

## SURFACE ACIDITY OF PALYGORSKITE-SUPPORTED RHODIUM CATALYSTS

JUANA HERRERO,<sup>1</sup> JESÚS A. PAJARES,<sup>2</sup> AND CARMEN BLANCO<sup>1</sup>

<sup>1</sup> Departamento de Química, Facultad de Ciencias, Universidad de Cantabria  
39005 Santander, Spain

<sup>2</sup> Instituto Nacional del Carbón, CSIC, Oviedo, Spain

**Abstract**—Infrared spectra of adsorbed pyridine have been used to obtain qualitative information on the nature of the interaction of pyridine with different rhodium catalysts supported on palygorskite and silica. Based on these data, qualitative definitions of the adsorption sites of these catalysts have been deduced. The catalysts were prepared with natural palygorskite, and palygorskite dehydrated *in vacuo* at 150°C and 400°C. In this way, catalysts were obtained that had different water contents and, therefore, different acidities. Lewis-bound pyridine was detected by infrared spectroscopy from room temperature to 500°C. The greatest acidity was found in a catalyst prepared with the palygorskite support dehydrated at 150°C before preparation of the catalyst. With this catalyst, strongly hydrogen-bound pyridine was observed when evacuation was carried out at temperatures between 150°C and 300°C. Catalysts prepared with the palygorskite support pretreated at 400°C did not exhibit strongly hydrogen-bound pyridine, and Lewis acidity decreased significantly. As expected, hydrogen-bound pyridine was also detected for rhodium supported on silica. However, it was desorbed at temperatures below 150°C. The results of the acidity studies follow the same pattern as those for 1-hexene double-bond migration under hydrogenation reaction conditions.

**Key Words**—Pyridine, Catalysis, Palygorskite, Rhodium, Surface acidity.

### INTRODUCTION

The activity and selectivity of a hydrogenating catalyst can be altered significantly by acid centers. For instance, Raythata and Pinnavaia (1983) found greater selectivity in the hydrogenation of 1-hexene with rhodium complexes immobilized in hectorite interlayers as compared to the reaction with a homogeneous catalyst. They attributed this selectivity to displacement of the protonic equilibrium in the reaction mechanism, the protons being due to the acidity of the clay. In carbon monoxide hydrogenation, CO insertion has been described if the catalyst contains Lewis-acid centers (Kellner and Bell, 1981; Ichikawa *et al.*, 1985; Fukuoka *et al.*, 1987). This CO insertion is favored by the formation of  $\mu$ -anchored carbonyls on the border between the metal and the Lewis-acid center.

On the other hand, when a metal that is active in hydrogenation is added to an acid catalyst there is a decrease in the normal levels of the coke deposits, which may produce deactivation of the catalyst. For instance, Matsuda *et al.* (1987) have found that adding a small amount of palladium prevents the deactivation of a pillared montmorillonite catalyst.

Clays used to be employed as acid catalysts in the petroleum industry (Grim, 1988). Recently, they have been used in several hydrocarbon conversions and in organic synthesis (Ballantine *et al.*, 1984; Laszlo and Moison, 1989). In these reactions, catalytic activity has been explained in terms of Brønsted and/or Lewis-acid centers contributing to the reaction mechanism.

To distinguish between Brønsted and Lewis-acid centers, infrared spectroscopy of a base chemisorbed on oxides has proven to be a suitable technique (Benesi and Winquist, 1978), particularly when the base is pyridine (Parry, 1963; Knözinger, 1976). The vibrational frequencies for pyridine shift, depending on the type of interaction with the oxide (Knözinger, 1976; Jacobs, 1984). The three forms of interaction are: 1. hydrogen bonding with surface hydroxyls, 2. Lewis acid-base interactions of the nitrogen lone pair with electron-deficient sites, and 3. protonation to form pyridinium ion. The technique has also been discussed by Farmer and Mortland (1966). In spite of the absence of the 1550  $\text{cm}^{-1}$  band of the pyridinium ion, they proposed the existence of a deformed pyridinium ion for saponite and montmorillonite *in vacuo* when strongly hydrogen-bound pyridine is formed.

Catalysts with different acidities can be obtained by varying the dehydration temperature (Td) before preparing the catalyst. The Td of an oxide, especially a clay, determines the type and concentration of the hydroxyl groups (Zhakarov and Yermakov, 1979; Lamb *et al.*, 1988), and thereby its acidity.

We have prepared heterogeneous catalysts in which the active hydrogenation species is rhodium and the acid agent is palygorskite, which constitutes the support (Herrero *et al.*, 1990). The catalysts were prepared by dehydrating palygorskite at 150°C or 400°C *in vacuo*, before the support and the hydrogenating species were put in contact. This heating and cooling pretreat-

Table 1. Supports and samples. References correspond to the study of pyridine adsorption by infrared spectroscopy.

Supports	Ref.	Precursors	Ref.	Catalysts	Ref.
silica	Parry, 1963	[Rh]/SiO <sub>2</sub>	This work	Rh <sub>x</sub> /SiO <sub>2</sub>	—
palygorskite	Blanco <i>et al.</i> , 1988	[Rh]/paly	This work	Rh <sub>x</sub> /paly	This work
paly-150	Blanco <i>et al.</i> , 1988	[Rh]/paly-150	—	Rh <sub>x</sub> /paly-150	This work
paly-400	—	[Rh]/paly-400	—	Rh <sub>x</sub> /paly-400	This work

paly-150 and paly-400 denotes palygorskite pretreated *in vacuo* at 150°C and 400°C, respectively.

ment *in vacuo* allowed us to control the water content. This would not have been possible at atmospheric pressure because palygorskite adsorbs water reversibly, if it has been evacuated at 150°C, and irreversibly if it has been evacuated at 400°C.

The catalysts prepared were active in the hydrogenation of 1-hexene. Since the isomerization of 1-hexene is considered as a suitable reaction to study the activity of acid catalysts (Abbot *et al.*, 1985), we present the results of the double-bond migration of 1-hexene under hydrogenation conditions. In addition, the adsorption of pyridine on some of these catalysts was followed by means of infrared spectroscopy, showing the important influence of the pretreatment conditions, particularly the Td of the clay, on the acidity of a clay catalyst.

## EXPERIMENTAL

### Materials

Palygorskite is a fibrous clay whose tetrahedral-octahedral-tetrahedral layers, analogous to those of sepiolite, are discontinuous, with channels along the fiber axis (Bradley, 1940). The palygorskite used was from the deposit at Serradilla, Cáceres, Spain. A <2- $\mu$ m fraction was provided by TOLSA, SA. Detailed properties of this palygorskite have been described, and acid properties have been studied by means of infrared spectroscopy of pyridine adsorption in previous papers (González *et al.*, 1989; Blanco *et al.*, 1988). Palygorskite pretreated *in vacuo* at 150°C and 400°C, called paly-150 and paly-400, respectively, lost 14% and 20% w/w due to water.

The catalysts were prepared in two stages. First, an organometallic, cationic rhodium complex, [Rh(nbd)(Me<sub>2</sub>CO)<sub>x</sub>]ClO<sub>4</sub> (nbd=2,5-norbornadiene), was reacted with the natural or dehydrated support in acetone solution at room temperature under an inert atmosphere. The resulting solid is called the precursor and is denoted [Rh]/support. Second, the precursor was reduced with hydrogen in acetone solution at atmospheric pressure and room temperature. At this stage, rhodium metal particles formed and the resultant solid, denoted Rh<sub>x</sub>/support, is the catalyst. Rhodium metal loading varied between 0.6 and 1%. Details of the synthesis and characterization of the samples are described elsewhere (Herrero *et al.*, 1990). The oxidation state of rhodium was three or one for precursor samples, and

zero for catalyst samples, as deduced from X-ray photoelectron spectroscopy (XPS). A list of precursors and catalysts is given in Table 1.

### Adsorption of pyridine

Self-supported wafers of ~5 mg/cm<sup>2</sup> (for catalysts with palygorskite support) and ~30 mg/cm<sup>2</sup> (for catalysts with silica support) were placed in a quartz sample holder. This sample holder is part of an evacuable Pyrex infrared cell with CaF<sub>2</sub> windows, coupled to a 10<sup>-5</sup> Torr vacuum system. The wafers were evacuated for at least 2 hours prior to pyridine adsorption, either at room temperature or at 150°C. The latter temperature was chosen to see if the reversible state of folded palygorskite, which has half of its coordinated water at this temperature (Van Scoyoc *et al.*, 1979), is also observed in precursors and catalysts. Afterwards, the sample was exposed to pyridine at its room temperature vapor pressure. After 30 minutes' exposure, and subsequent evacuation at room temperature, the infrared spectrum was registered. Finally, new spectra were recorded after 2 hours of evacuation at various temperatures from 100°C to 500°C.

Infrared spectra in the 4000–1100 cm<sup>-1</sup> range were taken at the beam temperature, 35°C, using a Perkin-Elmer 577 spectrometer equipped with a wedge attenuator in the reference beam. Abscissa accuracy was  $\pm 4$  cm<sup>-1</sup> from 4000 to 2000 cm<sup>-1</sup>, and  $\pm 2$  cm<sup>-1</sup> from 2000 to 200 cm<sup>-1</sup>. Ordinate accuracy was  $\pm 1\%$  transmittance.

It has been shown (Hughes and White, 1967; Blanco *et al.*, 1988) that it is useful to record the  $\nu$ OH region to help deduce the pyridine bonding. If a  $\nu$ OH band disappears after pyridine adsorption, it is inferred that a pyridinium ion has been formed. If pyridine adsorption results in the disappearance of a  $\nu$ OH band and the simultaneous appearance of another  $\nu$ OH band at a lower frequency, it may be concluded that hydrogen-bonded pyridine has been formed.

The entire surface of palygorskite is accessible to pyridine since the cross-sectional area of this base, 0.313 nm<sup>2</sup> (Kung and Kung, 1985), is less than that of the palygorskite channel, 0.64  $\times$  0.89 nm (González, 1988). The temperatures at which the bands corresponding to the pyridinium ion, coordinated pyridine, or hydrogen-bonded pyridine disappear provide us with a qualitative measure of the strength of the acid sites.

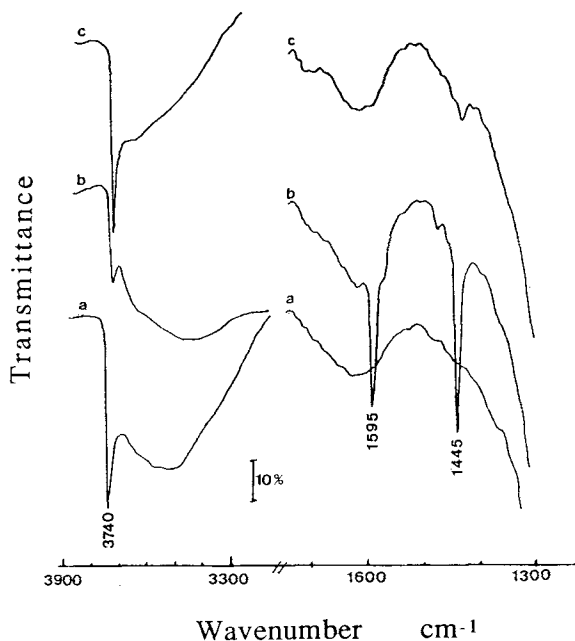


Figure 1. Infrared spectra from pyridine adsorbed on a self-supported wafer of  $[\text{Rh}]/\text{SiO}_2$ . (a) Original sample evacuated at room temperature; (b) after pyridine adsorption and evacuation at room temperature; (c) after evacuation at  $150^\circ\text{C}$ .

At  $100^\circ\text{C}$  or lower, spectra in the  $1600\text{ cm}^{-1}$  region are not easy to see because of the  $1620\text{ cm}^{-1}$  band for water. One of the difficulties in the reproducibility of the experiments was that the number of adsorption-desorption runs had a slight influence on the intensity of some bands, particularly those of the hydroxyl region after evacuation at  $150^\circ\text{C}$ . Another problem was the fact that the vacuum system remained contaminated with pyridine, in spite of efforts to eliminate it after each adsorption with a liquid-nitrogen trap washed after each use. We attempted to adsorb pyridine on a catalyst prepared in the same way with montmorillonite as support (denoted  $\text{Rh}_x/\text{mont}$ ), but failed because of the difficulty in forming wafers with this sample.

#### Hydrogenation of 1-hexene

Experiments were carried out in a round-bottomed flask fitted with a side arm and septum to allow injection and sampling for gas chromatography. The flask was connected to a gas burette that allowed pumping of the system and hydrogen dosing. The catalyst suspension (a quantity equivalent to  $0.02\text{ mM}$  rhodium in  $10\text{ ml}$  acetone) was evacuated in the hydrogenation flask and then  $\text{H}_2$  (at  $1\text{ atm}$ . pressure) was admitted. After one hour of prehydrogenation, 1-hexene ( $2\text{ mM}$ ) was admitted. Isomerization rates to *cis*,2-hexene were followed with a Perkin-Elmer Sigma 3 GC, using a  $\frac{1}{8}\text{ in} \times 4\text{ m}$  column packed with  $15\%$   $\beta\beta'$ -oxidipropionitrile Chromosorb W 80/100 mesh.

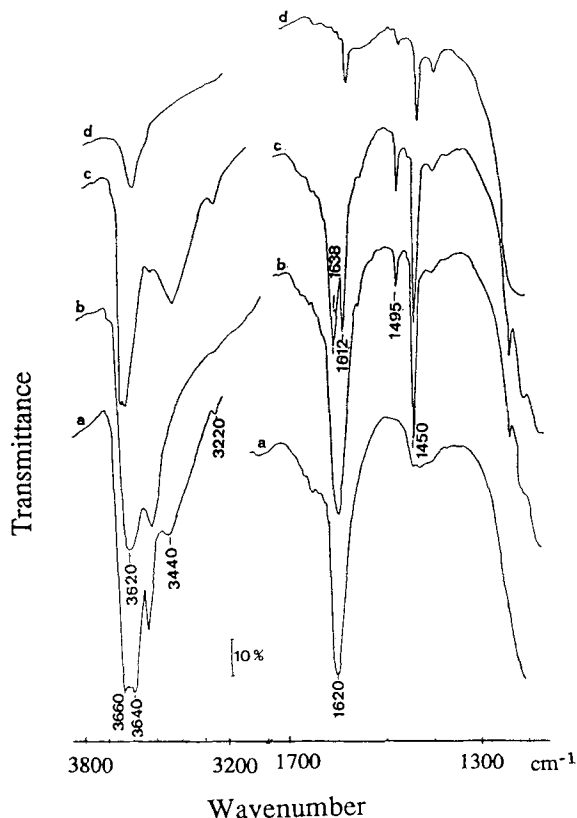


Figure 2. Infrared spectra from pyridine adsorbed on a self-supported wafer of  $\text{Rh}_x/\text{paly-150}$ . (a) Original sample pretreated by evacuation at  $150^\circ\text{C}$ ; (b) after pyridine adsorption and evacuation at room temperature; (c) after evacuation at  $150^\circ\text{C}$ ; (d) after evacuation at  $400^\circ\text{C}$ . (There are no significant differences between the spectra of  $[\text{Rh}]/\text{paly}$ ,  $\text{Rh}_x/\text{paly}$  and  $\text{Rh}_x/\text{paly-150}$  samples.)

## RESULTS

### Pyridine adsorption

$[\text{Rh}]/\text{SiO}_2$ . The spectrum of pyridine adsorbed on this catalyst precursor is shown in Figure 1 (curve b). Bands appear at  $1595$  and  $1445\text{ cm}^{-1}$ , and there is a decrease in the  $3740\text{ cm}^{-1}$  band and formation of a broad band at  $3500\text{ cm}^{-1}$ . These changes are attributed to pyridine that is hydrogen-bound to hydroxyl groups. After evacuation at  $150^\circ\text{C}$ , these bands disappear and only very small bands, at  $1600$  and  $1450\text{ cm}^{-1}$ , remain (Figure 1, curve c).

$[\text{Rh}]/\text{paly}$ . The spectrum obtained from pyridine adsorbed on this precursor is given in Figure 2 (curve b). Bands appear at  $1450$  and  $1495\text{ cm}^{-1}$ . In the region of the hydroxyl groups, an increase is observed in the bands for the coordinated water in palygorskite at  $3510$  and  $3620\text{ cm}^{-1}$ . This masks the bands at  $3660$ ,  $3640$  and  $3610\text{ cm}^{-1}$  corresponding to structural hydroxyls in the folded state (Van Scoyoc *et al.*, 1979). The bands

Table 2. Wave number ( $\text{cm}^{-1}$ ) of bands for pyridine adsorbed on samples [Rh]/paly,  $\text{Rh}_x/\text{paly}$  and  $\text{Rh}_x/\text{paly-150}$ . OH (structural) denotes OH coordinated to octahedral cations inside the structure. The 3510, 3620 and 1620  $\text{cm}^{-1}$  bands of the coordinated water at 20°C disappear at 150°C *in vacuo*.

	At 20°C, unfolded paly	At 150°C, folded paly
$\delta\text{H}_2\text{O}$	1620	—
$\nu\text{OH}(\text{H}_2\text{O})$	3510, 3620	—
$\nu\text{OH}$ (structural)	—	3660, 3640
$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{Si-O-Si, Si-O-Al} \end{array}$	—	3440, 3220
Bpy	—	1638
Lpy + Bpy	1495	1495
Lpy	1448	1450
Lpy	1612	1615
$\text{Mn}^+(\text{H}_2\text{O})\text{-py}$	1225	1230
H-py	1595	—

at 3430–3440 and 3220–3230  $\text{cm}^{-1}$ , described for folded palygorskite (Blanco *et al.*, 1988) also disappear. These changes suggest that the adsorption of pyridine on the inner surface of palygorskite has caused the folded palygorskite to return to its initial unfolded state.

After evacuation of this precursor at 150°C, the following spectral features are observed (spectrum c, Figure 2): 1. the water bands disappear,  $\delta\text{H}_2\text{O}$  at 1620  $\text{cm}^{-1}$  and  $\nu\text{OH}$  at 3620  $\text{cm}^{-1}$  and 3510  $\text{cm}^{-1}$  (Serna *et al.*, 1977; Blanco *et al.*, 1988). This does not occur for palygorskite itself, even at temperatures higher than 400°C *in vacuo* (Van Scoyoc *et al.*, 1979; Blanco *et al.*, 1988). 2. Two bands appear at 1638 and 1612  $\text{cm}^{-1}$  that are assigned to pyridinium ion and Lpy (Lewis-bound pyridine), respectively. Note the absence of a band in the 1550  $\text{cm}^{-1}$  region that would normally accompany the one at 1638  $\text{cm}^{-1}$ , both described for pyridinium ion. A slight increase is observed in the frequencies of the bands assigned to Lpy at 1612, 1495 and 1450  $\text{cm}^{-1}$ . 3. The bands for the structural hydroxyls (3660, 3640  $\text{cm}^{-1}$ ) and those for hydrogen bound

to the oxygen of the  $\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{Si-O-Si and Si-O-Al} \end{array}$  linkages (3440, 3220  $\text{cm}^{-1}$ ) reappear. The two latter bands are much more intense than those in the original sample.

Pyridine readsorption leads to the same spectrum in the hydroxyl region as for the original sample; the water bands are recovered. This process of adsorption-desorption of pyridine is reversible, as described for palygorskite (Blanco *et al.*, 1988). There is a correspondence between the appearance (disappearance) of bands in folded palygorskite and their disappearance (appearance) in unfolded palygorskite (Table 2).

After evacuation at 300 and 500°C, the hydroxyl region of the spectra is as in palygorskite under the same conditions. The bands assigned to Lpy, at 1612, 1495 and 1450  $\text{cm}^{-1}$ , persist after treatment at 500°C, but with lesser intensity (Figure 2, spectrum d).

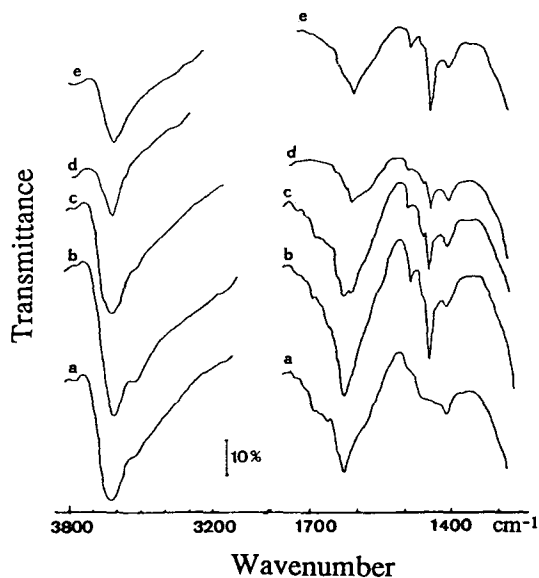


Figure 3. Infrared spectra of pyridine adsorption on  $\text{Rh}_x/\text{paly-400}$ . (a) Original sample evacuated at 150°C; (b) after pyridine adsorption and evacuation at room temperature; (c) after evacuation at 150°C; (d) after evacuation at 400°C; (e) after readsorption of pyridine.

After pyridine had been adsorbed (i.e., after spectrum c) water adsorption was performed on the sample in two ways. 1. When water adsorption at room temperature was followed by evacuation, all pyridine was replaced by water and the original spectrum of palygorskite was registered. An analogous replacement of pyridine by water at room temperature has been described under different conditions, except for temperature, for other clays (Farmer and Mortland, 1966; Adams *et al.*, 1975). 2. When water was adsorbed at 150°C, part of the Lewis-acid centers was converted into Brönsted-acid centers, as has been described by Rupert *et al.* (1987). There was a decrease in the 1450  $\text{cm}^{-1}$  band and a new, small band at 1550  $\text{cm}^{-1}$  appeared. The 1638  $\text{cm}^{-1}$  band was not observed, due to the fact that this band, if it existed, was superimposed on the broad water band. The pyridinium ion formed was weakly bound because it disappeared after evacuation at room temperature. The enhancement of Brönsted acidity by the addition of water has frequently been observed with solid acids.

*Rh<sub>x</sub>/paly.* We have not observed significant differences in the wave numbers of the bands registered for pyridine adsorbed on this sample and those of [Rh]/paly, its precursor. Nevertheless, the  $\text{Rh}_x/\text{paly}$  1638  $\text{cm}^{-1}$  band, and its accompanying bands in the hydroxyl region at 3440 and 3220  $\text{cm}^{-1}$  persist at higher evacuation temperatures (up to 300°C) than the corresponding precursor.

Table 3. Rate of *cis*,2-hexene formation by Rh/support catalysts.<sup>1</sup>

Support	% Rh	Catalyst mg	Rate of <i>cis</i> ,2-hexene formation mol <i>cis</i> ,2-hexenemol <sup>-1</sup> (Rh)min <sup>-1</sup>
SiO <sub>2</sub>	0.65	344	2.6
paly-400	0.95	211	7.7
mont	1	210	7.7
paly	0.85	257	8.5
paly-150	0.95	211	12

<sup>1</sup> Reaction conditions: 1-hexene, 2 mM; catalyst, 0.02 mM of Rh; volume of acetone solution, 10 cm<sup>3</sup>; temperature, 20°C; P<sub>H<sub>2</sub></sub>, 1 atm. Calculated from GC chromatography data assuming all rhodium is on the surface of the support.

*Rh<sub>x</sub>/paly-150*. Qualitatively, the results of pyridine adsorption for this catalyst are similar to those of the two previous samples. However, after pyridine adsorption and evacuation at 150°C the spectrum of this sample shows a cleaner split between the bands at 1638 and 1612 cm<sup>-1</sup>.

All three catalysts and precursor supported on palygorskite ([Rh]/paly, Rh<sub>x</sub>/paly and Rh<sub>x</sub>/paly-150) had more intense bands at 3440, 3220, 1612 and 1495 cm<sup>-1</sup> than those observed for palygorskite alone in an analogous study (Blanco *et al.*, 1988). In addition, since the bands at 1612 and 1495 cm<sup>-1</sup> remained more intense at 300°C for these three samples than for the support alone, we propose that the number and strength of acid centers are greater in these three samples than in palygorskite.

*Rh<sub>x</sub>/paly-400*. Spectra for pyridine adsorbed on this catalyst are shown in Figure 3 (curve b). Only bands corresponding to Lpy appear. These bands are of lesser intensity and disappear at lower temperatures than the corresponding bands of the preceding samples. Nevertheless, bands attributed to Lpy still appear in the spectrum even when the sample is evacuated at 400°C (Figure 3, curve e).

#### Double bond migration of 1-hexene

The rates of *cis*,2-hexene formation by the different catalysts are shown in Figure 4 and Table 3. The conversion of 100% 1-hexene to *n*-hexane was achieved in a few minutes (2–7 minutes depending on the catalyst used), under the conditions described (Herrero *et al.*, 1990). The maximum quantity of *cis*,2-hexene was produced by Rh<sub>x</sub>/paly-150 and the minimum by Rh<sub>x</sub>/SiO<sub>2</sub>, which yielded an insignificant amount. It was necessary to make certain assumptions in order to obtain these values. The rates of conversion to *n*-hexane were calculated only for the first minute, although the conversion rate after this first minute varies for different catalysts. In addition, for a good comparison, it would be necessary to know the rhodium dispersion. Nevertheless, the sequence of these catalysts in relation to their activity in the double-bond migration is the

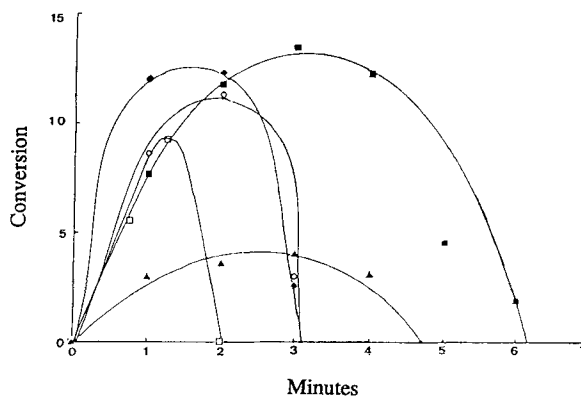


Figure 4. Isomerization of 1-hexene to *cis*,2-hexene by Rh<sub>x</sub>/support. Reaction conditions: 1-hexene, 2 mM; Rh, 0.02 mM; P<sub>H<sub>2</sub></sub>, 1 atm.; volume of acetone solution, 10 cm<sup>3</sup>; room temperature. The curves correspond to different supports: ▲ SiO<sub>2</sub>; □ palygorskite evacuated at 400°C; ◇ palygorskite; ◆ palygorskite evacuated at 150°C; ■ montmorillonite. Palygorskite and montmorillonite are not active under these conditions.

same as for the increase and strength of the acid centers monitored by pyridine adsorption.

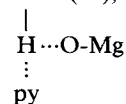
## DISCUSSION

### Hydrogen-bound pyridine

Interaction between the hydroxyl groups of an oxide and pyridine is the weakest of the three modes of adsorption. Consequently, pyridine can be pumped off readily (Parry, 1963; Kung and Kung, 1985). For the [Rh]/SiO<sub>2</sub> catalyst, the only form of interaction observed was pyridine hydrogen-bound to the hydroxyl groups of silica. The same interaction at the same temperature was described by Parry (1963) for silica. We have not observed bands that would correspond to Lpy species, with rhodium being the Lewis-acid center. The absence of Lpy may be due to the fact that the quantity of rhodium is too small to be detected by this method. On the other hand, the adsorption properties of a catalyst with a silica support in powder form could be different from those of pelleted samples.

### Strongly hydrogen-bound pyridine

In the temperature range between 150°C and 300°C, the presence of hydroxyls strongly bound to pyridine by hydrogen is detected in the spectra of samples with paly and paly-150 supports, especially since the latter support provides better splitting of the 1638 and 1612 cm<sup>-1</sup> bands. The νOH vibrations of hydroxyls with bands at 3440 and 3220 cm<sup>-1</sup> are probably due to a bond with pyridine,



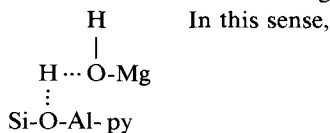
formed pyridinium ion in the sense of Farmer and

Mortland (1966). This deformed pyridinium would be indicated by bands at 1638, 1495 and 1230  $\text{cm}^{-1}$  (Table 2).

Pyridine forms a much stronger hydrogen bond with the hydroxyl groups of palygorskite than it does with silica. Consequently, a temperature greater than 200°C is necessary to remove it. Moreover, the band at 1595  $\text{cm}^{-1}$ , which in the samples supported on silica corresponds to an O–H–py bond, does not appear in the spectra of the palygorskite samples. Thus, it appears that the hydrogen bonding of pyridine with the palygorskite samples is different from that described in the literature for silica and other oxides (Parry, 1963; Kung and Kung, 1985).

The nature of the hydrogen bonding of pyridine is centered on the assignment of the 1638  $\text{cm}^{-1}$  band. There are two different species that may account for this band. On the one hand, it could correspond to the bending frequency of coordinated water,  $\delta\text{H}_2\text{O}$ , shifted to higher wave numbers due to the strong hydrogen bond (bands at 3420 and 3220  $\text{cm}^{-1}$ ). Ryskin (1974) found an increase in the bending frequency of water when there is a hydrogen bond in aquocomplexes of other minerals. On the other hand, it could correspond to a deformed pyridinium ion involved in a hydrogen bond, in which the proton is out of the plane of the ring. Consequently, the  $\nu_{19b}$  of the pyridinium ion, at 1550  $\text{cm}^{-1}$ , which reflects in-plane N–H bending, does not appear. Such a deformed pyridinium ion has been described by Farmer and Mortland (1966), who found that water cannot be removed from  $\text{Mg}^{2+}(\text{HOH}, \text{NC}_5\text{H}_5)$  in Mg-montmorillonite; residual water molecules ionize to give pyridinium ions on heating in a vacuum. In palygorskite, the so-called coordinated water is bound to octahedral Mg on the edges of the structure. Thus, based on the study of Farmer and Mortland (1966), it seems possible that a deformed pyridinium ion could be formed. Although the two possibilities discussed above are different, they both involve strongly hydrogen-bound pyridine.

However, these hypotheses must be viewed with caution because another process, due to pyridine adsorption itself, may simultaneously enhance surface acidity. It has been shown that pyridine adsorption can change the strength of acid centers. Pyridine coordinated to Lewis-acid centers near the oxygen of the tetrahedral layer can increase its donor capacity (Flockart *et al.*, 1967; Jacobs, 1984). The result would be a polarization of the coordinated water to octahedral Mg or to exchange cations:



the spectra show that the bands assigned to water polarization at 3420 and 3220  $\text{cm}^{-1}$  are more intense after two pyridine adsorptions than after one.

When the evacuation temperature is increased, the amount of strongly hydrogen-bound pyridine reaches a maximum at 150°C, and declines thereafter as the surface approaches dehydration. At this acidity maximum, when the palygorskite contains one of its two molecules of coordinated water, the spectra registered for catalysts  $\text{Rh}_x/\text{paly}$  and  $\text{Rh}_x/\text{paly}-150$  suggest interesting catalytic properties. The results of the double-bond migration reaction show the same qualitative trend. The catalyst with highest acidity is  $\text{Rh}_x/\text{paly}-150$ . The rate of *cis*,2-hexene formation at room temperature by  $\text{Rh}_x/\text{paly}-150$  is significantly higher than that of the other catalysts. The lack of strongly hydrogen-bound pyridine on  $\text{Rh}_x/\text{paly}-400$  is due to the absence of coordinated water in this catalyst. As a consequence of its lower acidity, this catalyst has greater donor capacity.

#### Pyridine bound to Lewis centers

Lewis-acid centers are found in all catalysts and precursors supported on palygorskite. The fact that the intensity of the bands assigned to Lpy is lower for  $\text{Rh}_x/\text{paly}-400$  than for the other catalysts may seem paradoxical. With alumina, or other more common supports (Hughes and White, 1967), the concentration of Lewis-acid centers increases when the temperature is increased. The Lewis-acid centers in the catalysts that we have prepared are tetrahedral Al, octahedral Al on the edges of the structure, exchange cations, and rhodium. After treatment at 400°C, the exchange cations may migrate into the hexagonal holes. Hence, they would be saturated and no longer behave as Lewis-acid centers. This migration of cations with increasing temperature has been found in montmorillonite (Farmer, 1974).

It is worth noting that there is no significant difference in relation to pyridine adsorption between the precursor designated  $[\text{Rh}]/\text{paly}$  and the catalyst,  $\text{Rh}_x/\text{paly}$ . The oxidation states, as determined by XPS, for rhodium in the precursor and catalyst are three and zero, respectively (Herrero *et al.*, 1990). Therefore, the oxidation state of rhodium does not significantly influence the wave number of the 8a vibration (1612  $\text{cm}^{-1}$ ) of Lpy. For organometallic rhodium complexes with pyridine and related ligands the  $\nu_{8a}$  (Pinilla *et al.*, 1980) appears near the same wave number (1592–1618  $\text{cm}^{-1}$ ). It does not seem possible to establish a correspondence between band position and the metal cation (aluminum, exchange cation, or rhodium) to which pyridine is coordinated, and its charge. Kung and Kung (1985) found the same lack of correspondence for other transition metal cations.

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