

Controlling the softness–hardness of Pd by strong metal–zeolite interaction: cyclisation of diallylmalonate as a test reaction

Avelino Corma,* Hermenegildo García,* and Antonio Leyva

Instituto de Tecnología Química CSIC-UPV, Avda. de Los Naranjos s/n, 46022, Valencia, Spain

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Abstract

The cycloisomerisation of diallylmalonate to form cyclopentenes is demonstrated here to be a specific test reaction for hard Lewis acid sites in palladium-containing zeolites. We have found a correlation of the cycloisomerisation efficiency for a series of palladium-supported zeolites with the hardness of their framework as previously reported by quantum chemical calculations. Thus, the catalytic activity decreases and eventually disappears when the softness of the zeolite framework increases, the optimum in the activity being achieved when palladium is hosted in hard zeolite frameworks. In this way, the cycloisomerisation yield decreases in the series HY (Si/Al 15) \approx HBeta (Si/Al 12.5) > HZSM-5 (Si/Al 15) > (Si)Beta (Si/Al ∞) > H,NaBeta (Si/Al 12.5) > HNaY (Si/Al 2.6) > NaY (Si/Al 2.6) > NaBeta (Si/Al 12.5) \approx (Si,Ge)Beta.

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1. Introduction

Palladium-catalysed C–C forming reactions are among the most versatile tools in modern organic synthesis due to their chemoselectivity in the presence of a large variety of functional groups as well as to the high yields and mild conditions required for the reaction [1–3]. Although many details of the reaction mechanism still remain unveiled, it is widely accepted that palladium metal acts in some catalytic steps as a Lewis acid site accepting an electron pair. In this regard, the influence of the ligands on the activity of palladium complexes in solution for cross-coupling reactions has been frequently rationalised as arising from changes in the softness and hardness of the palladium atom considered as Lewis acid [4]. In a palladium complex, the local hardness at the palladium atom depends on the hardness–softness of the ligand considered as a base. The harder the ligand, the harder the palladium atom in the complex.

A general tendency in catalysis is to transform a successful homogeneous catalytic reaction into a heterogeneous

process in which the catalyst can be easily recovered from the reaction mixture and reused. In addition, heterogeneous catalysis minimizes wastes contributing to the development of greener chemical transformations and facilitating the design of continuous flow processes [5–7].

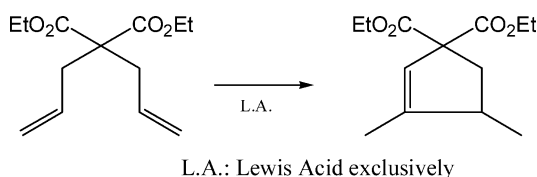
The simplest way to convert a homogeneous into a heterogeneous catalyst is to deposit the active species onto a high surface area inorganic carrier [8–10]. Recent examples in which palladium salts or complexes have been adsorbed into porous aluminosilicates have been published [11–14]. When adsorbing a Pd species onto inorganic oxides, the influence of the interaction of the Pd with the inorganic support on its softness–hardness has been frequently ignored, and the properties of the Pd species are considered sometimes as independent on the nature of the carrier despite that large variation in catalytic activity is sometimes observed from one support to another. However, it is reasonable to consider that in those cases in which free palladium ions or weak complexes are supported on an inorganic oxide, the negative oxygens of the inorganic support can interact with the palladium species in a way that resembles the formation of a coordination bond. The solid surroundings around the metal ion would act like a “macroligand,” being able to replace other weak ligands from the coordination sphere of the

* Corresponding authors. Fax: (+34)963877809.
E-mail addresses: acorma@itq.upv.es (A. Corma),
hgarcia@quim.upv.es (H. García).

metal. By tuning such metal/support interaction, it could in principle be possible to gain some control on the softness–hardness of the Pd center and, therefore, some change on the activity and selectivity of the solid palladium catalyst should be possible by varying the nature of the support.

Herein, we demonstrate the advantage of using a model reaction to assess experimentally the extent to which the catalytic activity of a palladium site can be modified upon adsorption onto zeolites of different composition. These remarkable variations in activity can be rationalised based on the consideration of soft–hard Lewis acid interactions between the palladium metal ion and the zeolite host. The hardness–softness principle as introduced in 1963 by Pearson is a qualitative concept for explaining the relative affinities between acids and bases that cannot be rationalized based on electronegativity or other related macroscopic properties [15,16]. Despite the fact that the hard–soft acid–base theory is qualitative, there have been proposals to define a quantitative scale associated with the energy, geometry, and size of the frontier molecular orbitals of the interacting acid and base. In this way, two approaches based on quantum mechanical principles using perturbation molecular orbital theory [17] and density-functional theory have been used to develop a quantitative scale for the hardness–softness of acids and bases [18]. In these theoretical methodologies, the larger the difference between the energy of the highest occupied orbital (HOMO) of the donor atom and the lowest unoccupied orbital of the acceptor atom (LUMO), the larger the charge control and hard–hard interactions prevail. On the other hand, when the above HOMO–LUMO energy difference is small, the soft–soft interactions become predominant and the interaction is controlled by molecular orbital overlapping rather than by electrostatic interactions. Based on these principles the hardness–softness character of a given zeolite framework can be determined by calculations of the frontier orbitals energy [19–21]. Thus, our assumption is that the local hardness–softness at the palladium Lewis acid sites is modulated by the zeolite framework considered as a ligand, following the rule that the softer the zeolite framework the softer the palladium atom in this palladium–zeolite complex. Our purpose is to correlate the current knowledge on zeolite framework hardness–softness based on these theoretical calculations with experimental results based on a test reaction.

Aimed at this objective, we have selected as a model reaction the cycloisomerisation of diethyl 2,2-diallylmalonate ester (Scheme 1), that is a reaction that has been previously reported to be catalysed by Pd(II) complexes acting



Scheme 1.

as Lewis acid [22–27], and studied the influence of a consistent series of various zeolite frameworks with different hardness–softness on the catalytic activity of the Pd atoms. The series of zeolites has been purposely selected based on existing literature reports to represent a wide range of hardness–softness character in the zeolite framework. We have found a correlation of the cycloisomerisation efficiency of the supported Pd catalyst with the hardness of the zeolite framework. The catalytic activity decreases dramatically from 100% conversion to 0% when the softness of the zeolite framework in the series increases, the maximum activity being achieved when Pd is hosted on hard zeolite frameworks. This trend parallels that observed in solution in which the activity of Pd²⁺ ion for the cycloisomerisation reaction requires hard ligands to occur [27]. In other words, variations on the chemical composition of the zeolite framework modifies consistently in a controllable way the activity of zeolite-supported Pd Lewis acid site in a manner that can be rationalised through the softness–hardness interaction concept. Thus, Pd-containing hard zeolites are highly active for the cycloisomerisation while Pd-containing soft zeolites are inactive to perform the reaction.

Also as the outcome of our study, we propose the cycloisomerisation of diethyl diallylmalonate as a test reaction specific for hard Lewis acid sites. Given the current interest on supported noble metal catalysts for cross-coupling reactions and green Lewis acid solids in general, a reliable test reaction can be a very important tool for assessing the softness–hardness variations on the metal site by interaction with the support.

2. Experimental and methods

2.1. Preparation of the zeolites

NaY, HBeta, and HZSM5 were commercial zeolites (PQ-CBV100, PQ-CBV811, and PQ-CBV3020, respectively). HY was obtained from NaY by three consecutive Na⁺ to NH₄⁺ ion exchanges at room temperature using aqueous solutions of ammonium acetate of 0.4, 0.5, and 0.6 M concentration and a solid–liquid ratio of 10. The intermediate NH₄⁺-Y sample was calcinated at 500 °C in an open atmosphere to provide HY. USY zeolite was obtained by self-steaming HY at 500 °C for 12 h followed by exhaustive washings with 1 M NH₄PF₆ solution. H,NaBeta was obtained from commercial HBeta through ion exchange at room temperature with 0.2 M NaHCO₃ solution and a solid–liquid ratio of 10. The sodium content was determined by chemical analysis after dissolving the zeolite with concentrated aqueous HF acid at 60 °C. NaBeta was obtained from HBeta by complete Na⁺-to-H⁺ ion exchange following the same procedure as for HY. (Si)Beta and (Si,Ge)Beta were synthesized using tetrapropylammonium chloride as a structure-directing agent and TEOS (tetraethoxysilane) and germanium oxide as silica and germanium sources, respec-

tively. HF was used as mineralising agent. The structure and crystallinity of (Si)Beta and (Si,Ge)Beta were confirmed by powder X-ray diffraction. The surface area of the zeolites prepared was measured by isothermal nitrogen adsorption using a Micromeritics ASAP2000 and the Si to Ge ratio was determined by chemical analysis.

2.2. Preparation of the catalysts

Pd^{2+} -exchanged zeolites were prepared according to the method of Zhang and Sachtler [28]. A solution of PdCl_2 (41.6 mg) dissolved in 0.1 M ammonium aqueous solution (25 mL) was stirred at room temperature for 24 h in the presence of zeolite (5 g). After this time, the solid was filtered, washed with distilled water (1 L/g), and dried. The final palladium content of the solid was determined by quantitative atomic absorption spectroscopy after zeolite was dissolved with concentrated HF. Alternatively, Pd^{2+} -containing catalysts were obtained by the incipient wetness methodology. Prior to adsorbing PdCl_2 the pore volume of each support was determined by adding dropwise water to the dry support until a wet paste is obtained. Then, the required PdCl_2 amount to achieve the target palladium content in the support (1 wt%) was dissolved in the volume corresponding to the pore of the support, in order to fill all the voids of the solid without losing metal. The solution was added dropwise to the dry support with a microneedle to achieve the better possible dispersion of the metal. The solid was stirred magnetically for 1 h. Finally, it was kept in a dry box under vacuum for 12 h.

2.3. FT-IR pyridine measurements

Pyridinium titration of HY, HUSY, and HBeta was performed by adsorbing pyridine at room temperature at its vapour pressure onto thermally dehydrated zeolite wafers in a greaseless quartz IR cell having CaF_2 windows. The zeolite wafers were prepared by pressing around 10 mg of the zeolite at 2 ton/cm² for 5 min. The spectrum was recorded at room temperature after outgassing the wafer at 300 °C under 10⁻² Pa reduced pressure.

2.4. Reaction tests

Diethyl 2,2-diallylmalonate (Aldrich, 0.5 mmol) and toluene (10 ml) were added to the previously dehydrated solid support and the suspension was magnetically stirred in a preheated oil bath at 110 °C. The course of the reaction was followed by stopping the stirring prior to taking a 0.1-mL sample of the supernatant solution that was subsequently analysed by GC (HP 5890 GC equipped with a 25-m capillary column of 5% phenylmethylsilicone) using nitrobenzene as external standard. At the end of the reaction the suspension was filtered and the solid submitted to exhaustive solid–liquid extraction with CH_2Cl_2 using a

micro-Soxhlet setup. The extract was concentrated under reduced pressure and analysed by GC. Mass balances higher than 95% were achieved in all cases.

The structure of isolated products was characterized by GC (comparison with authentic sample), GC-MS (Varian Saturn II, same column and conditions as GC) and ¹H NMR spectroscopy (Varian Gemini, 300 MHz, CDCl_3 as solvent).

3. Results and discussion

3.1. Palladium-containing zeolites

For the present work we have used three different zeolitic structures namely faujasite Y, Beta, and ZSM5. The nature of the charge-balancing cation and the zeolite framework composition have been varied in this study. Thus, the Si/Al ratio ranges from 2.4 to ∞ and a Ge-containing Beta zeolite has also been included in the series of supports. The charge-balancing cations studied were H⁺ (corresponding to Brønsted acid sites) or Na⁺ (zeolites devoid of any Brønsted acidity). The series of zeolites has been chosen on purpose to cover the widest possible range of hardness–softness variation. Our selection is based on previously existing reports in the literature about theoretical data on quantum chemical calculations that has shown that the zeolite framework softness depends on its chemical composition and on its crystal structure [20,29,30].

Pd(II) was ion-exchanged in the zeolites from a $\text{Pd(NH}_3)_4^{2+}$ complex followed by thermal ammonia desorption according to the method reported in the literature [28,31,32]. Diffuse reflectance UV–vis spectroscopy of the $\text{Pd(NH}_3)_4^{2+}$ zeolites and Pd^{2+} zeolites (Fig. 1) clearly indicates the success of the preparation procedure by observing a shift in λ_{max} of the zeolite from 300 nm [corresponding to $\text{Pd(NH}_3)_4^{2+}$ complex] up to 440–480 nm (attributable to ammonia free aquated Pd^{2+} ions). Alternatively, for comparison purposes, some other samples were prepared at 1%

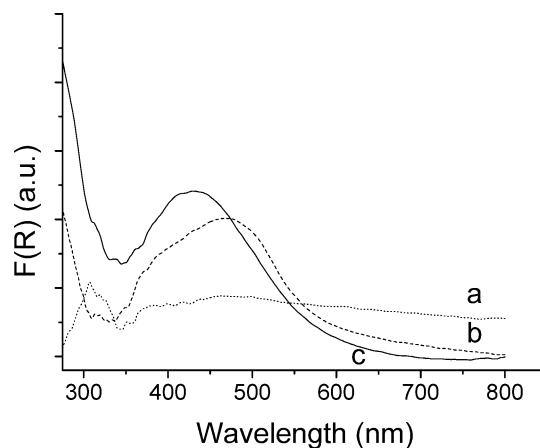


Fig. 1. Diffuse reflectance UV–vis spectra (plotted as the Kubelka–Munk function of the reflectance, R) of $\text{Pd(NH}_3)_4\text{-NaY}$ (a), $\text{Pd}^{2+}\text{-NaY}$ (b), and $\text{Pd}^{2+}\text{-HY}$ (c).

Table 1
Relevant analytical and physicochemical parameters of the zeolites used as support in the present work

Support	Support pore diameter (Å)	Support surface (m ² /g)	Si/Al
HBeta	7.5*5.7 6.5*5.6	730	12.5
NaBeta		730	12.5
(Si)Beta		460	∞
(Si,Ge)Beta		460	15 ^a
HY	7.4	780	15
NaY		780	2.6
Dealuminated USY		710	14
HZSM5	5.3*5.6	430	15

^a Si/Ge molar ratio, Al-free sample.

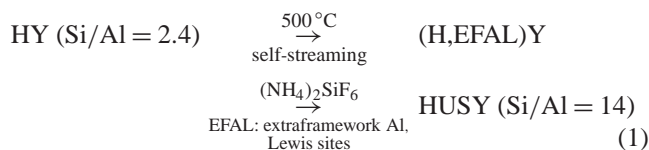
Pd wt using PdCl₂ as palladium source and following the incipient wetness procedure. In the case of (Si)Beta and (Si,Ge)Beta devoid of framework Al and, therefore, of any ion exchange capability, Pd was introduced exclusively by the incipient wetness method. The list of zeolites employed in the present work and their main analytical, textural and porosity data are summarized in Table 1.

3.2. Brønsted acid catalysis

The chemical structure of the products formed during the treatment of diallylmalonate with Brønsted or Lewis acids is contained in Chart 1. Diallylmalonate cyclisation discriminates in first place between Brønsted and Lewis acid sites. This was demonstrated by studying the activity of typical Brønsted acid sites either in solution or by using a purely Brønsted zeolite (Table 2, entries 2 and 14). In these cases cyclisation did not proceed, the products formed being those that arise from the C=C double bond migration from the terminal to an internal, more substituted position. Also hydrolysis of the ethyl ester group was observed in a lesser extent (Scheme 2). These results indicate that cycloisomerisation must be considered a specific Lewis acid-catalysed process in agreement with the reports describing the Pd catalysis for this reaction [22,24,25,27].

The purposely prepared Brønsted Y zeolite devoid of Lewis sites used to demonstrate the inability of Brønsted acid sites to promote the diallylmalonate cycloisomerisation was obtained starting from NH₄Y (Si/Al 2.6) that was dealuminated by mild steaming. Subsequently, extraframework

Al was completely removed by dissolving it using concentrated aqueous solution of ammonium hexafluorophosphate:



Extraframework Al is the species responsible for Lewis acid sites in zeolites [33,34]. This treatment has been previously used to obtain protonic USY zeolites free from Lewis acid sites [35]. To demonstrate spectroscopically the success of the treatment for removing Lewis acid sites, acidity of the resulting (NH₄)₂SiF₆-washed HUSY zeolite, particularly the relative population of Lewis sites, was determined by the pyridine adsorption–desorption method [36]. Thus, Fig. 2 shows the aromatic region of the IR spectrum for the HUSY samples before and after ammonium hexafluorophosphate washings. As it can be seen there, the starting dealuminated HY sample contains the characteristic bands at 1540 and 1455 cm⁻¹, corresponding to the pyridinium (Brønsted acid sites) and Lewis-coordinated pyridine, respectively. However, after the ammonium hexafluorosilicate treatment most of the 1455 cm⁻¹ band disappears and only the characteristic pyridinium band (Brønsted acid sites) remains. This sample of HUSY containing exclusively Brønsted acid sites is not able to effect the diallylmalonate cycloisomerisation (Table 2, entry 14).

A sample of HBeta zeolite in which pyridine titration shows also predominantly Brønsted acid sites behaves similarly as dealuminated USY giving rise predominantly to C=C double bond rearrangement, with only a minor amount of cyclopentenes being again present in the reaction mixture (Table 2, entry 2).

It has to be remarked that while pyridine titration is a well-established spectroscopic method to distinguish between Brønsted and Lewis acid sites [37–39], it does not provide any information about the softness–hardness of the Lewis sites, and, therefore, no spectroscopic titration of the hardness–softness of the Lewis acid sites has ever been reported for solids.

To reinforce the fact that Brønsted acid sites only promote C=C double bond isomerisation and ester hydrolysis without forming any trace of malonate cycloisomerisation, a control in the homogeneous phase using *p*-toluenesulfonic

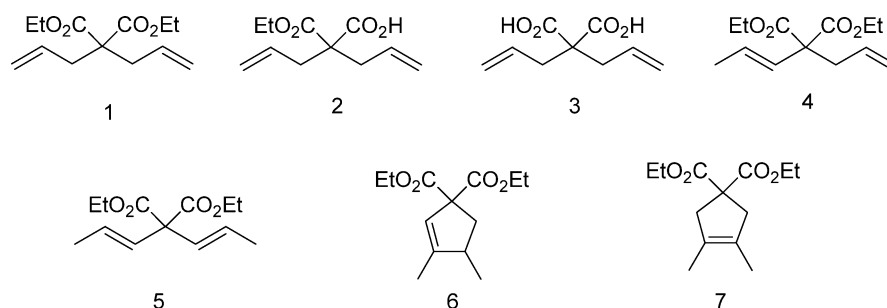


Chart 1.

Table 2

Results for the reaction of diethyl 2,2-diallylmalonate ester (0.5 mmol) in toluene (10 mL) after 1 h at 110 °C in the presence of Pd-containing zeolites (1 wt%, 266 mg)

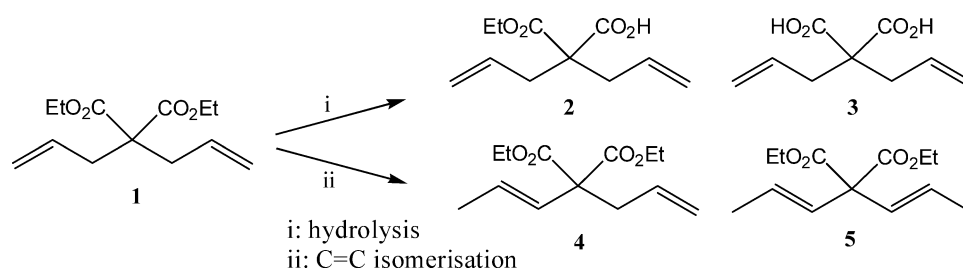
Entry	Catalyst ^a	Conversion (%)	Product distribution (%) ^b		TOF ^c (%/min)
			6 + 7 (6/7)	4 + 5 (4/5)	
1	PdCl ₂ (50%)	37	25 (∞)	12 (9.5)	13
2	HBeta	35	6 (0)	25 (1.3)	–
3	Pd ²⁺ -HBeta	100	100 (0.1)	–	944
4	PdCl ₂ -HBeta	100	79 (0.2)	20 (0.6)	374
5	PdCl ₂ -H,NaBeta	75	48 (0.2)	25 (0.9)	174
6	Pd ²⁺ -NaBeta	< 4	–	–	–
7	PdCl ₂ -NaBeta	< 1	–	–	–
8	PdCl ₂ -(Si)Beta	70	69 (33.5)	1	232
9	PdCl ₂ -(Si,Ge)Beta	< 2	–	–	–
10	Pd ²⁺ -HY	100	100 (0.1)	–	545
11	PdCl ₂ -HY	100	94 (0.1)	3	234
12	Pd ²⁺ -NaY	18	16 (0.4)	2	–
13	PdCl ₂ -NaY	< 4	–	–	–
14	HUSY desalum	38	Hydrolysis products	–	–
15	PdCl ₂ -USY desalum	83	69 (2.0)	12 (0.3)	96
16	PdCl ₂ -ZSM-5	89	76 (0.7)	13 (1.0)	230
17 ^d	<i>p</i> -Toluenesulfonic acid (25%)	30	–	25 (0)	–

^a Pd²⁺ corresponds to ion-exchanged catalysts and PdCl₂ to those others prepared by wet impregnation.

^b The number in brackets indicates the molar 6/7 or 4/5 molar ratio.

^c Defined as moles of (6 + 7) divided by Pd moles per unit of time.

^d 24 h.



Scheme 2.

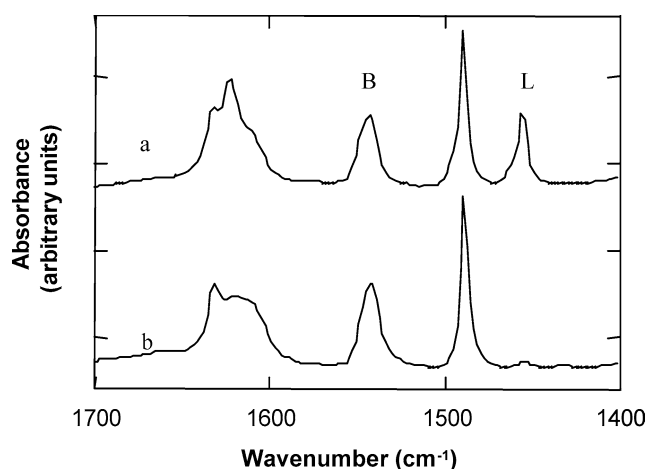


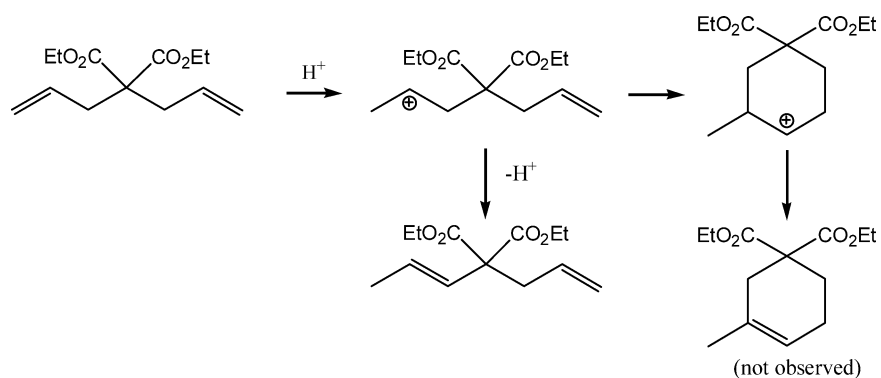
Fig. 2. FT-IR spectrum (aromatic region) of pyridine retained on (a) NH₄Y (Si/Al 2.6) and (b) dealuminated HUSY washed with (NH₄)₂SiF₆ after adsorption at room temperature and subsequent annealing (300 °C; 10⁻² Pa; 1 h). The intensities of Brønsted sites (B) for both samples are comparable whereas that of Lewis sites (L) are significantly decreased for HUSY due to the washings.

acid dissolved in toluene was carried out. The result (Table 2, entry 17) confirms the conclusion that Brønsted sites are not capable of promoting cyclisation of the starting malonate.

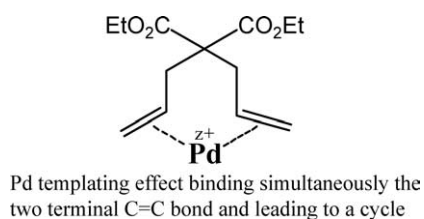
A likely rationalization to justify the occurrence of C=C double bond isomerisation and the failure of H⁺ to form cyclopentenes based on simple carbocation chemistry is shown in Scheme 3. It is important to note that according to Markovnikov's rule carbocation intermediacy could only lead to six-membered rings but never to five-membered rings. In contrast, formation of five-membered rings can be easily understood considering palladium as a Lewis acid that simultaneously coordinates with the two terminal C=C bonds. Scheme 4 illustrates the structure of the key palladium intermediate showing the templating effect leading to five-membered cycle formation.

3.3. Lewis acid catalysis

In contrast to the behaviour observed for zeolites in the H⁺ form, some of the Pd-containing zeolites give rise to the formation of cycloisomerisation products, their activ-



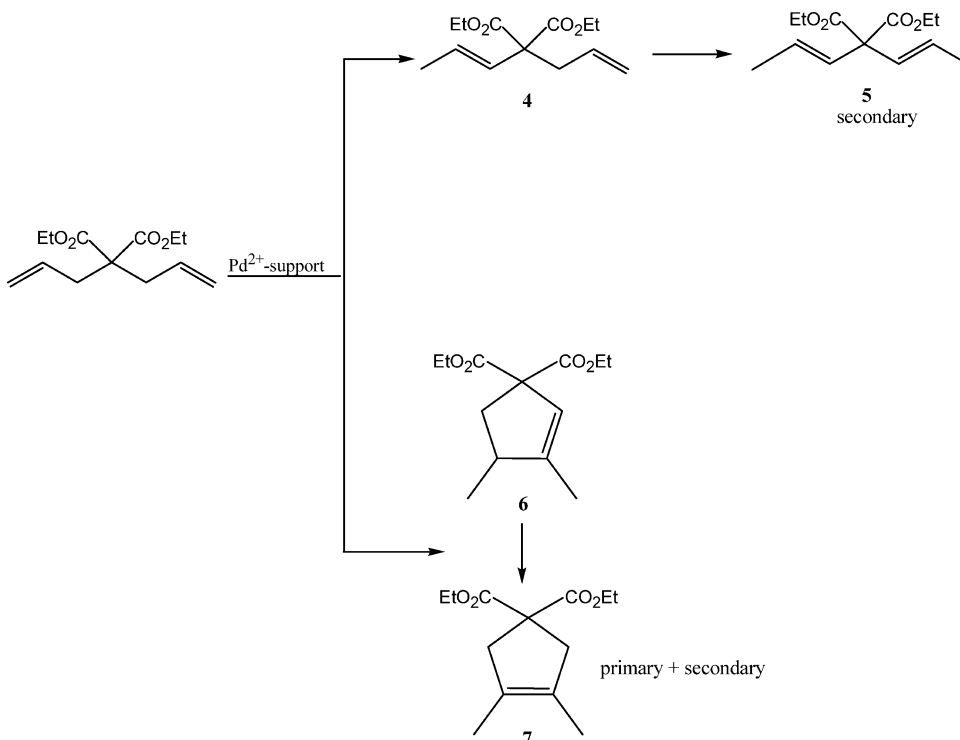
Scheme 3.



Scheme 4.

ity depending primarily on the zeolite framework chemical composition (Scheme 5). As representative examples of the catalytic activity of Pd-containing zeolites, the course of the reaction using Pd-containing HBeta and Pd-containing HZSM5 is shown in Figs. 3 and 4, respectively. As it can be seen in these figures, a small percentage of the crotonyl malonates **4** and **5** in which the C=C double bond has rearranged is also present in the reaction mixtures. As for pure Brønsted

acids, we believe that these by-products are formed through a Brønsted acid-catalysed mechanism, operating independently of the presence of Pd. However, as can be seen in Figs. 3 and 4, the product distribution for the Pd-containing acidic zeolites is dominated by the presence of the cyclised isomers **6** and **7**. Both isomers are primary products since they are formed since the initial reaction time, but we noted that the tri-substituted cyclopentene **6** is unstable under the reaction conditions and that it undergoes further isomerisation to the cyclopentene **7** having a four-substituted C=C double bond. This isomerisation is clearly demonstrated by performing an alternative experiment starting from compound **6** in the presence of PdCl₂-HBeta and observing its complete transformation into the four-substituted compound **7** (Fig. 5). Scheme 5 indicates the primary and secondary nature of compound **7** being formed directly from **1**, but also from product **6**. The driving force for this isomerisation is



Scheme 5.

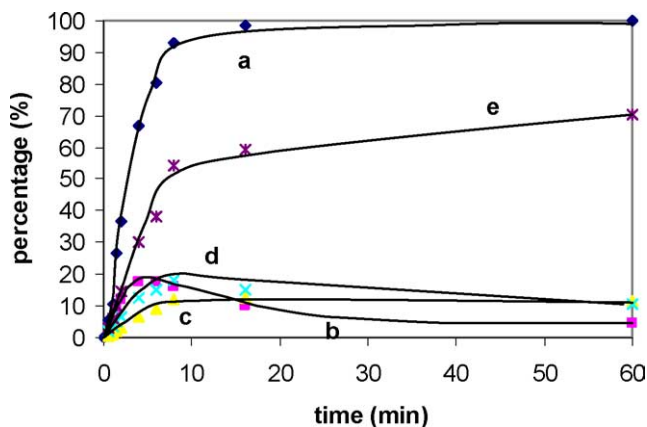


Fig. 3. Conversion of diethyl 2,2-diallylmalonate ester (a) and product distribution vs the reaction time for the cycloisomerisation of 0.5 mmol of reactant in toluene (10 ml) at 110 °C using PdCl₂-HBeta as catalyst (266 mg); (b) compound 4, (c) compound 5, (d) compound 6, (e) compound 7.

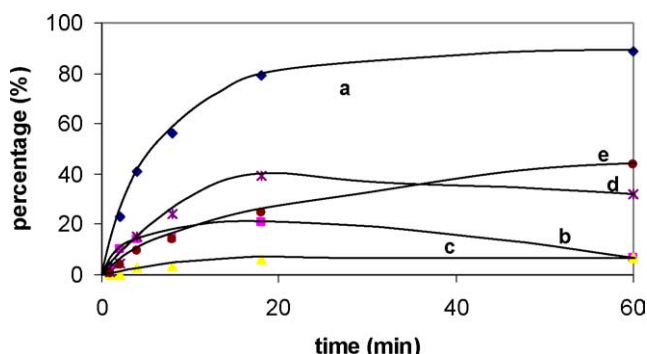


Fig. 4. Conversion of diethyl 2,2-diallylmalonate ester (a) and product distribution vs the reaction time for the cycloisomerisation of 0.5 mmol of reactant in toluene (10 ml) at 110 °C using PdCl₂-HZSM5 as catalyst (266 mg); (b) compound 4, (c) compound 5, (d) compound 6, (e) compound 7.

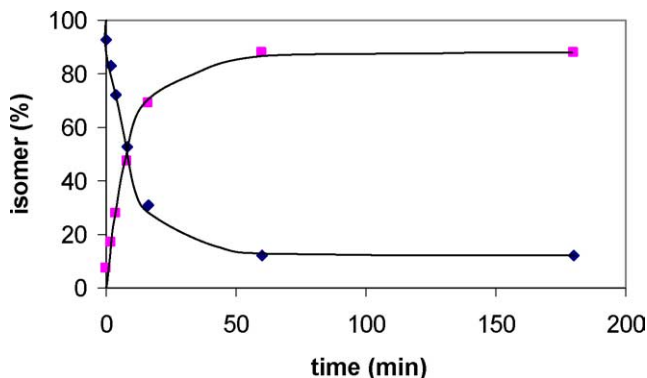


Fig. 5. Time-conversion plot for the isomerisation of cyclopentene 6 (◆) into cyclopentene 7 (■) for the reaction of 0.5 mmol of 6 in toluene (10 mL) at 110 °C using PdCl₂-HBeta as catalyst (266 mg).

the higher thermodynamic stability of compound 7 relative to the isomer 6 due to the higher substitution of the C=C double bond.

Interestingly, those samples in which Pd²⁺ has been introduced by ion exchange from Pd(NH₃)₄²⁺ exhibit qualitatively the same trend as those in which Pd²⁺ has been

introduced by the incipient wetness method in terms of activity toward cycloisomerisation. However, the initial activity of the ion-exchanged samples is somewhat higher than those prepared by impregnation and the actual 6/7 product distribution is also different. These quantitative differences between ion exchange and impregnation have already been observed previously in other processes catalysed by noble metal-supported zeolites and can be understood as arising from differences in the nature of the actual palladium species incorporated within the zeolite (Pd²⁺ in ion-exchanged vs. PdCl⁻ in impregnated samples) and the presence of adventitious Brønsted acidity (C=C bond isomerisation) introduced during the impregnation. Impregnation is, nevertheless, the preferred method for many industrial applications of noble metal-containing zeolites used in refining since it is experimentally the simplest incorporation procedure and no noble metal wastes are produced.

In order to have conclusive results in heterogeneous catalysis, one must be sure that the observed activity is due to the intrazeolitic Pd but not to any Pd species leached from the solid into the solution. To address this point, the reaction was carried out under the conditions shown in Table 2 using PdCl₂-HBeta as catalyst. However, in this case the reaction mixture was filtered “in hot” when the conversion was 25%, and the clear filtrate was allowed to react for 1 h. It was observed that removing the solid catalyst by filtration stops completely the reaction and the cycloisomerisation does not proceed any further in the solution in the absence of the solid catalyst. In other words, no homogeneous reaction is observed in this case. This is not surprising if one takes into account that in related precedents no leaching of Pd was also observed when using palladium-containing zeolites in toluene as solvent [11].

To confirm the ability of Pd acting as a hard Lewis acid to promote the cycloisomerisation a blank control in which PdCl₂ solid was used as catalyst in toluene was carried out and the results have also been included in Table 2 (entry 1). As it can be seen there, cyclopentenes are formed together with minor crotonyl products. Moreover, addition of *p*-toluenesulfonic acid does not vary much the product distribution and the cycloisomerisation rate, indicating that no cooperation between Brønsted and Lewis acid takes place. Thus, when using Pd²⁺-exchanged or supported zeolites in their H-form, no contribution of the Brønsted acid sites on the formation of cyclopentenes can be claimed.

From the series of catalysts studied, those in which palladium is present in zeolites containing H⁺ as charge-balancing cations exhibit high activity for the cycloisomerisation reaction. This is the case of zeolites HY, HUSY, HBeta, and HZSM-5 (Table 2, entries 3, 4, 10, 11, 15, and 16). When part of the protons are replaced by sodiums the activity of the Pd-containing zeolite decreases considerably (Table 2, entries 5, 6, 7, 12, and 13). Thus, for instance, the initial reaction rate of PdCl₂-HBeta decreases from 374 to 174 going from the H⁺ form to other H,NaBeta sample at 12% of Na⁺-to-H⁺ level exchange. Even more, a com-

plete Na⁺-to-H⁺ ion exchange causes the total deactivation of the Pd-containing zeolites, irrespective of whether they were prepared by ion exchange or wet impregnation. This activity trend can be rationalised as reflecting an increase on the local softness at the palladium metal ion (see below).

Another set of Pd-containing zeolites that was studied consisted of two Beta-zeolites devoid of any framework aluminum and therefore of any charge-balancing cation. The results obtained for PdCl₂-(Si)Beta and PdCl₂-(Si,Ge)Beta are also included in Table 2 (entries 8 and 9). As it can be seen there, the presence of framework germanium (8 wt%) is immediately reflected as a remarkable decrease on the activity of the catalyst for the cycloisomerisation. Again the relative activity of PdCl₂-(Si)Beta and PdCl₂-(Si,Ge)Beta can be understood as a reflection of the hardness–softness variation of the zeolite framework.

3.4. Zeolite framework hardness–softness and its relationship with the activity of the palladium Lewis acid sites for the cycloisomerisation

We propose that the catalytic activity of Pd²⁺-containing zeolites shown in Table 2 can be rationalised based on the reported data about the hardness–softness of the zeolite frameworks. Considering the zeolite as a “macroligand” coordinatively bonded to the active Pd sites, the harder the zeolite framework, the higher the local hardness at the palladium atom. According to the accepted reaction mechanism for the cycloisomerisation, Pd atoms must be electrophilic enough to bind to the π clouds of the terminal C=C bonds of diallylmalonate in the way depicted in Scheme 4, thus promoting the formation of the five-membered cycle [22,24,25,27]. Electrophilicity requires Pd atoms to be hard.

Hard acids have high-energy LUMOs and hard bases have low-energy HOMOs. In other words, the higher the energy of the LUMO of an acid the harder it is as an acid, while the lower the energy of the HOMO of a base the harder it is. Thus, from the point of view of the perturbation theory, we explain acid–base reactions and, in particular, the interaction between Pd metal ions and the zeolite framework mainly through the HOMO–LUMO interaction. In the case of zeolites [20,40] the energy of the zeolite frontier orbitals have been calculated as a parameter to evaluate their hardness–softness. In this way, there are reported theoretical calculations that estimate the influence of the chemical composition of zeolite on the relative hardness of the samples. Schoonheydt and co-workers [30] and Mortier and co-workers [29] have used the electronegativity equalization formalism for calculating the global electronegativity and hardness and the local softness in zeolites. The theoretical values obtained for hardness–softness in zeolites have already served to provide a conceptual understanding of the experimental results for electrophilic alkylation of aromatics with zeolites [20,41,42].

From all the precedents presented above, one can rank the hardness of the zeolite frameworks used in this work

considered as macroligand of Pd metal ions following the three rules emerging from the theoretical formalisms: (i) the higher the framework Al content, the harder the zeolite framework; (ii) the presence of germanium increases the softness of the zeolite; (iii) substitution of proton by alkali metal ions increases the zeolite softness. From these rules the series of zeolites can be ordered in decreasing hardness as follows: HUSY \approx HBeta \approx HZSM-5 > H,NaY \approx H,NaBeta > (Si)Beta > NaY > NaBeta > (Si,Ge)Beta. This order of zeolite hardness based on quantum chemical calculations coincides with that observed for the activity of the palladium-containing zeolites for the cycloisomerisation that is a specific Lewis acid-catalysed reaction.

4. Conclusions

In conclusion, it has been demonstrated that the activity of palladium catalyst depends on the match of its hardness–softness with the requirements of a particular transformation. Herein we have chosen the cyclisation of diallylmalonate and shown that it is a specific Lewis acid-catalysed reaction. We have also shown that the activity of a series of Pd-containing zeolites as catalyst varies in a wide range. By using the concept of hardness–softness of the zeolite framework we have provided a simple, predictive rationalisation of the reasons for such a wide variation on activity and propose the cyclisation of diallylmalonate as a test reaction to measure the relative softness of different solid Pd catalysts.

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