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Platinum Supported on [60]Fullerene-Grafted Silica as a New Potential Catalyst for Hydrogenation

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A Pt-based catalyst supported on a silica grafted with [60]fullerene was prepared and evaluated in the liquid-phase hydrogenation of cinnamaldehyde. Silanization of a large-pore silica was carried out with diethoxymethylsilane. [60]Fullerene was anchored on the modified silica through a hydrosilylation reaction with Si–H bonds, mediated by a Pt^0 Karsted catalyst. IR, ^{29}Si and ^{13}C MAS NMR spectroscopies, and N_2 adsorption–desorption provided evidence that [60]fullerene was covalently bonded onto the silica surface. [60]Fullerene was released at ca 950, 750, and 800 K in He, air, and H_2, respectively, even in the presence of 0.8 wt% Pt. The very high density of [60]fullerene grafting confers a strong hydrophobic character to the surface. A fairly good selectivity to cinnamyl alcohol was observed on this catalyst at cinnamaldehyde conversion above 90%. This behavior might be better explained by a specific interaction between the phenyl ring of cinnamaldehyde and the grafted [60]fullerene film than by a modification of the Pt d-band. The IR spectroscopy of adsorbed CO did not provide any evidence of an enhanced, or reduced, back-donation to $2\pi^*$ antibonding orbitals of CO, with respect to classical supported Pt catalysts.

1. INTRODUCTION

From their discovery, one decade before, fullerene-based materials have raised a huge number of studies to find applications. Catalysis, and in particular heterogeneous catalysis, has been envisaged as a potential field. Some specificities of fullerene-supported metal particles were thus proved in the Pd-mediated hydrogenation of alkenes and acetylene (1), the hydrogenations of cinnamaldehyde (2), CO, and 2-cyclohexanone (3) over Ru-based materials, and the disproportionation of cinnamyl alcohol on Pd/fullerene-black-soot (4). In particular, Ru_3C_{60} catalysts exhibited a higher selectivity for hydrocarbons in the CO hydrogenation at 473 K, compared to conventional Ru/C catalysts (3b). However, at higher temperatures, this behavior did not maintain due to reconstruction of the Ru phase.

In a short preliminary study we have shown that the [60]fullerene molecular compound can be covalently bonded on a silica support through Si–C bond formation (5). This composite material, called SiO_2–C_{60}, exhibited a high specific surface area and a good stability against thermal treatment, since the [60]fullerene moieties thus grafted are released at above 850 K, in Ar atmosphere. These interesting properties indicated that this material could constitute a potential candidate as a new class of carbon support in catalysis by metals.

The present work was aimed to prepare a Pt/SiO_2–C_{60} catalysts and to evaluate its thermal stability in various atmospheres. This catalyst was tested in the hydrogenation of cinnamaldehyde, chosen as model reaction. Pt-based catalysts are commonly exhibiting a rather low selectivity to cinnamyl alcohol (6). A possible effect of a metal–support interaction between Pt particles and SiO_2–C_{60} could be thus identified.

2. EXPERIMENTAL

2.1. *Preparation of Pt/SiO_2–C_{60}*

In order to anchor [60]fullerene on SiO_2, a stepwise strategy based on the prefunctionalization of SiO_2 by Si–H groups followed by hydrosilylation reaction engaging [60]fullerene was employed (5).

A suspension of silica (Spherosil XOA400, Rhône Poulenc, dried under vacuum at 423 K for 24 h) in a mixture of diethoxymethylsilane/hexane (1/2) was heated to 333 K in Ar for 48 h. The resulting solid was washed with THF to remove unreacted alkoxysilane and its condensation products with moisture. The solid thus obtained was suspended in 1,2-dichlorobenzene containing both [60]fullerene and Pt^0 as catalyst (Pt divinylsiloxane Karsted, Rhône Poulenc) and heated at 398 K in Ar for 48 h. The brown solid, isolated by filtration, was washed with 1,2-dichlorobenzene until a clear supernatant was obtained.

SiO_2–C_{60} hereupon prepared was activated in vacuum at 373 K overnight. After cooling to room temperature, Pt was

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deposited on SiO_2–C_{60} as Pt 2,5-pentanedionate ($Pt(acac)_2$, Aldrich). $Pt(acac)_2$ (20 mg) was dissolved in THF (10 cm^3, SDS, 99.3%), then contacted for 48 h with SiO_2–C_{60} (1 g). THF was removed by evaporation and the solid was dried in a vacuum at 353 K overnight. The resulting solid was calcined in air at 573 K for 3 h, then reduced in a stream of diluted hydrogen (H_2/N_2, 10/90, vol/vol) at 623 K for 3 h. The Pt/SiO_2–C_{60} catalyst contains 0.8 wt% Pt and 3.42 wt% C, as determined by chemical analysis.

2.2. *Characterizations*

The Pt/SiO_2–C_{60} catalyst was characterized by adsorption–desorption of N_2 at 77 K, TG-DSC experiments in various atmospheres, FTIR and NMR spectroscopies.

Adsorption and desorption isotherms of N_2 were determined using a Micromeritics ASAP2000 apparatus. Before the admission of N_2 pulses at 77 K, the sample was outgassed at 623 K overnight in a vacuum. BET and BJH methods were used to derive the specific surface area and the pore size distribution from the adsorption and desorption isotherms, respectively.

TG-DSC experiments were carried out in a SETARAM TG-DSC-111 apparatus, with fully programmable heating and cooling sequences, sweep gas valve switchings, and data analysis. About 30 mg of sample were placed in an alumina crucible. Heating was then started at 5 K min^{-1} from room temperature to 1073 K on-stream (flow: 20 cm^3 min^{-1}) of He, synthetic air or H_2/Ar mixture (3/97, vol/vol).

H_2 chemisorption was carried out in a conventional static apparatus. The sample was reactivated in H_2 at 623 K overnight, outgassed at 623 K for 2 h at a pressure of 2×10^{-4} Pa. A first isotherm was determined in the 0–20 kPa range. A back isotherm was then determined after evacuation at room temperature of the sample for 30 min at 2×10^{-4} Pa. The H_2 uptake was estimated by the extrapolation to zero pressure of the linear part of the isotherms. The first isotherm gives the total amount of chemisorbed hydrogen (H_{tot}); the second isotherm gives the reversible part of chemisorbed hydrogen (H_{rev}); the difference between the two isotherms gives the irreversible part of chemisorbed hydrogen (H_{irr}).

The FT-IR study was carried out at room temperature using a Nicolet 320 FTIR instrument with a resolution of 2 cm^{-1} and a MCT detector. The spectra obtained were analyzed in the 4000–1300 cm^{-1} spectral region. Self-supporting wafers were prepared under a pressure of 3 ton cm^{-2}. The wafers were activated *in situ* in the IR cell (KBr windows) in a vacuum at 673 K overnight and the spectra were recorded at room temperature. For FTIR spectroscopy of adsorbed CO, the wafer was activated at 623 K in H_2 for 3 h. The cell was then evacuated at 2×10^{-4} Pa for 3 h at the same temperature. CO was then introduced at room temperature at full coverage of the Pt particles ($\theta_{CO} \approx 1$). Finally, the sample was desorbed under vacuum at increasing temperatures up to 473 K. Spectra were recorded after each operation.

The MAS NMR spectra were taken at 59.6 MHz for ^{29}Si and 75.4 MHz for ^{13}C in solid state NMR (Bruker AM 300). The ^{29}Si spectra were obtained using a CP and ^1H decoupling sequence, the ^{13}C spectra were obtained using a single pulse acquired delay sequence with a HP ^1H decoupling. The spectral widths used were 15 and 25 kHz. The pulse widths were 5.8 and 4.8 μs and the relaxation delays were 10 and 60 s for the ^{29}Si and ^{13}C NMR, respectively. The shifts were referred to tetramethylsilane. The spectra were done at a spinning frequency of 5 kHz. Typically, 10,000 scans were accumulated for each nuclei.

2.3. *Hydrogenation of Cinnamaldehyde*

The experimental set up for the hydrogenation of cinnamaldehyde was reported in detail previously (7). In short, the reaction was carried out in a 100 cm^3 batch reactor. The prereduced Pt/SiO_2–C_{60} sample (0.26 g) was reactivated *in situ* in *i*-propanol (40 cm^3) at 383 K and under 4.5 MPa H_2 pressure for 2 h. After cooling to room temperature, the cinnamaldehyde was charged and the reaction started at 383 K under 4.5 MPa H_2 pressure with a reactant concentration of 7.9×10^{-4} mol cm^{-3}. Micro-samples were withdrawn and analyzed on a gas chromatograph (Varian 3300 equipped with FID detector) using a DB wax capillary column (30 m × 0.32 mm ID). The calibration was done by using synthetic mixtures of pure components.

3. RESULTS AND DISCUSSION

The first point to be discussed is the reality of a chemical bond occurring between [60]fullerene and silica.

The IR spectroscopy of the unmodified SiO_2 presents the lattice and O−H vibrations at ca 2000–1600 and 3745 cm^{-1}, respectively (Fig. 1a). Upon condensation of $MeSiH(OEt)_2$ with SiO_2, in addition to the above-mentioned bands, other bands corresponding to C−H (ca 3000–2880 cm^{-1}), Si−H (ca 2170 cm^{-1}), C−C, and Si−C (ca 1400–1300 cm^{-1}) vibrations modes were also observed (Fig. 1b). The significant decrease in the OH band intensity at 3745 cm^{-1} provides evidence of the grafting of $MeSiH(OEt)_2$. Finally, the IR spectrum of SiO_2–C_{60} (Fig. 1c) shows vibration modes of [60]fullerene at 1428 cm^{-1} and revealed some decrease in the intensity of the Si−H band. The ^{29}Si and ^{13}C NMR spectra (Figs. 2, 3) confirm that [60]fullerene has been indeed grafted on silica, after reaction with the Si−H groups. For the parent SiO_2, three signals at δ −90.8, −101.2, and −110.0 corresponding to $(SiO)_2Si^*(OH)_2$, $(SiO)_3Si^*(OH)$, and $(SiO)_4Si^*$, respectively, were observed in the ^{29}Si spectrum (Fig. 2a). Upon condensation of $MeSiH(OEt)_2$ with SiO_2 (Fig. 2b), the intensity of the signals at δ −90.8 and −101.2 decreased significantly with respect to the signal

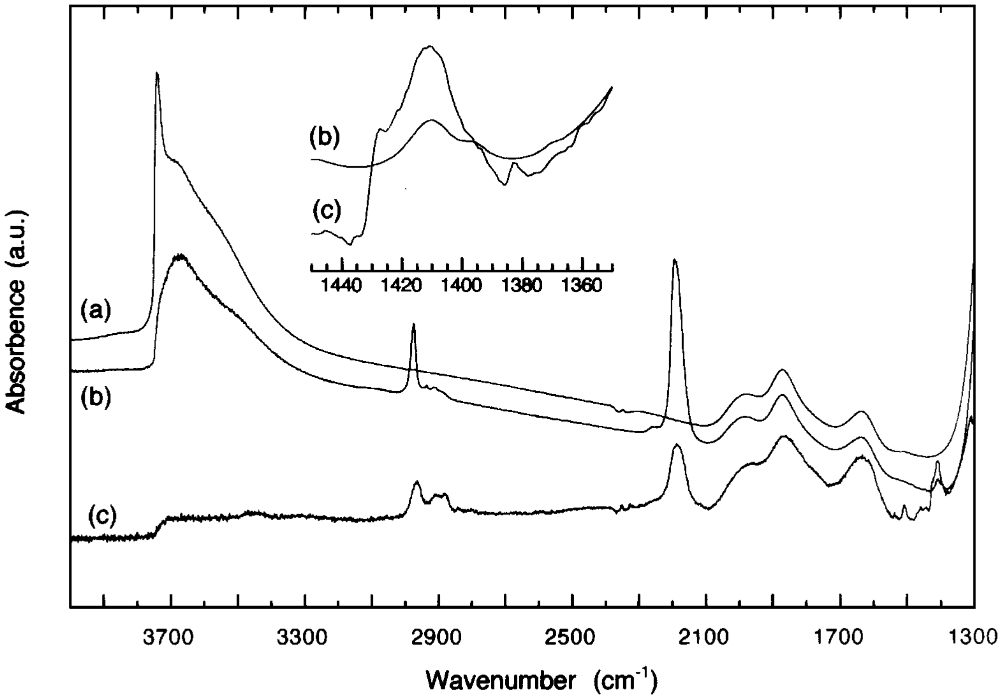


FIG. 1. IR spectra of SiO_2 (a), alkoxide-modified SiO_2 (b), and SiO_2–C_{60} (c).

at δ −110.0, indicating the conversion of Si–OH groups into Si–O–Si bonds. The spectra (Figs. 2b, c) show that additional siloxane bridges, likely between Si–OEt and Si–OH, were being formed during the hydrosilylation reaction. Moreover, some unreacted silanol groups remain in the final SiO_2–C_{60} material, very likely in hidden sites. On the other hand, while for the parent SiO_2 no signal was detected between δ 0 and −70, for the functionalized material, two peaks at δ −24.4 and −31.2 were observed. These signals may correspond to Si atoms of the types (SiO)Si*H(Me)(OEt) and $(SiO)_2Si^*H(Me)$. Concerning SiO_2–C_{60} (Fig. 2c), in addition to the above-mentioned signals, a peak at δ 8.6 was observed. While the signal between δ −20 and −40 may be attributed to unreacted Si–H groups, the presence of signals at higher field (δ 8.6 and −10.2), which may be assigned to conversion of (SiO)Si*H(Me)(OEt) and $(SiO)_2Si^*H(Me)$ into $(SiO)Si^*C_{60}(Me)(OEt)$ and $(SiO)_2Si^*C_{60}(Me)$, respectively, is a clear-cut argument in the favor of the addition of [60]fullerene to Si–H groups.

The ^{13}C MAS NMR study of SiO_2–C_{60} (Fig. 3b) revealed seven peaks at δ −1.78, 9.26, 17.1, 58.9, 81.4, 105.5, 145.5, and 209.8. Peaks at δ −1.78, 17.1, and 58.9 should correspond to Si–C^*H_3, Si–$OCH_2C^*H_3$, and Si–$OC^*H_2CH_3$, respectively. The decrease of the peaks at δ 17.1 and 58.9, with respect to the alkoxide-modified SiO_2 (Fig. 3a), confirms the additional siloxane bridge formation during the hydrosilylation process. The broad peak between δ 140 to 150 was previously assigned to the nonequivalent C atoms of [60]fullerene bonded to silica (5). On the other hand, a small and very sharp peak at δ 143.6 seems to exist on the right-hand side of this broad band. It is very likely due to a contribution of the undifferentiated C atoms of residual unbonded [60]fullerene (8). The small and broad band appearing at 105.5 could tentatively be assigned to the sp_3 C of [60]fullerene bonded to Si. Goze *et al.* (9) indeed observed a band at δ 72 in [60]fullerene unidimensional polymers, obtained by cycloaddition of [60]fullerene molecules under high pressure and temperature. This band was assigned to the sp_3 C atoms which link the [60]fullerene moities. The bands at 81.4 and 209.8 could be attributed to spinning side bands of the 145.5 main band.

There are thus strong arguments, from FTIR spectroscopy and ^{13}C, ^{29}Si MAS NMR studies, that [60]fullerene molecules are covalently bonded to silica. The strength of this bond was appreciated from TG experiments (Fig. 4). For unmodified SiO_2, there were two weight losses below 370 and at ca 870 K corresponding to the release of physisorbed H_2O (ca 5–6 wt%) and dehydroxylation (2.5 wt%), respectively (Fig. 4a). The release of H_2O (ca 1.5 wt%) was lower upon condensation of $MeSiH(OEt)_2$ (Fig. 4b). Additional dehydroxylation and the loosing of alkoxysilane fragments occurred with this material at above 473 K. Finally, the very low weight loss (0.5 wt%) at low temperature for SiO_2–C_{60} provided evidence of the high hydrophobicity of the surface (Fig. 4c). On the other hand, the weight loss with a maximum rate occurring at 950 K very likely corresponds to the release of [60]fullerene after Si–C bond cleavage. The [60]fullerene powders in inert gases, N_2 or Ar, sublime at ca 870 K (10). On the other

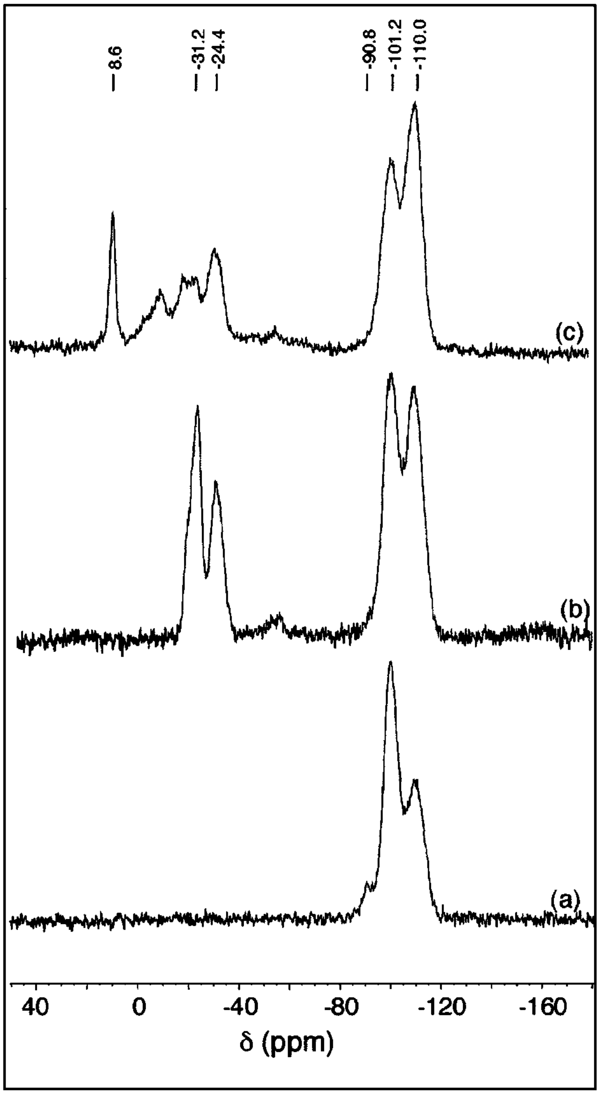


FIG. 2. ^{29}Si MAS NMR spectra of SiO_2 (a), alkoxide-modified SiO_2 (b), and SiO_2–C_{60} (c).

hand, the maximum desorption rate of [60]fullerene from $Al_2O_3(0001)$, in UHV chamber, ranged from 550 to 600 K (11). Part of the weight loss occurring between 500 and 800 K is likely due to residual 1,2-dichlorobenzene solvent used during the grafting of [60]fullerene.

On the other hand, the IR band at ca 2170 cm^{-1} ($\nu_{Si–H}$) in SiO_2–C_{60} (Fig. 1c) provides evidence that part of the $(\equiv SiO)_3Si–H$, of the alkoxide-modified SiO_2, has not reacted with [60]fullerene. This appears quite normal if considering the diameter of the [60]fullerene ball (ca 1.1 nm) which hinders the access to potentially reactive $(\equiv SiO)_3Si–H$ sites (density of Si–OH is about 4.4 nm^2). The surface of the parent silica is 337 m^2 g^{-1} (Table 1); it thus contains 7.5×10^{19} silanol g^{-1} approximately. The ca 3.3–3.8 wt% of [60]fullerene released at temperature higher than 600 K (Fig. 4c), with respect to the alkoxysilane grafted

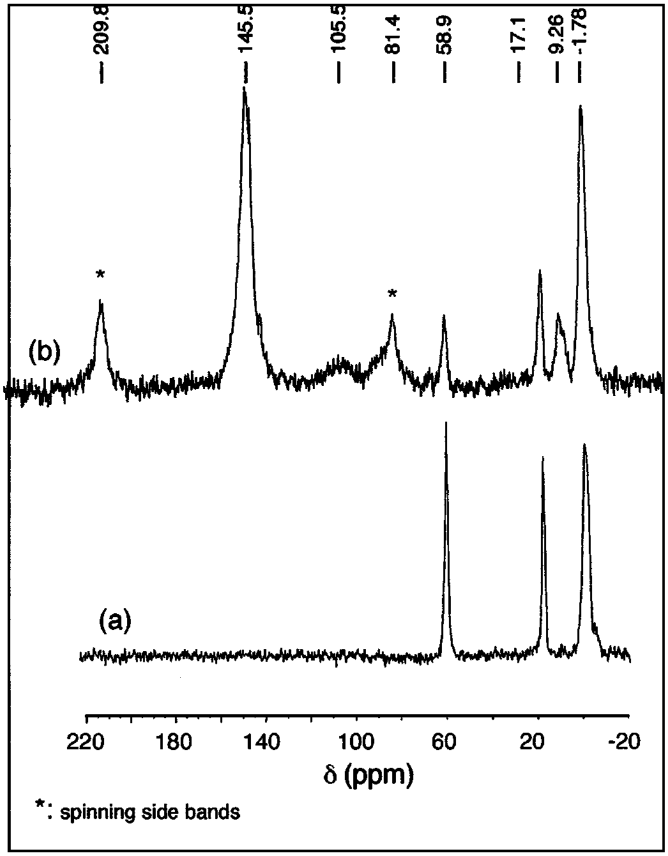


FIG. 3. ^{13}C MAS NMR spectra of alkoxide-modified SiO_2 (a), and SiO_2–C_{60} (b).

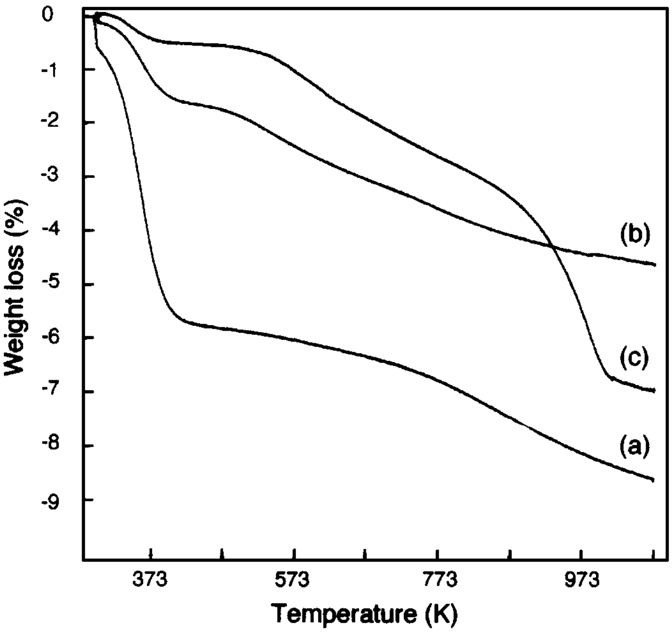


FIG. 4. TG profiles in He of SiO_2 (a), alkoxide-modified SiO_2 (b), and SiO_2–C_{60} (c).

TABLE 1

Some Properties of the Samples

Sample	S_{BET} (m^2 g^{-1})	Mean pore size (nm)	Pore volume (cm^3 g^{-1})	(H_{irr}/Pt)
SiO_2	337	10.8	0.92	—
Pt/SiO_2–C_{60}	266	9.7	0.50	0.36

silica, represents about 27–31 × 10^{18} molecules g^{-1}. As a result, 1/3 of the alkoxysilane groups should be grafted with [60]fullerene, and the coverage of the silica surface with bonded [60]fullerene appears very high.

Table 1 reports the textural properties of SiO_2 and SiO_2–C_{60}. There is a decrease of 1.1 nm ($\approx$10%) in the mean pore size which is correlated with 20 and 45% decreases in the specific surface area and pore volume, respectively. Moreover, the energetic term c, in the BET equation, decreases from 147 to 43. This emphasizes a very clear shift from an hydrophilic (SiO_2) to an hydrophobic (SiO_2–C_{60}) surface. The bonding between silica and [60]fullerene can be pictured as shown in Scheme 1.

The aim of this work was to develop a Pt/SiO_2–C_{60} as a new potential catalyst for hydrogenation. The stability of the bonding between silica and [60]fullerene, which is high for SiO_2–C_{60} in He atmosphere, has been therefore evaluated for Pt/SiO_2–C_{60} in both air and H_2 atmospheres. Figure 5 shows the two TG profiles. After the initial H_2O release below 370 K ($\approx$1 wt%), a second weight loss, centered at ca 750 K in air and 800 K in H_2, occurred. The weight loss above 400 K, ca 3.5 wt%, merely corresponds to the C content of Pt/SiO_2–C_{60}, from chemical analysis. Both were accompanied with an exothermic event, and CO_2 with H_2O evolutions were identified by mass spectrometry, during the treatment in air. These experiments show that calcination in air and reduction in diluted H_2 of Pt/SiO_2–C_{60} at temperatures lower than 573 and 623 K, respectively, do not initiate the bond cleavage between silica and [60]fullerene.

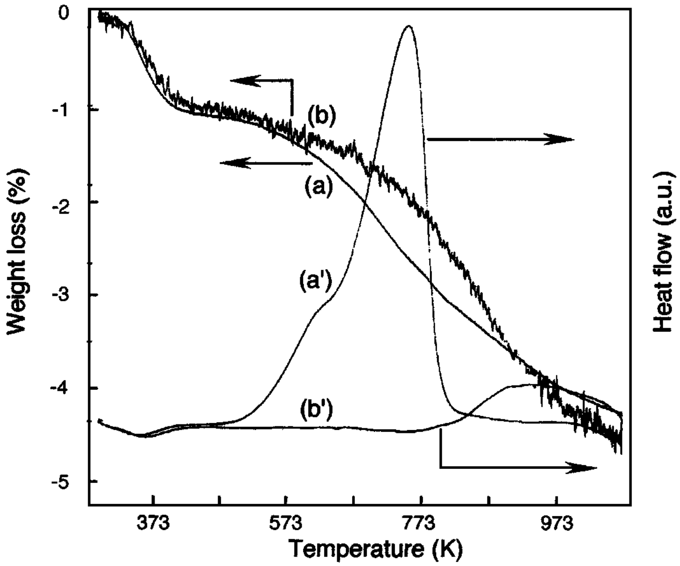
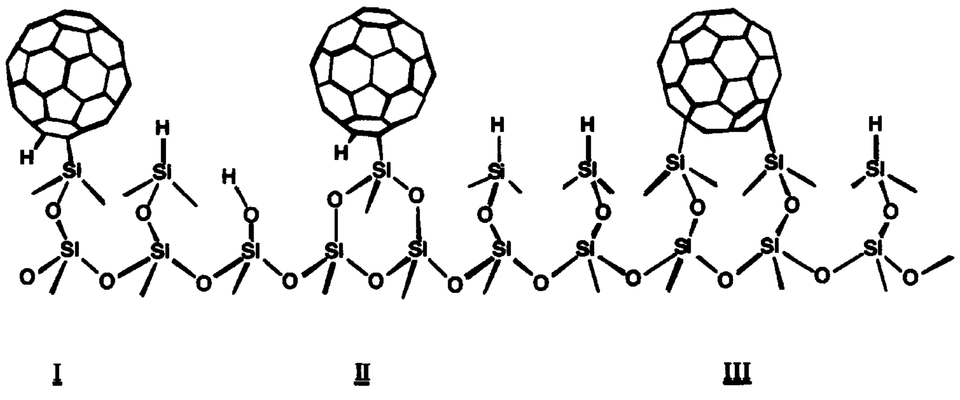


FIG. 5. TG and heat flow profiles of Pt/SiO_2–C_{60} in air (a, a′) and hydrogen (b, b′).

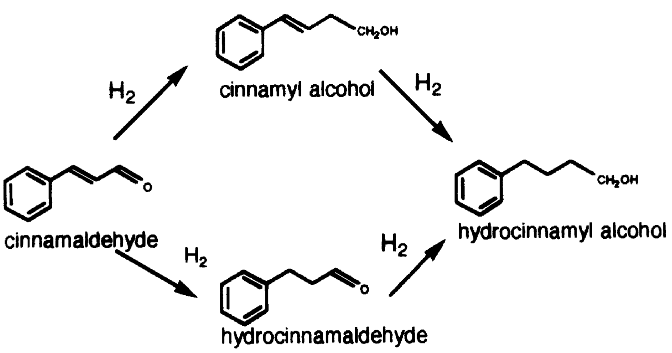
It comes out that such a material can be activated, and regenerated eventually, without any great modification of the grafted silica surface.

The irreversible part of H_2 taken up by the catalyst at room temperature (H_{irr}/Pt) is 0.36 which indicates a mean size of Pt particles around 3.0 nm.

The catalytic properties of this new material, for the liquid phase hydrogenation of cinnamaldehyde, have been tested. It is well established that the hydrogenation of α,β-unsaturated aldehydes occurs through the classical pathway shown in Scheme 2. Our results are fully in line with this network of parallel and consecutive reactions. Figure 6 shows the composition of products as a function of cinnamaldehyde conversion. It is noteworthy to point out the high selectivity for cinnamyl alcohol (up to 89%) which was maintained until high conversion of cinnamaldehyde. This is a fairly good selectivity to cinnamyl alcohol which



SCHEME 1. Various species of [60]fullerene bounded on the silica surface.



SCHEME 2. Formal reaction scheme of cinnamaldehyde hydrogenation.

was not reported for medium-sized Pt particles supported on an inorganic carrier (12), or on activated carbon (6, 13). The origin of this behavior could be ascribed to (i) geometric effects (particles morphology), (ii) electronic effects (d-band modifications), and/or (iii) specific interaction at the borderline between Pt particles and the [60]fullerene film. At this moment, it was impossible to identify any structural change of Pt particles induced by the SiO_2–C_{60} support.

An IR spectroscopic study of adsorbed CO has been carried out to show any modification of the Pt d-band. Figure 7 shows the IR spectra after CO adsorption on Pt/SiO_2–C_{60} and then desorption at increasing temperatures. A band of low intensity appeared at 2080 cm^{-1} at full CO coverage (Fig. 7a), which corresponds to linearly adsorbed CO on Pt.

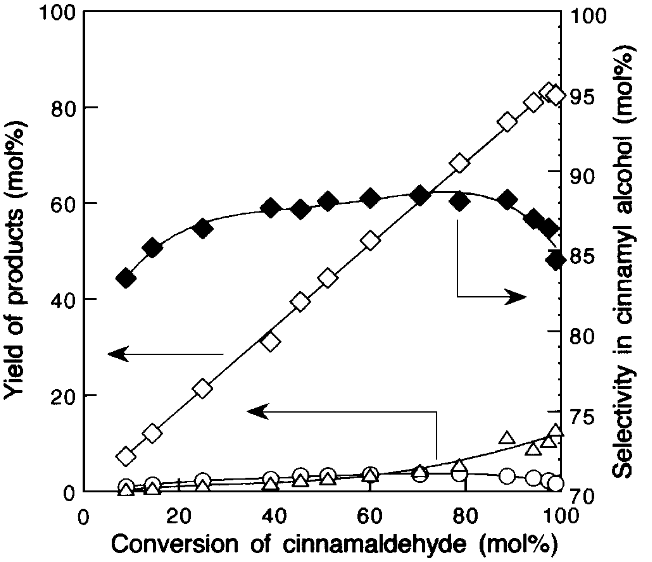


FIG. 6. Yield of products and selectivity to cinnamyl alcohol for the hydrogenation of cinnamaldehyde over Pt/SiO_2–C_{60} catalyst as a function of cinnamaldehyde conversion; (◇) cinnamyl alcohol, (○) hydrocinnamaldehyde, (△) hydrocinnamyl alcohol, (◆) cinnamyl alcohol selectivity. $T_R = 383$ K, $C_{\text{cinnamaldehyde}} = 7.9 \times 10^{-4}$ mol cm^{-3}, $P_{\text{hydrogen}} = 4.5$ MPa, catalyst weight = 0.26 g.

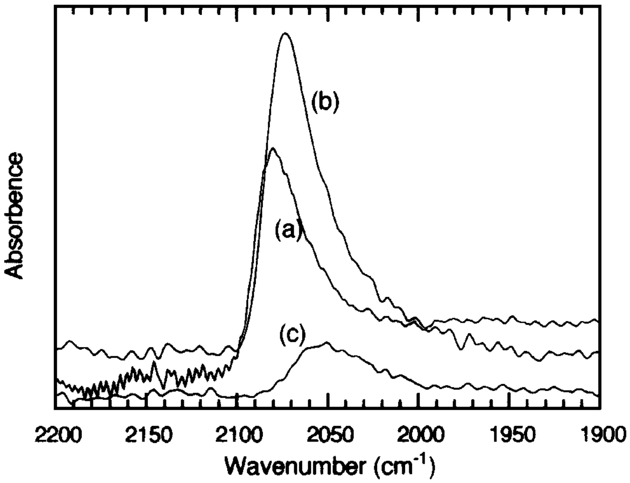
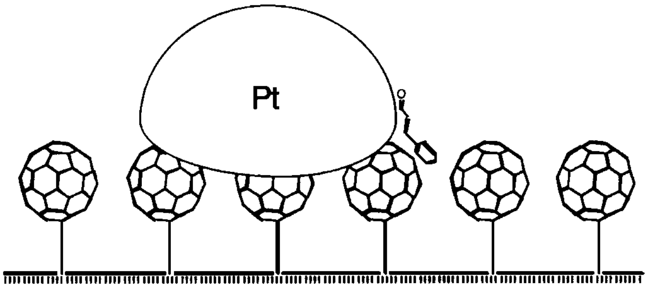


FIG. 7. Difference infrared spectra before and after CO adsorption on Pt/SiO_2–C_{60} at 298 K under 2.6 kPa CO pressure (a), and after evacuation at 298 K (b) and 473 K (c).

This band shifted to 2055 cm^{-1} at low coverage, after desorption at 473 K (Fig. 7c). This is due to the disappearance of dipole–dipole coupling between neighboring adsorbed CO. The position of isolated singleton CO at 2055 cm^{-1} compares fairly well with ν_{CO} found on Pt catalysts of medium dispersion in low interaction with alumina (14) or silica (15). This means that back-donation from the Pt d-band to $2\pi^*$ anti-bonding orbitals of CO is similar for these catalysts, which emphasizes no great specificity of the Pt d-band due to the presence of SiO_2–C_{60} support. The occurrence of electronic effects for determining the specific behavior of Pt/SiO_2–C_{60} in the hydrogenation of cinnamaldehyde becomes, therefore, questionable.

Finally, a joint adsorption of cinnamaldehyde on both Pt and [60]fullerene at their borderline might be suggested. In this picture (Scheme 3), the phenyl ring will be attracted by [60]fullerene favoring, thus, an orientation of the α,β-unsaturated system for an adsorption by the C=O groups on the Pt particles. The strong interaction between [60]fullerene and benzene has been proved elsewhere (16). This adsorption, with preferred orientation through the



SCHEME 3. Interaction of cinnamaldehyde with grafted [60]fullerene and Pt particles.

C═O group towards the Pt surface, would explain the high selectivity to cinnamyl alcohol found with Pt/SiO_2–C_{60}.

4. CONCLUSION

The Pt/SiO_2–C_{60} catalyst exhibits unexpected high selectivity for the cinnamyl alcohol formation in the hydrogenation of cinnamaldehyde. This behavior could be due to a specific interaction between the phenyl ring and the grafted-[60]fullerene moieties at the periphery of the 3 nm Pt particles. This interaction would favor the adsorption of cinnamaldehyde on Pt through the C═O bond. The stability of the [60]fullerene film grafted on silica is high, since [60]fullerene fragments in Pt/SiO_2–C_{60} were released at ca 750 and 800 K in air and H_2, respectively. This stability upon thermal treatments makes the SiO_2–C_{60} material suitable as a new carbonaceous support in catalysis by metals.

REFERENCES

1. (a) Nagashima, H., Nakaoka, A., Tajima, S., Saito, Y., and Itoh, K., *Chem. Lett.*, 1361 (1992).
1. (b) Nagashima, H., Kato, Y., Yamaguchi, H., Kimura, E., Kawanishi, T., Kato, M., Saito, Y., Haga, M., and Itoh, K., *Chem. Lett.* 1207 (1994).
2. Planeix, J. M., Coustel, N., Coq, B., Brotons, V., Kumbhar, P. S., Dutartre, R., Geneste, P., Bernier, P., and Ajayan, P. M., *J. Am. Chem. Soc.* **116**, 7935 (1994).
3. (a) Braun, Th., Wolhers, M., Belz, T., Nowitzke, G., Wortmann, G., Uchida, Y., Pfänder, N., and Schlögl, R., *Catal. Lett.* **43**, 167 (1997).
3. (b) Braun, Th., Wolhers, M., Belz, T., and Schlögl, R., *Catal. Lett.* **43**, 175 (1997).
4. Datta, A., Khwaja, H. I., Kelkar, R. Y., Saple, A. R., and Datta, M., *J. Chem. Soc. Chem. Commun.* 851 (1996).
5. Planeix, J. M., Coq, B., de Ménorval, L. C., and Medina, P., *J. Chem. Soc. Chem. Commun.* 2087 (1996).
6. Giroir-Fendler, A., Richard, D., and Gallezot, P., *in* "Heterogeneous Catalysis and Fine Chemicals" (M. Guisnet, J. Barrault, C. Bouchoule, D. Duprez, C. Motassier, and G. Pérot, Eds.), p. 171. Elsevier, Amsterdam, 1988.
7. Coq, B., Kumbhar, P. S., Moreau, C., Moreau, P., and Warawdekar, M. G., *J. Mol. Catal.* **85**, 215 (1993).
8. Taylor, R., Hare, J. P., Abdul-Sada, A. K., and Kroto, H. W., *J. Chem. Soc., Chem. Commun.* 1423 (1990).
9. Goze, C., Rachdi, F., Hajji, L., Nuñez-Regueiro, M., Marquez, L., Hodeau, J. L., and Mehring, M., *Phys. Rev. B* **54**, 3676 (1996).
10. Chen, H. S., Kortan, A. R., Haddon, R. C., and Fleming, D. A., *J. Phys. Chem.* **96**, 1016 (1992).
11. Tokmakoff, A., Haynes, D. R., and George, S. M., *Chem. Phys. Lett.* **186**, 450 (1991).
12. Schröder, U., and de Verdier, L., *J. Catal.* **142**, 490 (1993).
13. da Silva, A. B., Jordao, E., Mendes, M. J., and Fouilloux, P., *Appl. Catal. A: General* **148**, 253 (1997).
14. de la Cruz, C., and Sheppard, N., *Spectrochimica Acta* **50A**, 271 (1994).
15. Primet, M., *J. Catal.* **88**, 273 (1984).
16. (a) Balch, A. L., Catalano, V. J., Lee, J. W., and Olmstead, M. M., *J. Am. Chem. Soc.* **114**, 5455 (1992).
16. (b) Atwood, J. L., Koutsantonis, G. A., and Raston, C. L., *Nature* **368**, 229 (1994).
16. (c) Williams, R. M., Zwier, J. M., and Verhoeven, J. W., *J. Am. Chem. Soc.* **116**, 6965 (1994).