benzene.

Based on results above, we deduced that hydrogen binding on γ site, maybe belonging to defect site on Pt catalyst, should play an important role during benzene hydrogenation. The results of figures 1–3 clearly shown that small amount of hydrogen remaining on the Pt surface can strongly boost the hydrogenation rate of adsorbed benzene. The IR spectra of co-adsorption experiments for benzene and CO show that benzene could bond to the γ site of CO adsorption, and adsorbed benzene led to less hydrogen atoms binding to the γ site. Although the reduction in the amount of hydrogen on the γ site may result from a shift to α and β sites, the hydrogen adsorbed on α and β sites appeared less efficient for benzene hydrogenation even if adsorbed benzene did not reduce the amount of hydrogen adsorption on Pt. When the Pt surface was treated by hydrogen, the residual hydrogen on surface could first bind on the γ site resulting in adsorbed benzene being completely hydrogenated by subsequent hydrogen. To compare with the study of co-adsorption of hydrogen and benzene on Pt(110) surface, the results in this paper appear the difference between supported Pt catalyst and single crystal surface. On Pt(110) surface, pre-benzene was proposed to form a highly distorted form, maybe a dienyl species, resulting in progress of benzene hydrogenation, but pre-adsorbed hydrogen led to that benzene adsorbed molecularly on hydrogen adlayer, then desorbed intact [4]. These results are apparently different with the benzene hydrogenation on actual Pt catalyst.

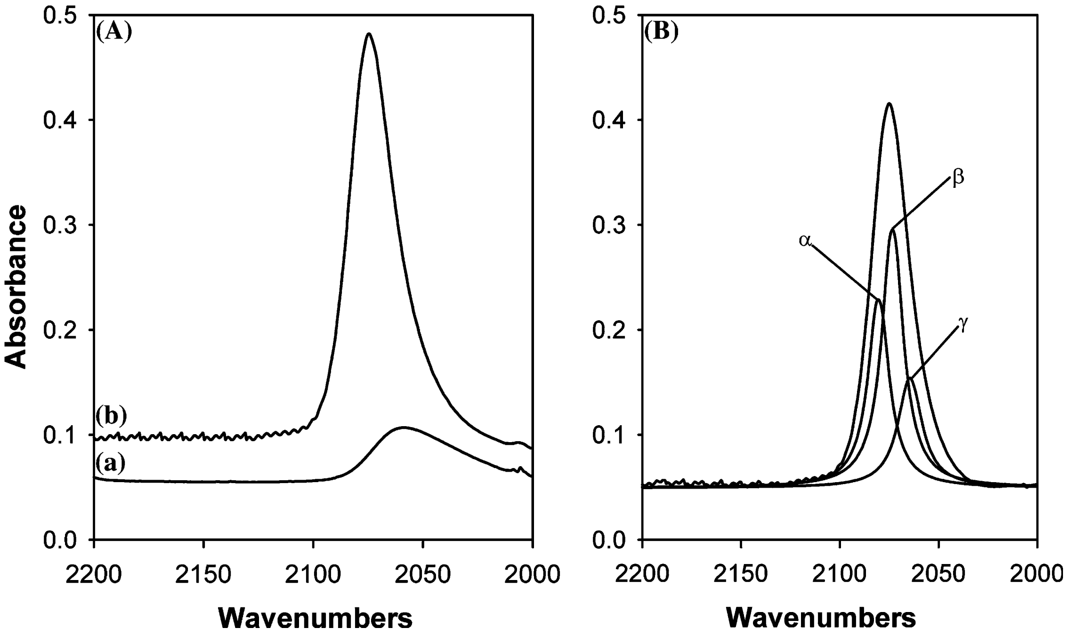

Figure 7. Part (A): IR spectra of various CO exposures to 30 torr benzene covered Pt/SiO_2 surface. (a) 10 torr CO dosed onto 30 torr benzene covered Pt/SiO_2 surface; (b) 30 torr CO dosed onto 30 torr benzene covered Pt/SiO_2 surface. Part (B): Deconvolution after IR spectra of subtracting figure 7A (a) from figure 7A (b).

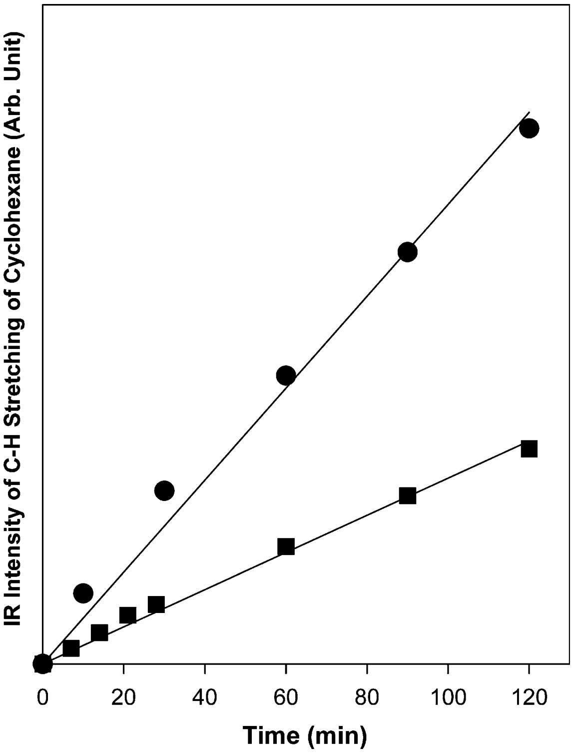

Figure 8. Plot of peak intensities for the C–H stretching (2800–3000 cm^{-1}) region of cyclohexane as function of reaction time for the IR spectra in figures 1 and 5: the circle symbol is for figure 1 and the square symbol is for figure 5.

On the surface Pt/SiO_2 catalyst, pre-adsorbed hydrogen binding on some defect sites can auxiliary accelerate reaction.

4. Conclusion

In summary, we have found that defect sites on surface of Pt/SiO_2 catalyst play an important role during benzene hydrogenation. FT-IR studies of co-adsorption experiments of benzene and CO show that three types of atop sites for hydrogen adsorption on the Pt surface dominate the reaction rate during benzene hydrogenation. Benzene and hydrogen can competitively bond to the γ site, defect sites such as kinks or edges, found by CO adsorption (CO stretching at 2067 cm^{-1}). Most of adsorption sites for α and β sites are still available for hydrogen adsorption even if 20 torr benzene and 10 torr CO exposed to the Pt/SiO_2 surface at 298 K. But hydrogen adsorbing on both α and β sites provide less efficient for hydrogenation of adsorbed benzene. When hydrogen adsorbs on the γ site prior to benzene the hydrogenation rate of benzene will be significantly accelerated.

Acknowledgements

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