Gas-phase hydrogenation of acetonitrile over Pt and Pt–Pd supported on mesoporous solids: influence of the metallic precursor


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Abstract

Gas-phase hydrogenation of acetonitrile has been chosen as a test reaction to evaluate the catalytic behaviour of supported bimetallic catalysts prepared from dinuclear complexes precursors. Thus, Pd/Pt supported on zirconium doped mesoporous silica catalysts, with total metal loading of 1 and 2 wt.%, have been obtained by incipient wetness impregnation by using [PdPtCl₂(m-dppm)₂], after removing the ligands by calcination and subsequent reduction with H₂. These catalysts have been compared with supported platinum or palladium/platinum catalysts with similar metal loadings prepared from classical inorganic salts ([Pt(NH₃)₄](NO₃)₂, PdCl₂ and H₂PtCl₆·C₁₆H₂O). The metal-based catalysts have been characterized by powder XRD, adsorption–desorption of N₂ at 77 K, TEM, H₂-TPR and NH₃-TPD. A remarkable high degree of metal dispersion was attained when using the dinuclear precursor, giving rise to the highest yield of triethylamine in the gas-phase hydrogenation of acetonitrile, with a selectivity toward this tertiary amine close to 100%.

Keywords: MCM-41; Dinuclear complex; Platinum; Bimetallic catalyst; Mesoporous solid; Hydrogenation of acetonitrile

1. Introduction

Lower aliphatic amines serve as raw materials in water treatment chemicals, pesticides, surfactants, solvents and animal feed supplements, among other uses. As well, they can be also used in rubber chemicals, pharmaceuticals, solvents and plastics. The production of amines is usually carried out by liquid-phase hydrogenation reactions under high temperatures and hydrogen pressures, in the presence of metallic catalysts.

An alternative procedure is the gas-phase hydrogenation of nitriles, which seems to allow a better control of the selectivity pattern, by suitable choice of the nature of support (acid–base properties) and active phase (type of metal, metal particles sizes) [1–7]. Thus, Verhaak et al. [5] have reported that catalysts based on nickel supported on basic supports favour the formation of the primary amine in the gas-phase hydrogenation of acetonitrile. This fact led to these authors to propose a bifunctional mechanism for this reaction, where the hydrogenation step is accomplished on the metallic centres, whereas the acid function, located on the support, catalyzes the transamination reaction leading to secondary and tertiary amines. However, this mechanistic model failed when it was applied to other catalytic systems [3,8], where all reaction steps converting nitriles into different amines seemed to take place on the surface of metal sites.

Regarding the influence of the supported metal on the selectivity toward the different amines, it is largely accepted
that nickel-based catalysts lead the reaction toward primary amines, whereas noble metal catalysts seem to favour the formation of higher amines. The Arai group has extensively studied the behaviour of platinum supported on different supports, and they have evaluated the effects of metal particle size and supports on the gas-phase hydrogenation of acetonitrile [8–10]. They observed the influence of the support on the specific activity and the selectivity, as in the case of platinum catalysts supported on alumina and titania, respectively. However, the preparation method of different support materials and platinum precursors (impregnation or ion-exchange) seemed to have also a strong influence on the selectivity toward diethylamine or triethylamine.

On the other hand, there is a great deal of interest in the search of new precursors to get tailored metal particles sizes. In this sense, Guari et al. [11] have reported the use of organometallic precursor for the growth of gold nanoparticles within the pores of mesoporous solids, with a strict control of the metal particles size, by a two-step procedure implying the anchoring of the gold precursor and the subsequent chemical reduction. Organometallic complexes have also been employed as precursors for the preparation of supported noble metal catalysts for the hydrogenation of aromatics [12]. They exhibited, after the removing of the ligands from the metal coordination sphere, a catalytic activity comparable to that shown by a commercial Pt/Al2O3 hydrogenation catalyst, even in the presence of dibenzothiophene. This catalytic performance seems to lie in a better metallic dispersion, rather than in the electronic or steric effects ascribed to the organometallic precursors.

The vertiginous development of the M41S family of mesoporous solids, from their discovery by researchers at the Mobil laboratories in 1992 until now, has opened new opportunities in sorption and catalysis, mainly due to their high specific surface areas, uniform pore-size distributions, and tunable acid/base and redox properties [13–16].

Recently, some of us have reported that catalysts based on nickel supported on different mesoporous materials are very active in the gas-phase hydrogenation of acetonitrile at 408 K, with selectivity toward the primary amine, in some cases, higher than 70 mol% for acetonitrile conversions close to 100% [17,18].

In this work, we report the behaviour of platinum and platinum/palladium supported on mesoporous silica catalysts in the gas-phase hydrogenation of acetonitrile. One of the main goals of this work was to evaluate the effect of introducing both metals (Pd/Pt) in the form of a dinuclear complex against the use of a mixture of salts. In that way, with the unique complex, the ratio 1:1 of metals would be already present in each molecule of the precursor and the homogeneity of the metallic dispersion could be improved. Other factors, such as the metallic content and the addition of zirconium to the mesoporous silica support, will also be evaluated.

2. Experimental

2.1. Preparation of catalysts

We have used two mesoporous supports of the MCM-41 type. One of them is made from pure silica, denoted as MCMSi, and the other is a silica doped with zirconium (Si/Zr molar ratio = 5), named SiZr-5.

The mesoporous MCM-41 silica support (MCMSi) was prepared by adding, under vigorous stirring, tetraethoxysilane (Aldrich, 98% ethanol solution) to an aqueous solution of hexadecyltrimethylammonium bromide (25 wt.%) (Aldrich) previously stirred at 353 K for 30 min. The surfactant/SiO2 molar ratio was 0.5. The pH was adjusted to 10–11 by addition of an aqueous solution of tetramethyammonium hydroxide (25 wt.%) and the resulting gel was stirred at room temperature for 4 days. The solid product was filtered off, washed with ethanol (2 × 200 mL) and dried at 333 K. In order to eliminate the surfactant, the solid was then calcined at 823 K for 6 h (1 K min−1 heating rate).

On the other hand, the mesoporous zirconium-doped silica support (SiZr-5) was obtained by following the procedure reported elsewhere [19].

Catalysts were prepared by using the incipient wetness method over the supports as pellets (0.2–0.3 mm). The dinuclear complex precursor ([PdPtCl2(µ-dppm)2]) was incorporated as a CH2Cl2 solution, while the monometallic precursors ([Pt(NH3)4](NO3)2, PdCl2, and H2PtCl6·6H2O) were introduced in aqueous solutions. Then, samples were dried in air at 333 K for 12 h, and calcined at 773 K for 4 h (2 K min−1 heating rate). Prior to catalytic tests, samples were reduced in situ at 673 K in a H2 flow of 50 mL min−1 for 60 min.

The catalysts prepared are summarized in Table 1. In the name of each catalyst, the number indicates the final metal wt.% in the calcined material. After this number, the metal or metals present are indicated and also the support used in each case (SiZr for SiZr-5 support, and Si for MCMSi). Catalysts obtained from the dinuclear complex are marked with B at the end of the name.

2.2. Characterization of catalysts

Powder X-ray diffraction patterns were obtained by using a Siemens D-501 diffractometer (Cu Kα-Source) provided

Table 1

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Precursor</th>
<th>Support</th>
<th>Metal (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1PtSi</td>
<td><a href="NO3">Pt(NH3)4</a>2</td>
<td>MCMSi</td>
<td>1</td>
</tr>
<tr>
<td>0.5PtSiZr</td>
<td><a href="NO3">Pt(NH3)4</a>2</td>
<td>SiZr-5</td>
<td>0.5</td>
</tr>
<tr>
<td>1PtSiZr</td>
<td><a href="NO3">Pt(NH3)4</a>2</td>
<td>SiZr-5</td>
<td>1</td>
</tr>
<tr>
<td>2PtSiZr</td>
<td><a href="NO3">Pt(NH3)4</a>2</td>
<td>SiZr-5</td>
<td>2</td>
</tr>
<tr>
<td>1PdPtSiZr</td>
<td>PdCl2, H2PtCl6·6H2O</td>
<td>SiZr-5</td>
<td>1</td>
</tr>
<tr>
<td>2PdPtSiZr</td>
<td>PdCl2, H2PtCl6·6H2O</td>
<td>SiZr-5</td>
<td>2</td>
</tr>
<tr>
<td>1PdPtSiZr-B</td>
<td>PdPtCl2(µ-dppm)2</td>
<td>SiZr-5</td>
<td>1</td>
</tr>
<tr>
<td>2PdPtSiZr-B</td>
<td>PdPtCl2(µ-dppm)2</td>
<td>SiZr-5</td>
<td>2</td>
</tr>
</tbody>
</table>

dppm = Ph2PCH2PPh2.
with a graphite monochromator. Textural parameters have been calculated from N2 adsorption-desorption isotherms, at 77 K, obtained by using a conventional glass volumetric apparatus (outgassing at 473 K and 10⁻⁴ mbar overnight). Pore-size distributions were calculated with the Cranston and Inkley method for cylindrical pores [20].

Transmission electron micrographs (TEM) of the catalysts were obtained by using a Phillips CM 200 Supertwin-DX4 microscope. Samples were dispersed in ethanol; a drop of the suspension was put on a Cu grid (300 mesh).

Temperature-programmed desorption of ammonia (NH3-TPD) was used to determine the total acidity of the supports and catalysts. Before the adsorption of ammonia at 373 K, the samples were treated at 823 K in a helium flow (50 mL min⁻¹) for 60 min. The NH3-TPD was performed between 373 and 823 K, with a heating rate of 10 K min⁻¹. The evolved ammonia was analyzed by an on-line gas chromatograph (Shimadzu GC-14A) provided with a thermal conductivity detector.

Hydrogen temperature-programmed reduction (H2-TPR) experiments were carried out between room temperature and 823 K, by using a flow of Ar/H2 (10 vol% of H2, 40 mL min⁻¹) and a heating rate of 10 K min⁻¹. Water produced in the reduction reaction was eliminated by passing the gas flow through a cold finger (188 K). The H2 consumption was analyzed by an on-line gas chromatograph (Shimadzu GC-14A) provided with a TCD.

The purity of the dinuclear complex [PdPtCl2(μ-dppm)2] was verified by 1H, 13C{1H} and 31P{1H} NMR using the following FT-spectrometers: Gemini FT-200 (for 1H NMR), Varian Unity FT-300 (for all the nucleus), Gemini FT-400 (1H NMR) and Innova FT-500 (1H and 13C NMR).

2.3. Catalytic tests

The gas-phase hydrogenation of acetonitrile was performed in a flow system operating at atmospheric pressure. A tubular Pyrex reactor (27 cm length, 7 mm o.d. and 3.6 mm i.d.) was used. Prior to any measurement, 0.05 g of sample (sieve fraction of 0.2–0.3 mm) was reduced in situ at 673 K under a hydrogen flow of 50 mL min⁻¹ for 60 min (heating rate of 10 K min⁻¹). After that, the hydrogen flow was bubbled through a saturator containing acetonitrile (Aldrich, 99.93 + wt.%, HPLC grade) at 281 K, thus, resulting in a feed with 6.5–7 mol% of acetonitrile, which was introduced into the reactor. The reactants and products were analyzed by using an on-line gas chromatograph (Shimadzu GC-14A) equipped with a flame ionization detector and a TRB-14 column. Tests were performed between 408 and 448 K, and a total flow rate of 88 mL min⁻¹ was used.

The conversion has been calculated from the measured acetonitrile concentrations of the effluent and the feed:

\[
\text{Conversion (\%) } = \frac{100 \times (\text{CH}_3\text{CN}_{\text{in}} - \text{CH}_3\text{CN}_{\text{out}})}{\text{CH}_3\text{CN}_{\text{in}}} 
\]

The selectivity was calculated from peak areas by considering the different factors in the flame ionization detector. The selectivity for the product \( i \) is defined as:

\[
\text{Selectivity}_i(\text{mol }\%) = \frac{100 \times (\text{corrected area})_i}{\text{sum of all corrected areas}}
\]

A series of preliminary experiments were carried out in order to rule out the existence of diffusional limitations under the experimental conditions used.

3. Results and discussion

3.1. Catalysts characterization

The characterization of the two mesoporous supports used in the present paper has been previously reported [19,21]. It was noted that incorporation of zirconium into the mesoporous silica produces a decrease in the long-range order as shown by the presence in the X-ray diffraction patterns of an unique and broad reflection at low diffraction angle, but the reflection lines corresponding to \( \text{ZrO}_2 \) (tetragonal or monoclinic) were never observed. As expected, the presence of zirconium into the silica framework enhanced the total acidity of the resulting mesoporous support.

Concerning the X-ray diffraction patterns of the catalysts, they exhibit, in all cases, the typical \( d_{100} \) low angle reflection of the hexagonal arrangement of channels, indicating that the structure is preserved not only after conforming the powdered supports as pellets but also after the impregnation and calcination processes. In general, unreduced catalysts which are synthesized using salts of monometallic Pt

![Fig. 1. Powder X-ray diffraction patterns of unreduced catalysts: (a) 1PtSi, (b) 0.5PtSiZr, (c) 1PtSiZr, (d) 2PtSiZr, (e) 1PdPtSiZr, (f) 2PdPtSiZr, (g) 1PdPtSiZrB and (h) 2PdPtSiZr-B.](image)
complexes show diffraction signals due to the presence of metallic platinum, which means that a fraction of Pt(II) is reduced during the calcination process (Fig. 1). These diffraction signals are not present for the other catalysts (except for 2PdPtSiZr), which points to a better metallic dispersion when the dinuclear precursor was employed.

The evaluation of the metal particles sizes and their distribution has been carried out by transmission electron microscopy. The micrographs displayed in Fig. 2 show that the size of the metallic particles varies with the type of bimetallic catalyst, being quite smaller for the catalysts obtained from the dinuclear precursor.

Fig. 2. Transmission electron micrographs and histograms of particle size of 2PdPtSiZr and 2PdPtSiZr-B catalysts.
Thus, for 2PdPtSiZr-B, most of the particles are smaller than 6 nm, being the mean particle size of 2.9 nm, while for the analogous 2PdPtSiZr, the mean value is 26.3 nm, since metal particles larger than 100 nm are observed in the corresponding micrograph. The differences in the mean metal particle sizes are also evident for the catalysts with a lower metal loading (1 wt.%), since the mean values found for 1PdPtSiZr and 1PdPtSiZr-B are 14.8 and 2.1 nm, respectively. These results confirm the much better metallic dispersion obtained for catalysts prepared from the dinuclear precursor, as it had been deduced from XRD.

This amelioration of the metal dispersion has been also reported for supported noble metal catalysts prepared from organometallic precursors [12], and this improved metallic dispersion is a major advantage against similar materials obtained from classical inorganic salts, conferring to these catalysts a greater sulphur resistance in the hydrogenation of aromatics.

Concerning the textural characteristic of the catalysts, these were evaluated by N₂ adsorption–desorption at 77 K. In all cases, the isotherms are of Type IV according to the IUPAC classification and reversible, with the typical inflexion of this family of mesoporous MCM-41 solids at low relative pressure. The adsorption–desorption isotherms and the corresponding pore-size distributions of catalysts are very similar to those of supports, revealing that no modification of the textural characteristics of support after the incorporation of the active phase has taken place. In Fig. 3, the isotherms and pore-size distributions of the SiZr-5 support and the 2PdPtSiZr-B catalyst are shown as an illustrative example. It is observed that the shape of the isotherms is very similar, excepting an increase in the adsorbed volume at high relative pressures and a slight shift of the band corresponding to the average pore radii toward low values, after the incorporation of the active phase onto the mesoporous support. Nevertheless, the specific surface area is not affected and the values obtained for most of the catalysts are very close to that of zirconium doped mesoporous silica, used as support. This indicates that the support is barely affected after the incorporation of these low percentages (1–2 wt.%) of active phase (Table 2). For bimetallic catalysts prepared from the dinuclear complex, the decrease is very low due to their better metal dispersion. This fact could also be attributed to the use of a non-aqueous solvent, dichloromethane, in the impregnation step, whereas water was used for the preparation of the other catalysts. The pernicious effect of water over the mesoporous structure of MCM-41-type solids has already been reported [22,23].

For monometallic catalysts, the decrease in the specific surface area after the introduction of the metallic phase is more pronounced, especially for 2PtSiZr. This reveals that the metal particles are blocking a fraction of the pores of the

<table>
<thead>
<tr>
<th>Textural characteristics of the supports and the noble metal-based catalysts</th>
<th>S_BET (m² g⁻¹)</th>
<th>V_p (cm³ g⁻¹)</th>
<th>Sac (m² g⁻¹)</th>
<th>ΣV_p (cm³ g⁻¹)</th>
<th>d_p (av) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCMSi</td>
<td>749</td>
<td>0.567</td>
<td>834</td>
<td>0.569</td>
<td>2.9</td>
</tr>
<tr>
<td>SiZr5</td>
<td>545</td>
<td>0.559</td>
<td>700</td>
<td>0.592</td>
<td>3.4</td>
</tr>
<tr>
<td>1PtSi</td>
<td>522</td>
<td>0.345</td>
<td>502</td>
<td>0.325</td>
<td>2.6</td>
</tr>
<tr>
<td>0.5PtSiZr</td>
<td>442</td>
<td>0.345</td>
<td>496</td>
<td>0.360</td>
<td>2.9</td>
</tr>
<tr>
<td>1PtSiZr</td>
<td>444</td>
<td>0.350</td>
<td>482</td>
<td>0.356</td>
<td>3.0</td>
</tr>
<tr>
<td>2PtSiZr</td>
<td>288</td>
<td>0.194</td>
<td>300</td>
<td>0.186</td>
<td>2.5</td>
</tr>
<tr>
<td>1PdPtSiZr</td>
<td>493</td>
<td>0.408</td>
<td>579</td>
<td>0.442</td>
<td>3.0</td>
</tr>
<tr>
<td>2PdPtSiZr</td>
<td>495</td>
<td>0.530</td>
<td>649</td>
<td>0.552</td>
<td>3.4</td>
</tr>
<tr>
<td>1PdPtSiZr-B</td>
<td>545</td>
<td>0.792</td>
<td>781</td>
<td>0.723</td>
<td>3.7</td>
</tr>
<tr>
<td>2PdPtSiZr-B</td>
<td>534</td>
<td>0.751</td>
<td>679</td>
<td>0.695</td>
<td>4.1</td>
</tr>
</tbody>
</table>

a: Pore volume at P/P₀ = 0.95.
b: Calculated by using the Cranston and Inkley method [20].
support. The lowest surface area was found for 2PtSiZr, because of the existence of large metal particles, previously observed by XRD.

On the other hand, it has been demonstrated that the acidity of the support exerts an important influence on the activity and selectivity in the gas-phase hydrogenation of acetonitrile [5,24,25]. For this reason, the acidity of the different supports and catalysts used in this study was evaluated by NH$_3$-TPD. This technique confirms the results already reported for other members of the MCM-41 family, which indicated that the incorporation of heteroatoms such as aluminium or zirconium into a silica matrix enhances the acidity of the inorganic framework. A preliminary study with the bimetallic catalysts was carried out, in order to evaluate the differences between different precursors. As can be observed in Fig. 4, the incorporation of the active phase produces in all cases an important decrease of the acidity with respect to the support. For catalyst 2PdPtSiZr-B, we measured the total acidity before and after the reduction process in order to get information of the material as it is used in the catalytic reaction. It is necessary to consider that the precursor is reduced in situ before the catalytic run. The catalyst loses half of its acidity after reduction, and in consequence all the other catalysts were studied under these conditions. This loss of acidity after reduction can be explained by accepting the existence of M$^{2+}$ ions neutralising acid sites of the support in unreduced catalysts, which can retain ammonia molecules forming amminocomplexes. The reduction of these species, after flowing hydrogen, produces a decrease of the total acidity of catalysts.

The catalysts prepared with salts precursors or mono-metallic complexes show a higher acidity, a fact that may be due to their larger metallic particles already observed from XRD (and TEM), which leave available a higher fraction of the acid sites of the support.

On the other hand, the H$_2$ temperature-programmed reduction (H$_2$-TPR) technique gives useful information about reducibility of the different species, and hence the strength of the metal-support interaction can be deduced.

In a previous paper, the H$_2$-TPR curves of pure Pd and Pt supported on SiZr-5, with 2 wt.% of metal loading, have been reported [26]. The monometallic palladium catalysts exhibited a negative peak at low temperature (353 K), together with a small H$_2$ consumption peak at 373 K and several broad and low intense peaks between 523 and 723 K, which were attributed to the reduction of PdO and PdO$_x$Cl$_y$ species, respectively. In the case of monometallic Pt catalysts, their H$_2$-TPR profiles present two peaks, one of them at low temperatures (373–473 K) with a low intensity, and another one between 573 and 673 K. The presence of these two peaks may reveal the existence of platinum in two different environments: the first peak could be assigned to the reduction of large platinum(II) oxide particles, while the less reducible platinum(II) species would be located in the inner region of the mesoporous framework, as either small PtO particles or Pt$^{2+}$ ions neutralising the cationic exchange sites, as well as PtO$_x$Cl$_y$ species.

For bimetallic catalysts obtained from the dinuclear precursor, a H$_2$ consumption peak is observed at 354 K which could be assigned to the reduction of Pd(II) to Pd(0) (Fig. 5). The negative peak observed in the TPR profiles at 405 K is characteristic of the palladium-containing catalysts, and it is attributed to the hydrogen desorption from decomposition of a palladium hydride previously formed at low temperature, accordingly to that previously observed by other authors [27,28]. At higher temperatures, the broad signal detected at 585 K could be assigned to the reduction of small metal oxide clusters, whereas the hydrogen consumption observed at 753 K could be attributed to both MO$_x$Cl$_y$ (M = Pd, Pt) species [29] and metal ions neutralising acid sites of the support.

The TPR curves for bimetallic Pd/Pt catalysts obtained from salts are very different. The hydrogen consumption below 500 K could be attributed to the reduction of both metals, although the contribution of the Pd reduction to this
peak could be more important. The peak centred between 550 and 600 K could be assigned to the reduction of small metal oxide particles and $\text{MO}_2\text{Cl}_2$ species. The negative peak due to the palladium hydride is not detected; and the hydrogen consumption at temperatures higher than 625 K is absent in the $\text{H}_2$-TPR curve of the 2PdPtSiZr catalyst. This latter fact corroborates the existence of large metal particles, already detected by XRD and TEM, on this catalyst, which are easily reducible.

3.2. Catalytic tests

All the catalysts previously characterized were tested in the gas-phase hydrogenation of acetonitrile at atmospheric pressure. The reaction products were ethylamine (EA), diethylamine (DEA), triethylamine (TEA), and methane.

The following standard experimental conditions were used: $T = 408$ K, $\text{F}/\text{W} = 104,000 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$, $\text{H}_2/\text{CH}_3\text{CN}$ molar ratio = 13. These conditions were chosen because previous studies [17,18] had evidenced that, as expected, low space velocities and high $\text{H}_2$/acetonitrile ratios increased the acetonitrile conversion, as well as high reaction temperatures. However, at higher temperatures, the appearance of cracking products, in some cases, limited the yield in amines and the catalysts deactivate faster due to coke deposition.

In addition, in our study, catalytic activity in the gas-phase hydrogenation of acetonitrile was only observed after the removing of the ligands of the coordination sphere of the supported bimetallic complex, and the subsequent reduction of the metallic phase.

Other fact to be taken into account is the sequence of impregnation and pelletization, being the best textural and catalytic results obtained, as expected, by impregnation of a support, previously pelletized. This sequence gives rise to catalysts where the active phase is more accessible to reactants. For this reason, in this study we have impregnated, in all cases, pellets with the different metal solutions, since the high pressure used to pelletize after the impregnation could produce that a part of the active phase was not accessible for the reactants.

In a first step, we have evaluated the influence of the support acidity on the catalytic behaviour by supporting platinum (1 wt.%) on two supports of different acidity: mesoporous silica and zirconium doped mesoporous silica. Thus, the 1PtSi and 1PtSiZr catalysts have been, respectively, obtained. For 1PtSi, the initial conversion was very low, the deactivation was observed, whereas 1PtSiZr initially converted all the acetonitrile, but with a high formation of cracking products ($\text{CH}_4$), and not very high selectivity toward higher amines (Fig. 6). After two hours of time-on-stream (TOS), at 408 K, 1PtSiZr reached the steady state with a conversion of 48% and a selectivity toward TEA of 63 mol%. The deactivation of platinum catalysts in the gas-phase hydrogenation of acetonitrile has already been reported [10], and it has been explained by considering that an acid support not only favoured cracking reactions (producing in some cases coke deposition over active sites), but also could suffer the strong linking of basic molecules such as amines to the acid sites producing the deactivation of the catalyst. We have found that the use of a more acidic support, SiZr-5, gives rise to a high selectivity to the tertiary amine, TEA, without formation of EA, maintaining an acetonitrile conversion, in the steady state, close to 50%.

Then, it is possible to state, from this preliminary study, that the support is very important for the gas-phase hydrogenation of acetonitrile, because the acid–base character of the support determines the metal-support interaction, and hence the electronic density of the metallic particles, which is in part responsible of the catalytic activity of these solids. The observed increment in the selectivity to TEA using the most acidic support, SiZr-5, seems to indicate the participation of acid sites in the condensation reactions giving rise to TEA and DEA, although this selectivity would mainly depend on the modification of the electron density on the metal particles. This fact might point to a bifunctional mechanism [5], although more information about the catalytic behaviour of this family of catalysts is necessary to unequivocally postulate a plausible mechanism.

Taking into account that the use of SiZr-5 gives better results than MCMSi in terms of activity and selectivity, we have also studied the influence of the metal loading by varying between 0.5 and 2 wt.% the amount of metal incorporated over the SiZr-5 support. All monometallic catalysts exhibit initial conversions near 100%, but a quickly deactivation always occurs. Conversion and selectivity after 15 h of TOS are shown in Fig. 7. The maximum conversion is obtained for 1PtSiZr (ca. 48%), whereas the lowest value (ca. 12%) is observed over 2PtSiZr, where large metal particles were detected by DRX, which leave available a smaller metallic surface.

The use of palladium-based catalysts for the gas-phase hydrogenation of acetonitrile has also been reported [3,30]. Thus, Pd supported on NaY preferentially leads to secondary...
amines in the hydrogenation of butyronitrile at low reaction temperatures [3], whereas Iwasa et al. [30] have recently shown that selectivity can be largely modified by formation of palladium alloy catalysts and working at different reaction temperatures. Moreover, it is well known that by alloying several transition metals, the catalytic performance can be modified. For these reasons, we have substituted a fraction of Pt by Pd in order to prepare bimetallic catalysts, but maintaining similar metal loadings (1 and 2 wt.%) and an atomic ratio 1:1. Our goal is not only to study the influence of the presence of Pd, but also the effect of the use of different metallic precursors to obtain bimetallic catalysts, on the acetonitrile hydrogenation. Thus, we have prepared a series of PdPt bimetallic catalysts by impregnation with a dinuclear complex and mixed salt precursors, on the SiZr-5 support.

In Table 3, the initial conversion and selectivity values are shown, and the corresponding values in the steady state are compared in Fig. 8. In the steady state, the acetonitrile conversion values, except for 2PdPtSiZr-B, are about 30% (Fig. 8). However, the selectivity toward TEA is much higher over catalysts obtained from the dinuclear precursor, reaching selectivity values higher than 85 mol% on these two catalysts (1 and 2 wt.%). Moreover, the production of DEA is negligible on these catalysts, whereas EA was never observed. By considering the values of conversion and selectivity toward TEA, the 1PdPtSiZr-B is among the bimetallic catalysts that exhibits the best TEA yield (26.1%). This finding is in contrast with the higher acidity of the 2PdPtSiZr catalyst. However, this TEA yield value is slightly lower than that corresponding to the 1PtSiZr catalyst (32.6%). This fact could be explained by taking into account that perhaps the synergic effect of Pd appears for higher loading of this metal, as shown by the work of Iwasa et al. [30], where percentages as high as 10 wt.% are used.

As conclusion, it is possible to state that the bimetallic 1PdPtSiZr-B catalyst shows a similar behaviour (referring to yield of TEA) in the gas-phase hydrogenation of acetonitrile than the monometallic platinum catalysts with the same percentage of metal, but improving the selectivity to TEA, perhaps due to the higher available metallic surface. This is because of the better metallic dispersion obtained when a bimetallic precursor was used, as it has been observed in the XRD patterns, where these catalysts did not showed the peaks corresponding to Pt(0) or these peaks were smaller than those obtained for the catalysts which were prepared from the mixture of salts.

Therefore, catalysts prepared from the dinuclear precursor show in general better results in terms of TEA selectivity than those prepared from a mixture of salts, which would facilitate the separation of the TEA from the other products. TEA is obtained as the major product, showing the catalyst 2PdPtSiZr-B full selectivity toward TEA, although its acetonitrile conversion in the steady state barely is higher than 15%.

The use of both an acidic support, such as SiZr-5, and dinuclear precursors leads to catalysts with a high degree of metal dispersion, where the strong metal-support interaction makes electron-deficient the small metal clusters. This could favour the adsorption of basic species such as DEA, which would be transformed into TEA by addition of alkyl groups to the N bonded intermediates, as postulated by Huang and Sachtler [31]. The subsequent hydrogenation of the resulting species on the metal sites and desorption increases the selectivity toward TEA.

Finally, concerning the mechanism of the gas-phase hydrogenation of acetonitrile over this series of Pt- and PdPt-based catalysts, it is evident from the results previously...
exposed and discussed, that much work it is still needed to postulate a mechanism which could explain the catalytic behaviour, since this seems to depend on factors such as the nature of support, type of active phase precursor and synergistic effect in bimetallic systems.

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