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A test reaction to assess the presence of Brönsted and the softness/hardness of Lewis acid sites in palladium supported catalysts

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Cyclic ethylene acetal of α-bromopropiophenone gives rise to three distinctive products, each one being specific to Brönsted, hard Lewis and soft Lewis sites, respectively. In the presence of Brönsted sites, hydrolysis of cyclic acetal forms the corresponding α-bromophenone. Hard or soft Lewis sites promote selectively a rearrangement of the phenyl or ethylenedioxy group to form 2-phenylpropionate ester or dioxine, respectively. This test reaction has been used to assess the influence of the support on the catalytic activity of palladium in zeolites. Three series of supports including alkali-exchanged faujasite, Beta zeolites and sepiolites have been tested. It has been observed that the nature of the zeolite plays an important role on the palladium selectivity, basic supports increasing the softness of the palladium Lewis sites. The catalytic test correlates well with electrochemical data about the reduction potential of supported palladium, XPS characterization of the oxidation state of palladium supported on the surface and activity in the Suzuki reaction.

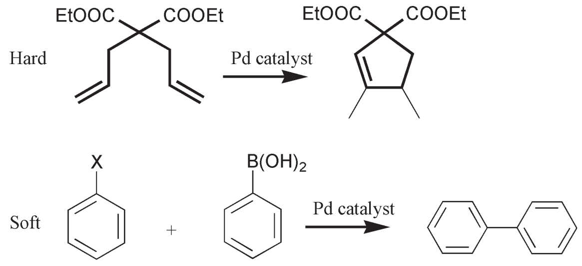
Introduction

The use of palladium catalysts for C–C and C–heteroatom coupling reactions is an area of much current interest due to the mild conditions required and the compatibility of these processes with the presence of other functional groups in the substrates.[1–4] While a considerable amount of work has been carried out in solution using soluble palladium complexes, heterogeneous catalysis offers the advantage with respect to homogeneous phase reactions of easier work-up in continuous flow or batch reactions, easy recovery of the catalyst and the possibility to reuse the solid. In this context, it has been reported that palladium, supported or ion-exchanged in porous aluminosilicates including zeolites and clays, can be convenient solid catalysts for the Heck and the Suzuki reactions.[3–5]

In this work, we want to demonstrate that the whole crystalline framework hosting palladium atoms acts as a macroligand modifying the electron density on the palladium atom and, therefore, the softness/hardness of the palladium species as a Lewis acid site. In homogeneous catalysis, modulation of the reactivity of palladium complexes by variation of the softness/hardness of the ligands is a general methodology to gain control over the activity and selectivity of palladium for coupling reactions,[6] but up to now, control of the softness/hardness has not been considered for palladium supported catalysts.

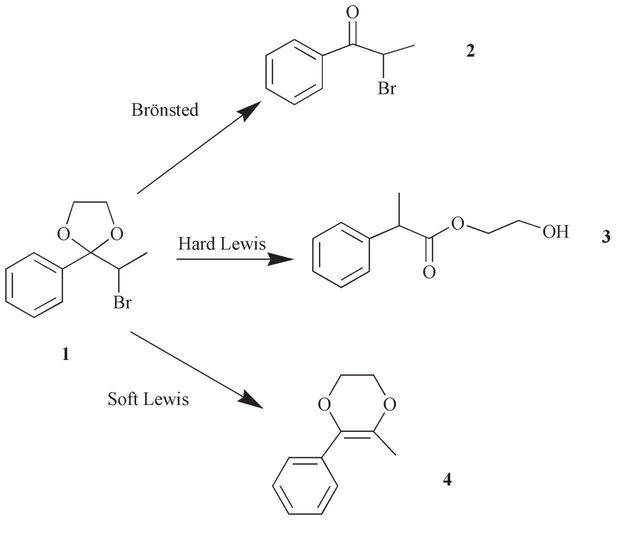
It has been established that some reactions, as for instance the cyclization of diallylmalonates with $PdCl^+$, requires hard palladium complexes while other processes only occur with soft palladium complexes, as for instance those being catalyzed by complexes having phosphines as ligands and in particular the Heck coupling with aryl halides (Scheme 1).

Herein, we propose a model reaction whose product distribution provides information, on the one hand, on the relative population of Brönsted and Lewis acid sites, and on the other hand, is able to assess quantitatively the hardness and softness of the Lewis sites. By using this reaction, we clearly demonstrate that modification of the framework chemical composition exerts a dramatic influence on the softness/hardness of the palladium species in the same manner as an organic ligand does in the case of molecular complexes. In this respect, the zeolite structure as a whole has to be considered as a macroligand.



Scheme 1

The reaction to probe the nature (Brönsted and soft/hard Lewis acid) of the sites is the hydrolysis *versus* the rearrangement of the cyclic acetal of α-bromopropiophenone (Scheme 2).[7,8] Thus, using "undried" organic solvents, the



Scheme 2

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presence of Brönsted sites leads to a complete hydrolysis of the cyclic ethylene acetal to α-bromopropiophenone. Lewis sites behave differently and by coordination with the bromine atom of α-bromopropiophenone, migration of the phenyl ring (hard Lewis site) or 1,2-alkoxy shift (soft Lewis site) occurs. Thus, there are three different products, each being specific to a particular type of site.

Here we are taking advantage of this reaction to show the extent in which we can modulate the softness/hardness of the palladium atoms supported on porous silicates when the chemical composition of the solid is modified. This information would be valuable in order to optimize the activity of palladium supported zeolites and related solids in heterogeneous catalysis.

Results and discussion

Aimed at demonstrating the influence of the nature of the zeolite support on the activity of the hosted palladium atoms, a set of catalysts having different compositions and different types of sites has been prepared. Table 1 contains the most relevant textural and chemical parameters of the solids.

Three series of catalysts containing palladium, all of them at 1 wt %, were tested for the reaction. One of them consisted of alkali metal ion-exchanged faujasite X. It is well-known that the basic strength of the framework oxygens in faujasites depends on the nature of the alkali metal ion, the basicity increasing along with the ionic radius of the alkali metal ion.[9] This variation in the basic strength of faujasites has been demonstrated both by using acidic probe molecules as well as by catalytic tests.[10–13] Therefore, by hosting palladium ion in this series of alkali faujasites the electron density of the framework oxygens surrounding the palladium Lewis sites should increase in the order NaX < KX < CsX. Also, the softness of the zeolite should increase in the same order NaX < KX < CsX. The results of the reaction of cyclic ethylene acetal **1** in the presence of Pd^{2+} containing alkali metal ion faujasites are summarized in Table 2.

Table 1 Main characteristics of the solid supports used in this work

Support	Pore diameter/Å	BET surface area/$m^2\ g^{-1}$	Si/Al atomic ratio
Faujasite X	7.4	570	1.4
Beta zeolite	7.4	666	12.5
Sepiolite	4.0	140	—

The reason for this selectivity in the rearrangement as a function of the hardness/softness of the Lewis sites is outlined in Scheme 3 and arises from the concurrent coordination of the Lewis acid site with the bromine and oxygen atoms (hard site) or bromine and the π system of the phenyl ring (soft sites) leading to aryl or alkoxy migration, respectively.

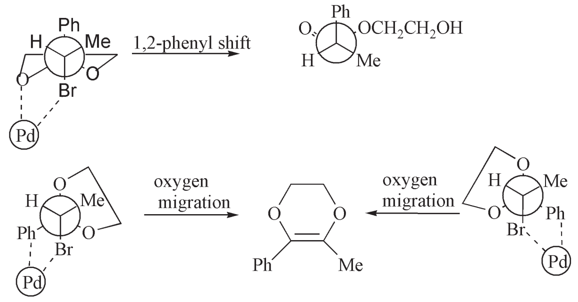
The selectivity of the migration is a consequence of stereoelectronic factors governing the concerted migration and bromine elimination, which requires that the migrating and leaving groups have to be *anti*-periplanar in order to maximize orbital overlapping.

The second series of catalysts were Beta zeolites differing in the nature of the charge balance cation (NaBeta, HBeta) or in the framework composition [(Si)Beta]. The results of the product distribution observed for the reaction of the cyclic ethylene acetal **1** in the presence of Beta zeolites are also listed in Table 2. From Table 2 it is clear that NaBeta zeolite without supported palladium is almost a nonacidic material, as expected from the pyridine titration data. Nevertheless, a slight activity for the rearrangement is observed, the ratio between hydroxyethyl ester to dioxine indicating the hard nature of the residual Lewis sites. At the other extreme, HBeta zeolite, with or without palladium, only hydrolyzes the acetal, which indicates that the activity arises exclusively from Brönsted acid sites. An intermediate situation in which both types of sites, Brönsted and Lewis, are simultaneously observed is $PdCl_2$–(Si)Beta, although the Lewis acid sites have to be considered hard since only formation of the ester is detected. The all-silica Beta zeolite, lacking framework aluminium, has a neutral framework and therefore does not contain any charge-compensating cation. The hard nature of the (Si)Beta was expected in view that Si^{4+} is more electronegative than Al^{3+} and this should lead to a reduced electron density on the framework oxygens, compared to those in the Al^{3+} coordination sphere.

The last series of catalysts that was tested for the rearrangement of α-bromopropiophenone cyclic acetal was sepiolite-supported $PdCl_2$. Sepiolite is a fibrous natural clay mineral with an ideal formula of $Mg_8Si_{12}O_{30}(OH)_4{\cdot}4H_2O{\cdot}nH_2O$. Its structure is formed of talc-like ribbons arranged in such a way that the tetrahedral sheet is continuous but inverts in apical directions in adjacent ribbons, generating uniformly sized parallelpiped intracrystalline tunnels (10.8 × 4.0 $Å^2$) along the fibre. As control, the activity of the natural sepiolite support was also studied. As shown in Table 2, the addition of $PdCl_2$ on the natural sepiolite introduces Lewis acidity, the ratio between ester to dioxine, indicating the prevalence of hard Lewis sites. As commented earlier for alkali metal ion faujasites, a certain degree of control over the basicity of the sepiolite support is possible by partial exchange of the

Table 2 Results of the reaction of cyclic ethylene acetal **1** (200 mg) in dichlorobenzene (15 ml) at 180 °C in the presence of the corresponding palladium containing solid (350 mg, 1 wt % Pd content) after 20 h of reaction time

		Product distribution (%)		
Catalyst	% Conversion	Propiophenone **2**	Ester **3**	Dioxine **4**
$PdCl_2$–NaX	10	0	0	10
$PdCl_2$–KX	34	0	0	34
$PdCl_2$–CsX	40	0	0	40
HBeta	100	100	0	0
NaBeta	4	0	3	1
$PdCl_2$–HBeta	100	100	0	0
$PdCl_2$–NaBeta	6	0	0	6
$PdCl_2$–(Si)Beta	7	5	2	0
Natural sepiolite	74	70	0	4
$PdCl_2$–natural sepiolite	50	0	45	5
$PdCl_2$–K^+ sepiolite	60	32	15	6
$PdCl_2$–Cs^+ sepiolite	26	0	10	16



Scheme 3

magnesium ions located at the edges of the sepiolite ribbons by alkali metal ions. In fact, the maximum basicity is expected for Cs^+ exchanged sepiolite. In good agreement, the resulting Cs^+ sepiolite used as the support of $PdCl_2$ exhibits a somewhat softer character, as assessed by the inverted product distribution with respect to the rest of the series, dioxine being the predominant product in this case.

In order for the above results to really reflect the influence of the nature of the support on the softness/hardness of Lewis acid sites, it is necessary to demonstrate that the products are stable under the reaction conditions and that the rearrangement reaction is truly heterogeneous, the contribution of palladium leached from the solid to the solution being negligible. Blank controls in which compounds **3** and **4** were treated in the presence of $PdCl_2$–KX show that these products are stable under the rearrangement conditions. Concerning the possibility of Pd^{2+} leaching, this has to be explored since the reaction could then occur in solution, promoted by leached palladium from the solid, instead of taking place on the solid support. If this were the case then the results shown in Table 2 would not reflect the interaction of the support with the Lewis acid but only the nature of the actual catalyst dissolved in the reaction medium.

In order to rule out the occurrence of the homogeneous reaction and to demonstrate that the results from Table 2 are really due to the sites present on the solid, leaching experiments were systematically carried out. In these experiments, the reactions were performed until half conversion was achieved and at this point the suspension filtered while the reaction mixture was still hot. Then, the resulting clear solution was surveyed for further conversion at the reaction temperature in the absence of any solid. What was observed in all cases is that the reaction does not progress when the solid is filtered out, thus confirming that the conversion of the acetal **1** occurs exclusively due to the sites present on the solid.

The reactivity data presented above indicate significant changes in the activity and selectivity of the adsorbed palladium species. We have taken this catalytic data as a reflection of the variation of the interaction of the palladium atom with the support due to changes in the composition. In order to support this interpretation we have correlated the catalytic data with electrochemical measurements of the reduction potential of palladium adsorbed on different supports. Fig. 1 shows the linear scan voltammograms in aqueous solution using lithium perchlorate as electrolyte of four selected samples compared to the response of $PdCl_2$ in solution. While the cathodic response of the $PdCl_2$–HBeta and $PdCl_2$–natural sepiolite systems, characterized by a reduction peak at −0.58 V *vs.* SCE, is very similar to that of $PdCl_2$, $PdCl_2$–KX and $PdCl_2$–CsX exhibit a prominent cathodic peak at −0.36 V *vs.* SCE, with a shoulder at lower potential for $PdCl_2$–CsX, that clearly do not correspond to any leached palladium species. The variation of the redox potential of Pd^{2+} depending on the support is also in line with the observed changes in reactivity, although they do not report specifically on the softness/hardness of the palladium.

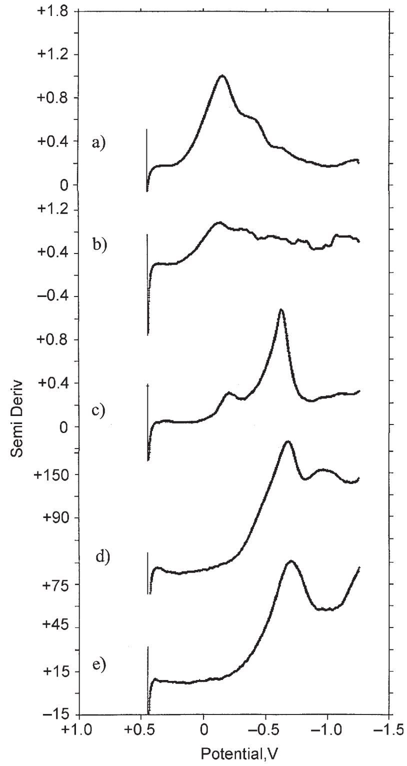


Fig. 1 Cathodic linear scan voltammograms of zeolite modified electrodes in water using 0.1 M $LiClO_4$ as electrolyte: (a) $PdCl_2$–CsX; (b) $PdCl_2$–KX; (c) $PdCl_2$–natural sepiolite; (d) $PdCl_2$–HBeta; (e) $PdCl_2$.

Leaching experiments, in which the solids were stirred in the aqueous electrolytic solution before measurements of the response of the clear filtrate, indicate that some palladium species exhibiting the same cathodic reduction as pure $PdCl_2$ are present. This is evidence that some palladium migrates from the solid to the solution under the conditions of the electrochemical experiments. However, the reduction potential of the leached palladium at −0.58 V is different from the potential measured for $PdCl_2$–KX and $PdCl_2$–CsX, thus confirming that the peak at −0.36 V *vs.* SCE is not to due leaching. Furthermore, by performing the electrochemical measurements in acetonitrile–water mixtures and using tetrabutylammonium perchlorate as electrolyte, the peak at −0.36 *vs.* SCE disappears. Given that in the electrochemical processes, the transfer of electrons from the working electrode to the probe has to be accompanied with the diffusion of electrolytes to maintain electroneutrality during each step of the redox process, the disappearance of electrochemical peaks using large electrolytes is an indication that the response corresponds to an intraparticle species. If a large electrolyte has its access into the pores restricted for steric reasons, then no electrochemical response can occur. In view of the above observations, that is, the shift in the reduction potential and influence of the electrolyte molecular size, we consider that the voltammograms of $PdCl_2$–KX and $PdCl_2$–CsX indicate a strong interaction of the palladium with the support, in agreement with the catalytic test. Moreover, the electrochemical measurements indicate that the reduction of palladium is easier and takes place at lower potentials when the support is a basic zeolite, this again being in agreement with an electron donation to the palladium by the support. Finally, XPS characterization of the outer most external layers of the $PdCl_2$ supported zeolites shows in all cases that the oxidation state of the palladium atoms in the fresh catalyst is +2, the amount of palladium(0) on the probed surface being undetectable.

To confirm that the results of the above test reaction can be useful to correlate the activity and selectivity of palladium supported zeolites in C–C coupling reactions, we performed the Suzuki reaction of bromobenzene and phenylboronic acid in toluene at reflux temperature in the presence of palladium supported on KX and on HBeta. While in the first case the reaction forms biphenyl in 87% yield at 24 h, under the same conditions but using HBeta the conversion of bromobenzene was only 10%. The above result indicates that the most appropriate supported palladium catalyst for the Suzuki requires soft palladium atoms rather than hard ones.

In summary, the results obtained for the rearrangement of the cyclic ethylene acetal of 2-bromopropiophenone show that the product distribution obtained depends in a consistent manner on the nature of the sites. Each type of site, either Brönsted or hard and soft Lewis acid sites, gives specifically a distinctive product. Particularly important is the finding that the softness/hardness nature of the Lewis sites can be assessed by simple measurement of the product distribution. Furthermore, given the current interest on Pd catalyzed reactions supported on inorganic solids, our data show that a wide range in the tuning of the electron density on the palladium can be achieved through modification of the support composition, this leading to a variation of its softness/hardness and as a consequence in its catalytic activity.

Experimental

Materials and methods

NaX was a commercial sample (Aldrich 13X). KX and CsX were obtained from NaX by three consecutive room temperature ion exchanges using KAcO and CsAcO aqueous solutions of increasing concentration (0.3, 0.4, and 0.5 M) and a solid–liquid ratio of 1:10. HBeta was prepared by hydrothermal crystallization using tetrapropylammonium as template, followed by calcination in air flow as reported.[14] The Si/Al ratio of HBeta determined by chemical analysis was 12.5. NaBeta was prepared from HBeta by ion exchange using a 0.6 M aqueous solution of $NaHCO_3$. All-silicon Beta zeolite was also obtained by hydrothermal crystallization under dynamic conditions, using aerosil as silicon source and tetrapropylammonium bromide as template at 140 °C as reported.[14]

Natural sepiolite was obtained from TOLSA (Vallecas, Spain) and was free from carbonate minerals. Potassium and cesium sepiolites were obtained by autoclaving natural sepiolite at 200 °C with a 1 M aqueous solution of NaOH for 6 h.[15] The resulting Na-sepiolite was thoroughly washed with distilled water and submitted to potassium or cesium (for sodium) exchange using KAcO or CsAcO, respectively.

$PdCl_2$ was deposited on the supports by ion exchange (case of X zeolite) or by the incipient wetness procedure (series of Beta zeolites and sepiolites). The latter method consists in dissolving the required weight of $PdCl_2$ to obtain 1 wt % in the final solid in the minimum amount of water to wet the dry supports before a slurry is obtained. During the dropwise addition of $PdCl_2$, the powdery solid is mechanically stirred to achieve maximum homogeneity.

Cyclic ethylene acetal (**1**) was obtained from α-bromopropiophenone (Aldrich) and ethylene glycol in toluene, using para-toluenesulfonic acid as catalyst and Dean–Stark equipment to azeotropically distill the water formed.

Catalyst test reactions

Test reactions were carried out by stirring magnetically a suspension of thermally dehydrated catalyst (350 mg), cyclic acetal (**1**; 200 mg) and 1,2-dichlorobenzene (15 ml) at 180 °C. Some of the catalysts were stirred in sodium carbonate solution at room temperature for 1 h and dried in an oven at 110 °C before using as catalyst. The course of the reaction was periodically followed by analysing the liquid phase by GC using a 30 m crosslinked phenylmethylsilicone capillary column. Besides unreacted substrate, the only products observed were α-bromopropiophenone, 2-hydroxyethyl-2-phenylpropionate and 2-phenyl-3-methyldioxine.

Electrochemistry and XPS measurements

Zeolite-modified electrodes were prepared, as previously described,[16,17] by transferring a few microlitres (typically 50 μl) of a dispersion of the zeolite (10 mg) in acetone (5 ml) to the surface of a freshly polished glassy carbon electrode (GCE; BAS MF 2012; geometrical area 0.07 cm^2). One drop of a solution of the Paraloid B72 (1%) in acetone was then added. The coatings examined contained 0.2–1.5 mg cm^{-2} of the dry zeolite.

$PdCl_2$-attached electrodes were prepared as described in the literature.[18,19] The sample (1–2 mg) was powdered in an agate mortar and pestle. The lower end of the electrode was gently rubbed over the powder and finally cleaned with a tissue paper. Linear potential scan voltammograms and differential pulse voltammograms were performed with a Metrohm E506 polarecord. A standard three-electrode arrangement was used, with a platinum auxiliary electrode, a saturated calomel reference electrode separated from the solution using a capillary salt bridge and a GCE electrode. Electrochemical measurements were conducted in water using 0.10 M $LiClO_4$ (Aldrich) as supporting electrolyte. All electrochemical measurements were performed at room temperature (298 K) in well-deaerated solutions under an atmosphere of argon.

XPS measurements were carried out at room temperature with a concentric hemispherical analyzer operated in the constant pass energy mode (50 eV). A Mg Kα X-ray source ($h\upsilon = 1253.6$ eV) was used. A vacuum of *ca.* 5×10^{-9} Torr was always attained in the analysis chamber during XPS recording. Charging effects were calibrated by the C(1s) line at 284.6 eV.

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