APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2002; **16**: 84–93

Preparation of rhodium catalysts on laminar and zeolitic structures by anchoring of organometallic rhodium

C. Blanco*, R. Ruiz, C. Pesquera and F. González

Dpto. de Ingeniería Química y Química Inorgánica, Universidad de Cantabria, Avda. de los Castros s/n, 39005 Santander, Spain

Received 18 April 2001; Accepted 15 October 2001

Rhodium catalysts supported on six different aluminosilicate structures were prepared by hydrogen reduction of a cationic organometallic rhodium complex anchored to the support. The *precursor* active phase was incorporated in acetone medium through ion exchange using $[Rh(Me_2CO)_x(NBD)]ClO_4$ as the metal precursor species, in which NBD is 2,5-norbornadiene and $(Me_2CO)_x$ is acetone. The effect of the structure and characteristics of the support on metal load and dispersion was studied in the heterogeneous catalysts thus prepared. The supports were characterized by X-ray diffraction, energy-dispersive X-ray analysis, volumetric adsorption and surface acidity. For the precursors and catalysts, the metal load was determined by UV–VIS spectra, the reduction temperature was determined by differential scanning calorimetry, and rhodium dispersion was measured by chemisorption. The structure of the materials used as supports had a great influence on the catalyst prepared. A higher metal content was achieved in the supports with laminar structures, whereas better dispersion was shown by the catalysts supported on zeolitic structures.

KEYWORDS: organometallic rhodium; montmorillonite; zeolitic products; catalyst preparation

Zeolites and zeolitic materials have an increasing role in heterogeneous catalysis, and are widely applied in large-scale industrial processes. Developments in the synthesis and characterization of zeolites have favored the design of materials that efficiently accelerate the reaction and which, therefore, help to achieve favorable thermodynamics and rates, as well as controlling the selectivity of a chemical reaction.[1]

Activity, selectivity and durability are characteristics that favor the use of heterogeneous catalysts in a wide range of chemical reactions under different pressure and temperature conditions. In view of their characteristics, natural and synthetic aluminosilicates have been used as catalysts and heterogeneous catalysts for a great number of active phases.[2] In addition, clays and zeolites have advantages as supports because they are chemically and physically robust, and inexpensive. Clays can easily be modified to improve their catalytic properties. For instance, in smectites, interlayer spacing can be adjusted by introducing substituents, by pillaring or solvent swelling, or even by transformation to new structures, and the acidic nature of the structure can also usefully be altered to improve their selectivity.[3] In any aluminosilicate, the porous structure provides a high surface area that enables it to receive high charges of a well-dispersed active component. Therefore, the industrial efficacy of aluminosilicates results from a combination of porosity and mechanical resistance.

Zeolites and zeolite-like products have regular pore and cage dimensions, which makes them different from other aluminosilicates. Most of the active sites are located in the molecular size pores and cages so that, during the reaction, the transforming molecules are subjected to steric limitations imposed by the zeolitic structure. This may change the course of the reaction, and product distributions are different from those obtained in the homogeneous phase. Hence these products possess molecular sieving properties, which is relevant in shape-selective catalysts.

The catalytic behavior of zeolites is also favored by their role as ion exchangers, which makes it possible to introduce a large variety of cations with different catalytic properties into their intracrystalline pore system. Acid sites, metal

---

*Correspondence to: C. Blanco, Dpto. de Ingeniería Química y Química Inorgánica, Universidad de Cantabria, Avda. de los Castros s/n, 39005 Santander, Spain.
E-mail: blancoc@unican.es
Contract/grant sponsor: Dirección General de Enseñanza Superior e Investigación y Ciencia; Contract/grant number: PB 98-1107.
Contract/grant sponsor: Comisión de Investigación Científica y Técnica; Contract/grant number: MAT99/1093-CO2-02.

DOI:10.1002/aoc.263

clusters and redox sites may occupy the intracrystalline voids of the zeolite. The presence of different kinds of active center influences the activity and selectivity of a given product. Therefore, the cation exchange capacity and crystallinity of zeolites make them particularly suitable for multifunctional catalysis, since they display the cooperative action of at least two chemical functions that perform complex catalytic transformations of molecules.

The combination of sieving properties and the location of the active sites in the pores (essential in shape-selective catalysis) enhances the catalytic activity of a given zeolite in a particular reaction.

The advantages of zeolites over other solids are, according to Espeel *et al.*,[4] their great acid strength and practically unlimited applicability to different types of catalysis. The main weaknesses are that they are very sensitive to deactivation by irreversible adsorption or pore blockage by heavy products, and also the incompatibility in size of molecules resulting from the fine chemicals area and the cages of the micropores.[4]

Metals supported on zeolites are prepared by incorporating the transition metal either by cation exchange or an impregnation procedure and then reducing the transition metal. The design of the supported catalyst is based mainly on the knowledge of the interaction and location of the active phase on the support. The metal dispersion in the catalyst depends on a number of factors, such as the textural characteristics of the support, the metal precursor used and the method of deposition selected, which influences the metal–support bond. The way the metal precursor is inmobilized and its subsequent activation[5] are of great importance, especially when metals from the platinum group are used. The high cost of these catalysts makes it necessary to optimize their catalytic yield and maximize the dispersion of the metal component, since the rate of chemical reaction is, in general, proportional to the number of surface metal atoms available. Highly disperse catalysts, containing small metal crystallites, have a high activity per gram of catalyst, and, therefore, a greater yield can be achieved.

Weitkamp *et al.*[6] have described the preparation of noble-metal clusters in different small-pore molecular sieves, *via* solid-state ion exchange. However, the synthesis of catalysts by the anchorage of organometallic complexes from organic media is poorly documented. In this study, we approached the problems in catalyst preparation by analyzing the influence of the structural characteristics of zeolites synthesized in a seawater medium[7] on their adsorption capacity, activation conditions and localization of their active centers.

In this study, the heterogeneous catalysts were prepared by anchoring an organometallic species to the support through ion exchange, as described previously[8–11] and based on the early work of Yermakov and Kusnetsov.[12] The addition of the precursor through ion exchange favored the stabilization of the metal against agglomeration inside the cavities of the zeolite. The activation process took place under mild conditions, and provided good dispersion and a small metal particle size for the catalyst.[13,14]

The aim of the study was to determine the effect of the textural and chemical characteristics of zeolitic products synthesized from a Spanish montmorillonite by alkaline treatment in a seawater medium and used as supports in heterogeneous catalysts. These products were tested for suitability against products prepared in the same way in distilled water medium and also with a pillared montmorillonite and with a purified sodium montmorillonite.

The study analyzed the influence of the support characteristics on the properties of the catalysts, which were prepared in an acetone solution by ion exchange with a cationic organometallic complex. Supports with different structures and textural characteristics were used to prepare the rhodium catalysts. We expected a substantially different rhodium–support interaction and, therefore, a different final metal dispersion in the laminar and zeolitic compounds.

EXPERIMENTAL

Supports

Supports were prepared from a montmorillonite supplied by GADOR,[15] designated BENa, after collecting the fraction below 2 μm and homogenization with NaCl. This material was used to synthesize a pillared clay and zeolitic products. The pillared clay was prepared by methods described elsewhere[16–18] using polyoxycations of aluminum and is designated BENPIL. The zeolitic materials were obtained through alkaline treatment of the montmorillonite.[7] In each case, 15 g of the starting montmorillonite was suspended in 100 ml of 6 M NaOH solution. The conditions of treatment and the media employed as solvent varied. When the medium was seawater the samples are denominated ZESE, and when distilled water was used, ZEDI. To designate the two conditions tested: a final P is added when the reacting mixtures were kept in an autoclave at 160 °C at autogeneous pressure for 24 h without stirring; a final X is added when the treatment took place at boiling point, using a reflux system with continuous stirring for 24 h. The samples were washed in dialysis membranes, oven dried at 105 °C, powdered and kept in a desiccator. The final products were, therefore, denoted: ZESEP, ZEDIP, ZESEX and ZEDIX.

Characterization of the samples was done by the following techniques. Powder X-ray diffraction (XRD) was performed in a Philips PW 1710 diffractometer, with Cu Kα radiation ($\lambda = 1.54178$ Å) at 40 kW and 25 mA. Energy-dispersive X-ray analysis (EDXRA) was carried out with a Jeol electron microscope (model JSM-T 330A) with a Link Analytical AN 10,000 microanalyzer. Specific surface area S_{BET} was determined from nitrogen adsorption isotherms at 77 K, using Micrometrics ASAP-2000 equipment.

The pyridine adsorption method was used to identify the nature and character of the surface acidic groups of supports, precursors and catalysts. IR spectra were obtained in an FTIR spectrophotometer, with diffuse reflectance, Perkin–Elmer Spectrum 2000, in the 4000–370 cm^{-1} range. Samples were degassed at 200 °C and then exposed to pyridine vapor. IR spectra were recorded after heating the samples at 35, 100, 200, 300 and 400 °C. IR spectra registered the desorption of pyridine, providing information not only of the kinds of acid center but also of their strength.

Catalysts

Catalysts were prepared by ion exchange, using acetone as the suspension agent (Me_2CO = acetone). The amount of metal incorporated is conditioned by the adsorption capacity of the support, which is related to the physical and chemical characteristics of the support surface. Support and solutions were used in the appropriate quantities to obtain metal loadings of 1 and 2.5 wt% assuming adsorption to be complete on the supports.

The precursor of the active phase used was a cationic rhodium complex, which was prepared by reacting $[Rh(NBD)Cl]_2$ (NBD = 2,5-norbornadiene) and $AgClO_4$ in acetone solution. After stirring for 50 min in the absence of light under argon, the solution was filtered through Kieselguhr, and the filtrate, corresponding to the rhodium complex $[Rh(Me_2CO)_x(NBD)]ClO_4$, was collected, as described previously.[8–11] The reaction that takes place is:

$$[Rh(NBD)Cl]_2 + 2AgClO_4 \xrightarrow[25\,°C]{(Me_2CO)_x,Ar} 2[Rh(Me_2CO)_x(NBD)]ClO_4 + 2AgCl\downarrow \quad (1)$$

The support was suspended in the above-mentioned filtrate, which contained the cation rhodium complex $[Rh(Me_2CO)_x(NBD)]^+$. The suspension was stirred in the absence of light under argon. After 7 days the resultant solid, denominated [Rh-x]/support (x indicates the theoretical percentage of incorporated rhodium), was filtered. The solid precursor was dried and kept in a desiccator. The schematic reaction is:

$$[Rh(Me_2CO)_x(NBD)]ClO_4 + (CE)support \xrightarrow[25\,°C]{(Me_2CO)_x,Ar} [Rh\text{-}x]/support(precursor) + (CE)ClO_4 \quad (2)$$

where CE denotes cation exchange in supports.

The amount of rhodium loaded was determined by UV–VIS spectroscopy (λ_{max} = 385 nm) as the difference between the metal concentration in the filtered liquid and that in the initial suspension. Measurements were made in a UV–VIS-MIR Perkin–Elmer Lambda-9.

Catalysts were prepared by decomposition and reduction of [Rh-x]/support (precursor) in flowing hydrogen, as described below, in the catalytic reactor. The reaction that takes place is as follows:

$$[Rh\text{-}x]/support(precursor) \xrightarrow[T]{H_2} Rh\text{-}x/support(catalyst) \quad (3)$$

The final characteristics of the catalyst depend on the temperature at which reduction takes place. Temperature controls the formation and nucleation of the metallic crystallites and, therefore, their size and distribution. The flow of hydrogen is also important because it affects the sintering of the metal.[12] The reduction and activation of the catalyst were performed under dynamic conditions, so that the reducing gas removes the water formed in the process (see reaction below), thus avoiding inhibition of the reduction of the catalyst and metallic dispersion.[19] Several factors that influence the reduction or activation of the heterogeneous catalysts make it advisable to reduce the catalysts *in situ* before they are used.[20]

The reduction temperature of the catalyst was determined with a SETARAM TG-DSC 111 thermobalance. A sample was heated in an $He + H_2$ gas flow from room temperature to 500 °C at a heating rate of 10 °C min^{-1}.

The metal dispersion is an indication of the efficiency of the incorporation procedure to 'disperse every metal atom' upon the support and thus have all the metal atoms available for reaction. This goal of atomically dispersed metal may not be realized for all cases, and thus the metal may reside as small clusters for which some of the 'interior' atoms are unavailable for reaction. The number of exposed metal atoms divided by the number of total metal atoms of the same kind in the catalyst sample times 100 is the percentage dispersion. Selective hydrogen chemisorption or selective hydrogen/oxygen chemisorption is often used to count the number of exposed metal atoms.

Rhodium dispersion was determined by H_2/O_2 chemisorption. The procedure of Benson and Boudart[21] involves adsorption of oxygen on the reduced metal, followed by hydrogen titration of the chemisorbed oxygen. The proposed stoichiometry is as follows:

$$RhO + \frac{3}{2}H_2 \longrightarrow RhH + H_2O \quad (4)$$

The advantage of this procedure is the Rh/H ratio (1:3), which gives higher sensitivity and, therefore, a smaller error. Measurement was performed with ASAP 2010C V.2.02 chemisorption apparatus.

Acidity in the catalysts was determined with the method described above for the supports.

RESULTS AND DISCUSSION

Characterization of the supports

The changes observed in the composition of the different samples analyzed by EDXRA (Table 1) showed a decrease in the SiO_2/Al_2O_3 ratio after the different treatments. In BENPIL, this is due to the intercalation of alumina pillars, whereas in the zeolitic products it is attributed to the solubility of the silica layer in the alkaline treatment used in their synthesis. The increase in sodium content in the zeolitic samples is a result of the treatment in NaOH. There is also a

Table 1. Ratios for the oxides in the supports, deduced from EDXRA

	BENa	BENPIL	ZEDIP	ZESEP	ZEDIX	ZESEX
SiO_2/Al_2O_3	5.56	3.53	2.90	3.05	3.00	2.86
Na_2O/Al_2O_3	0.36	0.03	1.52	1.51	1.13	1.30
K_2O/Al_2O_3	0.04	0.03	0.01	0.01	0.04	0.03
CaO/Al_2O_3	0.09	0.00	0.19	0.14	0.19	0.25
MgO/Al_2O_3	1.08	0.61	0.85	1.21	0.69	1.00
Fe_2O_3/Al_2O_3	0.10	0.10	0.07	0.10	0.10	0.11

higher Na_2O/Al_2O_3 ratio in the samples treated in the autoclave than in the samples obtained with the reflux method because of the more drastic conditions in the former.

The X-ray diffractograms for the starting montmorillonite and BENa showed the high purity of the sample. The pillaring process was confirmed by the values of the basal spacing $d_{(001)}$ of the montmorillonite intercalated with the corresponding aluminum oligomeric cations. The resulting basal spacing in BENPIL reached 18 Å.

Figure 1 shows the X-ray diffractograms of the zeolitic products. Although sodalite is present in all the samples synthesized, as a result of the NaOH concentration in the reaction mixture,[7] the medium employed is also of great importance because of the presence of anions such as Cl^-. As a result, the reflection peaks of sodalite are more intense in the ZESEP and ZESEX products than in those treated in distilled water.

A milder transformation was obtained in the ZE--X samples. The X-ray diffractograms show the characteristic peak of montmorillonite,[22] and a significantly increased intensity in the peaks associated with what are considered impure products: feldspar and quartz.

Thus a higher transformation is achieved under more severe conditions and in sea water than in their counterpart treatments. In addition, less heterogeneity is observed in the samples undergoing greater transformation.

The specific surface area (Table 2) analyzed by adsorption–desorption isotherms shows an increase in BENa (homogenized montmorillonite) and in the pillared sample. The increase up to 247 $m^2\ g^{-1}$ is related to the creation of micropores in the pillaring process. Of the zeolitic samples, those treated more severely (ZE--P) show values similar to those of the starting material, whereas the ZE--X samples present a slight increase. These results can be attributed to the formation in ZE--P of a structure with a pore size smaller than the nitrogen used in the isotherm analysis, whereas the resulting ZE--X products have a more open structure.

In most studies on the use of clays as catalysts or catalyst

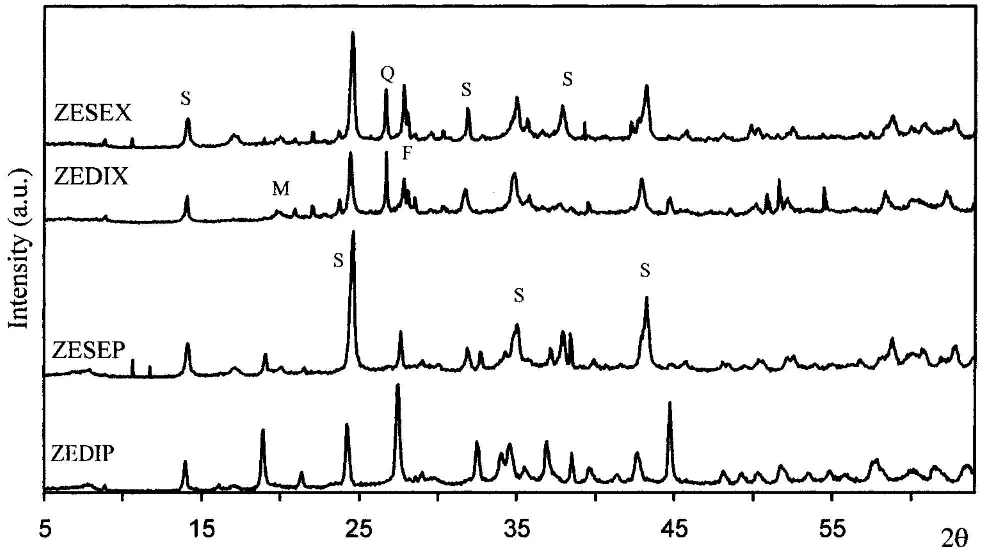


Figure 1. XRD of the zeolitic products synthesized with different treatment conditions and in different media: S = sodalite, M = montmorillonite, F = feldspar, Q = quartz.

Table 2. Specific surface area S_{BET} of the supports

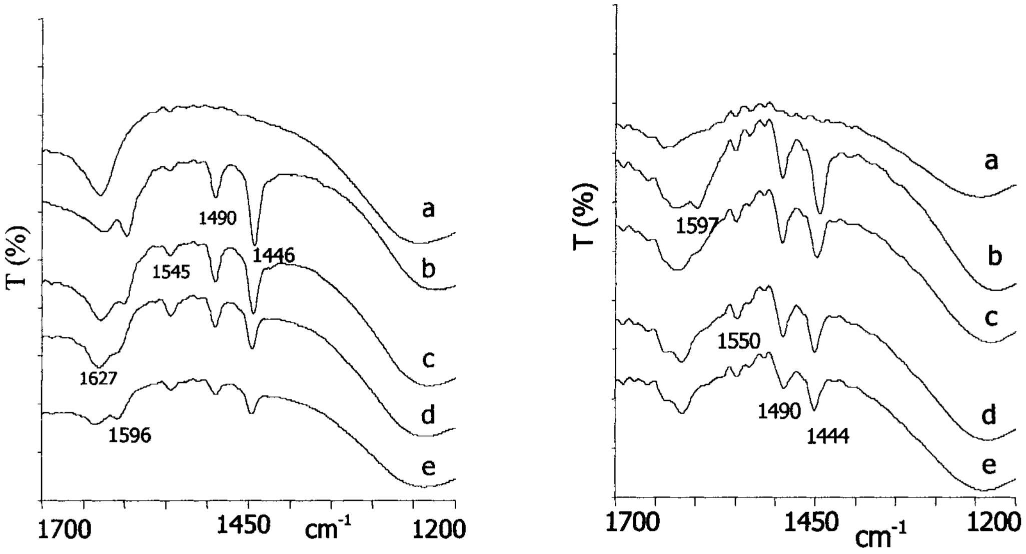
Support	S_{BET} ($m^2\ g^{-1}$)
BENT	64
BENa	87
BENPIL	247
ZESEP	70
ZEDIP	63
ZESEX	97
ZEDIX	90

supports, the surface acidity of the clays has been considered a determinant of their catalytic activity.[23] The importance of the knowledge of the nature, strength and number of acidic centers has been studied by several authors.[24–26] IR spectroscopy of a chemisorbed base is a powerful tool for the characterization of acidic groups in solids, and the use of pyridine was suggested by Parry[27] and Knözinger.[28] Several authors[29–33] have identified the characteristic bands of the pyridine bonds to the acidic centers.

The IR spectra of the supports with laminar structure (BENa and BENPIL) after reversible adsorption of pyridine are shown in Fig. 2. After pyridine saturation at room temperature, the spectra show bands associated with Lewis centers around 1595, 1490 and 1442 cm^{-1}, and others located around 1624 and 1540 cm^{-1} that denote Brönsted centers. Although no acidic Brönsted centers have been detected in sodium-homogenized montmorillonite by other authors using different methods,[30,34,35] the presence of physisorbed pyridine is indicated by the bands at 1600 and 1445 cm^{-1} associated with hydrogen bonds due to coordinated water in the samples. In the IR spectra of BENa [Fig. 2(I)], the intensity of the bands related to Lewis acid centers decreased as temperature increased. There was a parallel increase in the intensity of the bands attributed to Brönsted acid centers when the temperature was raised to 200 °C. The Brönsted acidity of montmorillonite arises from the exchangeable cations, which polarize the coordinated water molecules and produce an acidic proton. Its characteristic bands are easily identified after heating to 300 °C because of the complete loss of coordinated water. This loss is confirmed by the shift of the band of the pyridine bonded to the hydrogen of water molecules from 1597 to 1602 cm^{-1}, characteristic of the direct coordination of the base to exchangeable cations.

The BENPIL spectra [Fig. 2(II)] show slight differences, such as the increase in the strength of Lewis acid centers, with characteristic bands present even at 400 °C. The increase in Lewis acidity may be caused by the restructuring of the pillared clay, in which protonic centers are transformed into Lewis acid centers.

The acid–base properties in zeolites, as in clays, depend on the treatments applied in their modification and on the content in exchangeable cations.[36–38] The study of acidity in zeolitic supports is difficult because of the overlap from 1700 to 1200 cm^{-1} of the characteristic bands of zeolitic structures and those related to acid centers. Moreover, bands identified with acid centers correspond to exchangeable cations that



(I) (II)

Figure 2. IR spectra of adsorption–desorption of pyridine on BENa (I) and BENPIL (II). (a) at 200 °C without pyridine; pyridine desorption after heating at (b) 35, (c) 100, (d) 200 and (e) 300 °C.

are implicated in the formation of both Lewis and Brönsted centers.[39,40] To avoid the overlap of those bands, the spectra shown in Fig. 3 are the result of subtracting the spectrum of the starting sample evacuated at 200 °C and, for this reason, some curve peaks appear as positive, indicating a higher intensity of these bands in the starting sample.

The IR spectra of ZEDIP [Fig. 3(I)] show the characteristic band of Lewis acid centers around 1440 cm^{-1}, the intensity of which increases as the temperature rises. In the spectra of this sample, there is also a significant band at 1590 cm^{-1}, which Jacobs[29] related to Lewis acid centers, although other authors have indicated that it corresponds to pyridine hydrogen bonded to hydroxyls[41] and, therefore, to Brönsted acid centers. When the desorption temperature was increased, this band decreased and at the same time a new band appeared at 3560 cm^{-1} and increased with increasing temperature. This band is associated with the stretching vibration of hydroxyl groups of water coordinated with exchangeable cations. This finding confirms the second hypothesis. In the spectra of ZESEP [Fig. 3(II)] the intensity of the bands of both types of acid center decreased with heating up to 200 °C. The ease of desorption indicates that there were no real Lewis acid centers but that there were bonds between pyridine and exchangeable cations.[39] When

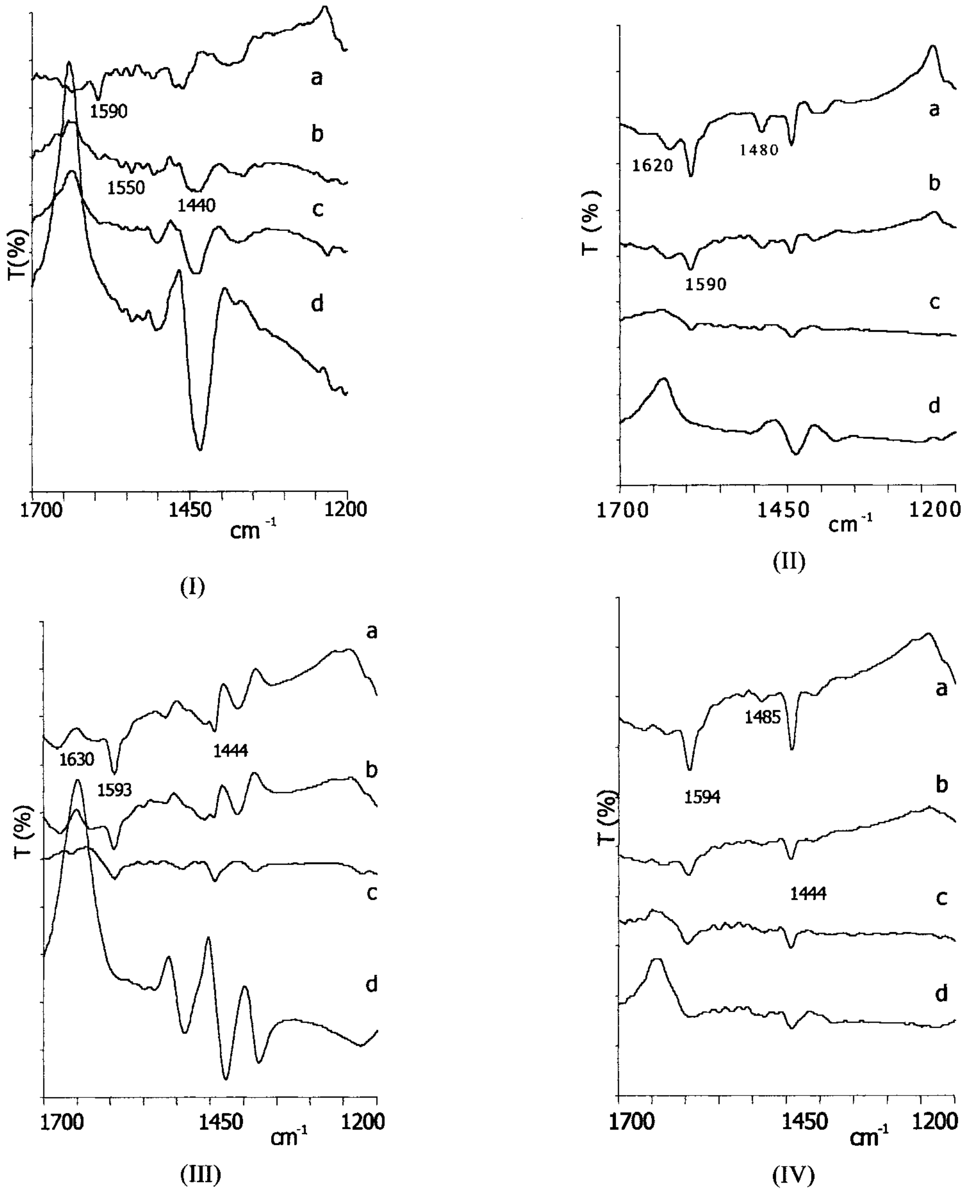


Figure 3. IR spectra of adsorption–desorption of pyridine on ZEDIP (I), ZESEP (II), ZEDIX (III) and ZESEX (IV); pyridine desorption after heating at (a) 35, (b) 100, (c) 200 and (d) 300 °C.

Table 3. Rhodium loading and rhodium dispersion in the heterogeneous catalysts at different reduction temperatures

Catalyst	Rh (%)	Dispersion (%)[a] $T_{red} = 200\,°C$	Dispersion (%)[a] $T_{red} = 300\,°C$
Rh-1/BENa	0.95	48	59
Rh-1/BENPIL	0.97	37	60
Rh-1/ZEDIP	0.93	109	130
Rh-1/ZESEP	0.96	78	108
Rh-1/ZEDIX	0.94	74	100
Rh-1/ZESEX	0.92	63	100
Rh-2.5/BENa	2.42	54	
Rh-2.5/BENPIL	1.86	42	
Rh-2.5/ZEDIP	1.82	115	
Rh-2.5/ZESEP	2.02	121	
Rh-2.5/ZEDIX	2.17	91	
Rh-2.5/ZESEX	1.54	89	

[a] Dispersion (%) = $\frac{N_S}{N_{tot}} \times 100 = \frac{\text{Number of metal atoms exposed at surface}}{\text{Total number of metal atoms present in the catalyst}} \times 100$

the sample was heated to 300 °C the band associated with Lewis acid centers increased and a slight shift occurred. This indicates differences in the environment and/or strength of the Lewis acid sites. The increase was higher in the ZEDIP sample. The ZEDIX spectra [Fig. 3(III)] are very similar to those of the ZEDIP sample although the intensity of the bands was diminished; in contrast, the ZESEX spectra [Fig. 3(IV)] show the high stability of the Lewis acid centers, the corresponding band appearing around 1440 cm^{-1} for all the temperatures tested.

In summary, all the samples have acid centers, whose strength and number vary depending on the particular structure of the constituent materials synthesized. The highest acidity was shown by the pillared clay BENPIL. The analysis of the zeolitic materials showed ZESEX and ZEDIP to have an apparently higher number of centers than their counterparts.

Catalyst characterization

The amount of metal retained in the different supports (when anchoring is by ion exchange) depends on the extent of the interaction between metal precursor and the support, i.e. on the number and strength of anchoring centers, the exchange capacity and the dimension of the channels in zeolites. The values for rhodium loading (Table 3) indicate that when the amount of rhodium was 1% the incorporation of the organometallic cation is almost complete; in contrast, when the amount of rhodium was increased to 2.5% the results differ according to the characteristics of the support. For BENa, the amount of metal incorporated was high regardless of the concentration of the organometallic cation. This can be attributed to the laminar structure of montmorillonites and their swelling capacity. The other supports show limitations in incorporating the rhodium complex, especially when the concentration of the rhodium complex was above 1%. In BENPIL, this may be due to a low cation exchange capacity (as incorporation of the pillaring complex was by ion exchange, this will have reduced the total cation exchange capacity).

The zeolitic products have a different degree of transformation depending on the treatment conditions and media employed in their synthesis, as seen in the characterization of the samples. These differences are reflected in the different metal loads. In these cases, it is necessary to take into account the sieve effect of the channels of these materials and, therefore, the dimensions of a cationic complex that is exchanged will be determined by its accessibility in these channels. The structure and the composition of the zeolitic compounds are more important than the specific surface area, and there is no evident correlation between S_{BET} and metal load.

One important aspect of heterogeneous catalyst preparation concerns determining the reduction temperature for the precursors at which the supported metal presents high activity for a given reaction, since low temperatures preserve the high dispersion attained after metal anchorage. The reducibility of the supported rhodium depends on the metallic species obtained in the reaction between the organometallic complex and the supports.[9,12,42] The differential scanning calorimetry curves in an He + H_2 gas flow for the different precursors are shown in Fig. 4. The precursors prepared on zeolitic supports show a small exothermic peak at around 160 °C, associated with the reduction of rhodium species to the metallic state. The slight exothermic peak in zeolitic precursors and its absence in [Rh-1]/BENa can be explained by the overlapping of processes

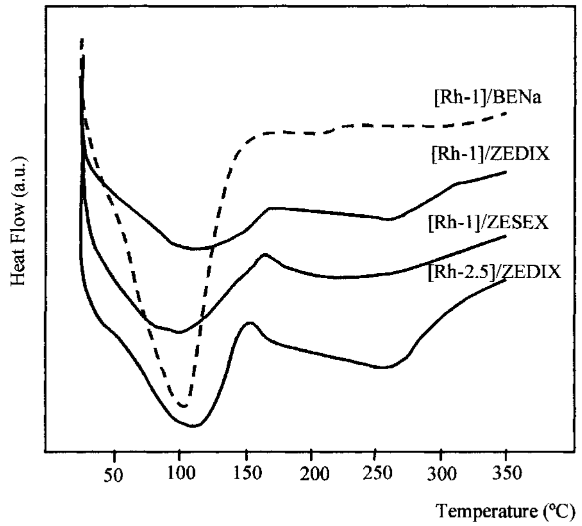


Figure 4. Differential scanning calorimetry curves in an He + H_2 gas flow of the precursors prepared on different supports.

such as the loss of physisorbed water on the zeolitic structure, loss of the water associated with the exchangeable cations, and also the decomposition of the organometallic active phase in the rhodium precursor. A more significant peak, situated at a lower temperature (150 °C), appeared in [Rh-2.5]/ZEDIX; this is due to the higher content of inmobilized metal. These values confirm the results of other authors[42] and show that by working at temperatures above 200 °C the complete reduction of the metal can be achieved.

The dispersion of the metallic phase can be varied by changing the method of metal deposition, the reduction temperature or the water partial pressure over the solid.[43,44] Table 3 shows that the resulting rhodium dispersion is not a function of the metal loading but of the structure of the support and of the reduction temperature. The nature of the support influences dispersion and, therefore, the size of the metallic particles.

The results (percentages of dispersion above 100%) confirm the lack of agreement in proposed stoichiometric values in hydrogen titration.[43,45] Differences depend on the temperature used for activation, because of the presence of incompletely reduced metallic particles, although they may be due to highly dispersed catalysts.[44] Water formation during the process can generate spillover phenomena, which may occur at room temperature.[46–48] The lower values of metal dispersion in all the catalysts when the activation temperature was 200 °C indicate incomplete reduction, whereas using higher temperatures increases the metallic particles exposed on the external surface. Differences in methodology with regard to reduction temperature or the migration of the reduced metal from within the structure to the surface must be considered when explaining the results obtained.

There was no correlation between metallic load and dispersion. Laminar structures (BENa and BENPIL) incorporated larger amounts of rhodium complex but had lower dispersion than the catalysts synthesized on zeolitic products. The influence of the support structure is also reflected in the results for the zeolitic products synthesized with different treatment conditions or in different media, which determine the channel dimensions and the number of anchoring centers in the resulting samples. Higher dispersion was achieved in the more transformed samples, ZE--P, than in ZE--X, and in those synthesized in distilled water (ZEDI-) than in sea water medium (ZESE).

When the theoretical metal load was 2.5% there was no significant increase observed in dispersion values in Rh-2.5/BENa and Rh-2.5/BENPIL, whereas in the heterogeneous zeolitic catalysts almost all the metallic particles were exposed. The results can be explained by the retention of rhodium within the laminar structures, which limits not only reduction but also the accessibility to its measurement.

The values obtained for metallic dispersion are similar to or higher than values reported by others authors[49–51] when the metallic active phase was incorporated by organometallic anchorage on traditional supports such as oxides or activated carbon.

Figure 5 shows the IR spectra of desorption of pyridine from catalysts supported on zeolites after the incorporation of rhodium. There was a decrease in the intensity and thermic strength of the characteristic bands for Lewis and Brönsted centers. All the catalysts under study presented a new shoulder around 1440 cm^{-1}, attributed to Lewis acid centres, thus indicating the presence of new acid centers due to the anchorage of rhodium.

CONCLUSIONS

From the results presented we conclude that the zeolitic materials synthesized are suitable for preparing heterogeneous catalysts by anchoring an organometallic complex by ion exchange.

The amount of metal immobilized and its dispersion depend on the characteristics of the different materials. Whereas the homogenized montmorillonite, BENa, incorporated almost all the rhodium present in the solution, the channel width in zeolites or the limited exchange capacity in BENPIL and zeolitic products resulted in lower values for the amount of cationic complex anchored. On the other hand, the same characteristics that limited the incorporation of the metal complex favored a higher dispersion in the external surface of the heterogeneous catalysts supported on zeolitic materials.

Although the analysis indicated that the reduction of rhodium to metallic species takes place at below 200 °C, complete reduction is reached at higher temperatures. This may be due to the location of the complex in the samples and its accessibility for reduction or to the migration of the

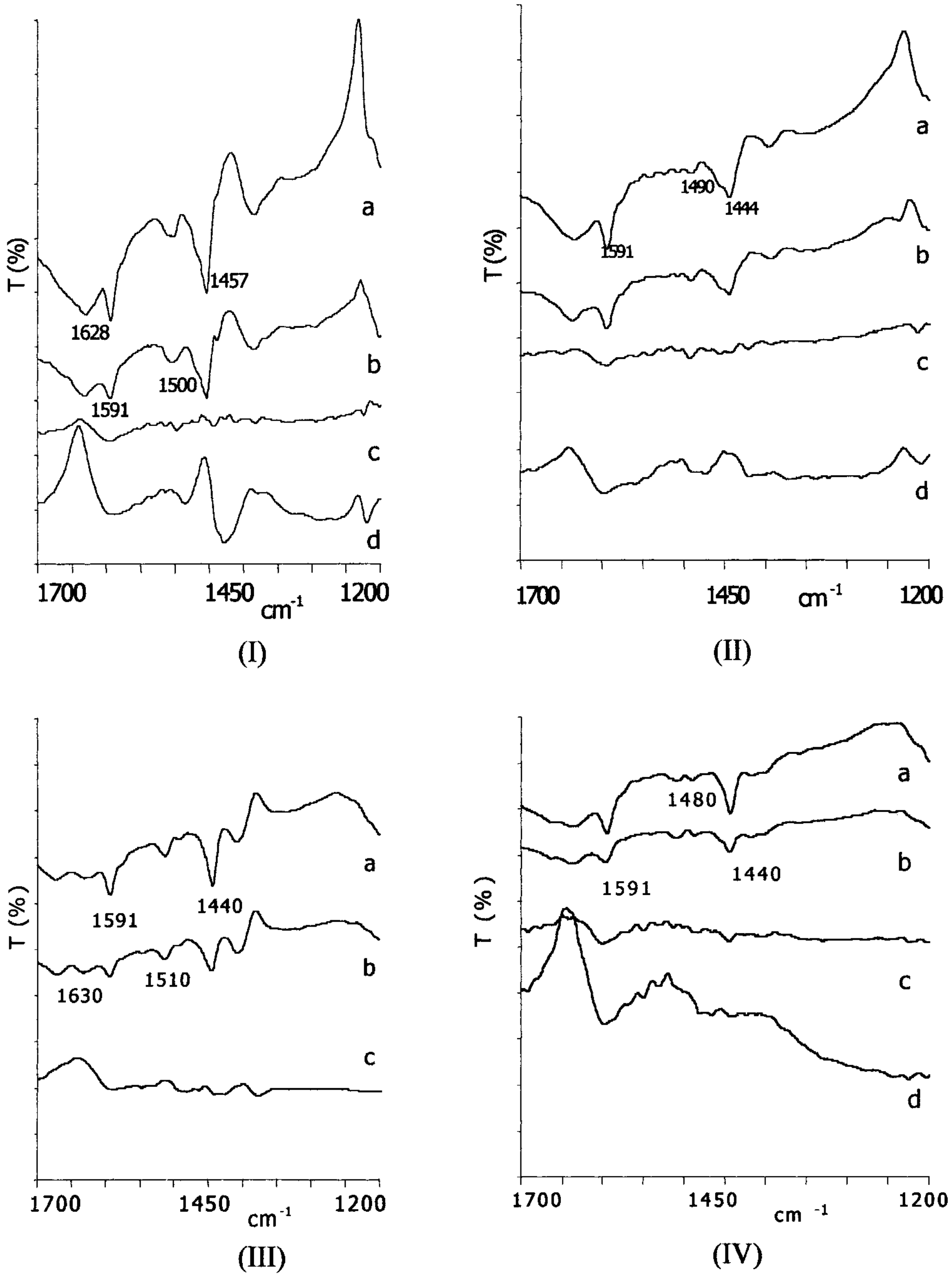


Figure 5. IR spectra of desorption of pyridine on catalysts: Rh-1/ZEDIP (I), Rh-1/ZESEP (II), Rh-1/ZEDIX (III) and Rh-1/ZESEX (IV), after heating at (a) 35, (b) 100, (c) 200 and (d) 300 °C.

complex from within the structure to the external surface with increasing temperature.

Acknowledgements

We wish to acknowledge the support of the DGESIC (Dirección General de Enseñanza Superior e Investigación y Ciencia) and CICYT (Comisión de Investigación Científica y Técnica) of the Spanish government who financed this work under projects Ref.: PB 98-1107 and MAT99/1093-CO2-02 respectively.

REFERENCES

1. Weitkamp J and Puppe L (eds). *Catalysis and Zeolites. Fundamentals and Applications*. Springer Verlag: Berlin, 1999.
2. Gianetto G, Montes A and Rodríguez G. *Zeolitas: Características, Propiedades y Aplicaciones Industriales*. Editorial Innovación Tecnológica EDIT: Universidad Central de Venezuela, Venezuela.
3. Chaloner PA, Esteruelas MA, Joó F and Oro LA. Homogeneous hydrogenation. In *Catalysis by Metal Complexes*, Ugo R, James B

(eds). Kluwer Academic Publishers: Northerlands, 1994; 241–256.

4. Espeel P, Parton R, Toufar H, Martens J, Hölderch W and Jacobs P. In *Catalysis and Zeolites. Fundamentals and Applications*, Weitkamp J, Puppe L (eds). Springer Verlag: Berlin, 1999; 377–429.
5. Brunell JP. In *Preparation of Catalysts II*, Delmon B, Grange P, Jacobs P, Poncelet G (eds). Elsevier Scientific Publishing Co.: Amsterdam, 1991.
6. Weitkamp J, Ernst S, Bock T, Kiss A and Kleinschmit P. In *Catalysis by Microporous Materials. Studies in Surface Science and Catalysis*, Beyer HK, Karge HG, Kiricsi I, Nagy JB (eds). Elsevier, Amsterdam, 1995; 278.
7. Ruiz R, Pesquera C, González F and Blanco C. Proceedings 13th International Zeolites Conference. *Surf. Sci. Catal.* 2001; **135**: 330.
8. Herrero J, Blanco C and Oro LA. *Appl. Organomet. Chem.* 1989; **3**: 553.
9. Herrero J, Blanco C, González-Elipe AR, Espinós JP and Oro LA. *J. Mol. Catal.* 1990; **62**: 171.
10. Herrero J, Blanco C, Esteruelas MA and Oro LA. *Appl. Organomet. Chem.* 1990; **4**: 157.
11. Herrero J, Fernández-Ferreras J, Renedo J, Lasa C, Blanco C and Benito I. *Appl. Catal. A: Gen.* 1992; **86**: 37.
12. Yermakov YI and Kuznetsov BN. *J. Mol. Catal.* 1990; **9**: 13.
13. Pajares JA, Reyes P, Oro LA and Sariego R. *J. Mol. Catal.* 1981; **11**: 181.
14. Herrero J, Blanco C, Prieto C, Dexpert H, Lahoz FJ and García J. *Jpn. J. Appl. Phys.* 1993; **32**(Suppl 2): 484.
15. Ruiz R, Blanco C, Pesquera C and González F. *Appl. Clay Sci.* 1997; **12**: 73.
16. Pesquera C, González F, Benito I, Mendioroz S and Pajares JA. *Appl. Catal.* 1991; **69**: 97.
17. González F, Pesquera C, Blanco C, Benito I and Mendioroz S. *Inorg. Chem.* 1992; **31**: 727.
18. Hernando MJ, Pesquera C, Blanco C, Benito I and González F. *Chem. Mater.* 1996; **8**: 76.
19. Zakharov VA and Yermakov YI. *Catal. Rev. Sci. Eng.* 1979; **19**: 67.
20. Richardson JT. *Principles of Catalysis Development*. Plenum Press: New York, 1989.
21. Benson JE and Boudart M. *J. Catal.* 1965; **4**: 704.
22. Rosenquist ITh. *Nor. Geol. Tidsskr.* 1959; **39**: 350.
23. Blanco C, Herrero J, Mendioroz S and Pajares JA. *Clays Clay Miner.* 1988; **36**: 364.
24. Forni L. *Catal. Rev.* 1973; **8**: 65.
25. Tanabe K. *Solid Acid and Bases*. Kodansha/Academic Press: Tokyo/New York, 1970.
26. Fierro JLG. Chemisorption of probe molecules. In *Spectroscopy Characterization of Heterogeneous Catalysts. Part B*, Fierro JLG (ed.). Elsevier: Amsterdam, 1990.
27. Parry EP. *J. Catal.* 1963; **2**: 371.
28. Knözinger H. *Adv. Catal.* 1976; **25**: 184.
29. Jacobs PA. The measurement of surface acidity. In *Characterization of Heterogeneous Catalysis*, Delannay F (eds.). Marcel Dekker: New York, 1984; 367–404.
30. Farmer VC. *The Infrared Spectra of Minerals*. Mineralogical Society: London, 1974.
31. Little LH. *Infrared Spectra of Adsorbed Species*. Academic Press: London, 1966.
32. Kung MC and Kung HH. *Catal. Rev. Sci. Eng.* 1985; **3**: 425.
33. Occelli ML and Tindwa RM. *Clays Clay Miner.* 1983; **30**: 22.
34. Billigham J, Breen C and Yarwood J. *Clay Miner.* 1996; **31**: 513.
35. Pesquera C, González F, Benito I, Blanco C and Mendioroz S. *Spectrosc. Lett.* 1992; **25**: 23.
36. Corma A, Pérez-Pariente J, Fornes V and Mifsud A. *Clay Miner.* 1984; **19**: 673.
37. Barthomeuf D. *Catal. Rev. Sci. Eng.* 1996; **38**: 521.
38. Stone FS. *Acta Cient. Venez.* 1973; **24**(Suppl. 2): 92.
39. Ward MD. Infrared studies of zeolite. Surfaces and surface relation. In *Zeolite Chemistry and Catalysis*, Rabo JA (ed.). American Chemical Society: Washington, DC, 1979.
40. Knözinger H. *Acta Cient. Venez* 1973; **24**(Suppl. 2): 76.
41. Herrero J, Pajares JA and Blanco C. *Clays Clay Miner.* 1991; **39**: 651.
42. Herrero J, Fernández-Ferreras J, Blanco C and Benito I. *J. Mol. Catal.* 1993; **79**: 165.
43. Fuentes S and Figueras F. *J. Catal.* 1980; **61**: 443.
44. Coq B and Figueras F. *J. Mol. Catal.* 1987; **40**: 93.
45. Anderson JR. *Structure of Metallic Catalysts*. Academic Press: New York, 1975.
46. Bernal S, Calvino JJ, Cifredo GA, Rodríguez-Izquierdo JM, Perrichon V and Laachir A. *J. Chem. Soc. Chem. Commun.* 1992; 460.
47. Bernal S, Botana FJ, Calvino JJ, Cauqui MA, Cifredo GA, Jobacho A, Pintado JM and Rodríguez-Izquierdo JM. *J. Phys. Chem.* 1993; **97**: 4118.
48. Bernal S, Calvino JJ, Cifredo GA, Gatica JM, Pérez-Omil JA, Laachir A and Perrichon V. *Stud. Surf. Sci. Catal.* 1994; **82**: 507.
49. Thorton E, Knözinger H, Tesche B, Rafalko J and Gates BC. *J. Catal.* 1980; **62**: 117.
50. Graydon WF and Langan MD. *J. Catal.* 1981; **69**: 180.
51. Foley HC, DeCanio SJ, Tav KD, Chao KJ, Onuferko JH, Dybowsky C and Gates BC. *J. Am. Chem. Soc.* 1983; **105**: 3074.