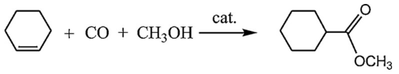
pressure (ca. 5 atm) and then heated up. At the working temperature the pressure was adjusted to the desired value (typically 50 atm total pressure) and maintained constant throughout the experiment (i.e. 2 h) by continuously supplying the carbon monoxide from the reservoir. At the end of each experiment the reactor was quickly cooled to room temperature and vented. The solid was recovered by filtration, washed and dried under vacuum. To determinate the amount of leaching it has been measured the amount of Pd on the solid before and after the reaction by using the ICP technique (the % of leaching has been expressed as [[(g of Pd in the solid before reaction)-(g of Pd in the solid after reaction)]/(g of Pd in the solid before reaction)]x100. The qualitative and quantitative analysis of the liquid was performed by using the GC–MS and GC technique. The conversion has been expressed as: [(initial moles of cyclohexene – final moles of cyclohexene)/ initial moles of cyclohexene] * 100; In all experiments the material balance has been verify and the selectivity to ester was 100 %

2.7. Recycling experiments

The pre-catalyst was recovered from the reaction solution through a simple filtration. It was thoroughly washed many time with methanol and acetone and then dried under vacuum. The solid was weighted and reused in the next reaction. In this case we prefer to evaluate the catalytic activity in term of TOF (Turnover Frequency: moles of ester/(moles of Pd*h)) which was calculated by considering that all the amount of metal deposited on the surface was active in the catalysis. This is because during the recycling operations part of the catalyst (usually < 5 %) could be lost. The leaching in the successive reactions was measured through the ICP analysis of the liquid phase. The next reaction was carried out following the same procedures above described (section 2.5).

3. Results and discussion

The methoxycarbonylation of cyclohexene (reaction 2) has been efficiently carried out by using a heterogeneous catalyst precursor, based on Pd metal deposited on an unsolvable support (Tables 1 and 2). Although it was widely reported that such reaction is not catalyzed by Pd metal [1–3,26–33], we found that by adding free PPh_3 and TsOH, similarly to the homogeneous catalytic systems [26–33], it can readily form the active species and lead to the ester in high yield.



(2)

3.1. Influence of different supports on the catalytic activity

The Table 1 shows the activity of several Pd_{metal}-supported heterogeneous catalysts which has been compared with the activity obtained by using the homogeneous $[Pd(PPh_3)_2(TsO)_2]/PPh_3/TsOH$ (1/50/60) system, previously studied by some of the authors [30,31].

All the pre-catalysts tested lead to good conversion regardless of porosity and specific surface area of the support. Among these, Pd_{metal} on Carbon (Pd/C), Pd_{metal} on polyketone (Pd/PK) and Pd_{metal} on cellulose (Pd/cell) lead to comparable conversions (81–83 %), whereas Pd_{metal} on ion exchange resins lead to different results (entries 5–7). In particular, Pd_{metal} on Dowex 1-X8 leads to the worse conversion (42 %, entry 5), whereas Pd_{metal} on Amberlyst IRC 50 and Pd_{metal} on Amberlyst 15 lead to the best conversions (92-91 %, entries 5, 6), which are almost comparable to the conversion obtained by using the homogeneous catalyst (93 %, entry 1).

All the heterogeneous catalysts have been readily recovered at the end of reaction by using a simple filtration apparatus. The leaching of the metal measured was very poor when Pd/Amberlyst IRC 50 (3 %) or Pd/Amberlyst 15 (3 %) has been used (Table 1, entries 5 and 6) whereas it is higher when Pd/Dowex 1-X8 (3 %) is used (entry 7). Moreover, based on our previous work [40], it has been deposited a dosed amount of ferrimagnetic Fe_3O_4 (magnetite) on the surface of some supports in order to allow an easier recovery of the catalyst by using an external magnetic field.

Table 2 shows that the addition of Fe_3O_4 decreases the conversion of cyclohexene (entries 4–9) and that it differs consistently from the amount of cyclohexane methyl ester effectively detected in solution; Unfortunately, at the end of the reaction all the catalysts have lost the initial magnetic properties. By increasing the amount of Fe_3O_4 on the support the cyclohexene conversion slightly change and it further decreases the amount of ester detected in solution (entries 4–6). As in such experiments the material balance is not satisfied (not further by-products were detected), we suppose that both cyclohexene and/or its ester could be chemisorbed on the Fe_3O_4 causing also the lost of its magnetic features. This point was not further investigated because it was not in the aim of the present work. However, on the light of such results we decided to avoid the use of Fe_3O_4 and to optimize the reaction conditions by using the precursor Pd/Amberlyst IRC 50, which leads to the best result.

3.2. Influence of PPh_3 and TsOH on the catalytic activity and on the leaching of palladium

The Fig. 1 shows that, in absence of PPh_3 and at constant acid concentration (for instance TsOH/Pd = 60/1), the reaction is not catalyzed by Pd/Amberlyst IRC 50. However, by increasing the PPh_3/Pd molar ratio the catalyst become active and the conversion passes through a maximum of 92 % when it is *ca.* 50/1.

At PPh_3/Pd lower than *ca.* 45/1, the leaching of Pd measured was less than 5 % of the initial metal deposited on the support. On the other hand, at PPh_3/Pd higher than 45/1 the lost of metal rapidly increases, reaching *ca.* 15 % when PPh_3/Pd is ca. 120/1 (conversion of *ca.* 50 %).

According with the studies on the homogeneous catalysis [26–33], it is plausible that PPh_3 reacts with the Pd_{metal} deposited on the surface of the support forming solvable Pd(0) complexes. Such a complexes are transformed in the active species (probably Pd(II)-H) through reaction with the acid which increases the catalytic activity (see the Fig. 2). However the conversion passes through a maximum because the increase of free PPh_3 concentration stabilizes the inactive Pd(0) species against the active Pd(II)-H ones, causing a decrease of catalytic activity (see the Fig. 1 and reaction mechanism).

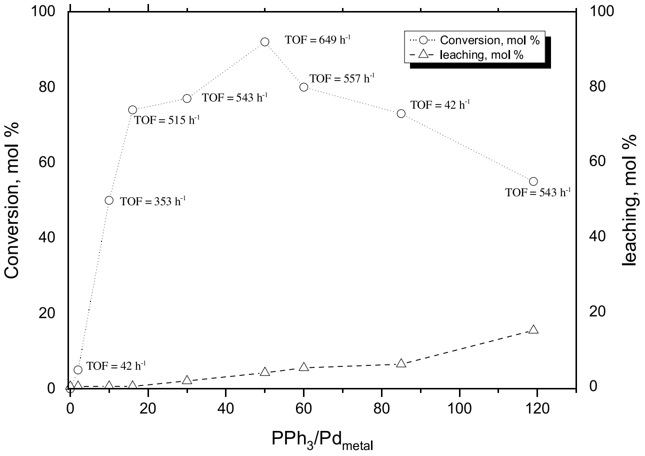


Fig. 1. Influence of PPh_3 on the catalytic activity of Pd/Amberlyst IRC 50 (3 %). Run conditions: Pd/Amberlyst IRC 50 = 50 mg (Pd 3 % w/w); Pd/TsOH = 1/60 mol/mol; Cyclohexene = 19.74 mmol (2 mL), solvent = MeOH (8.0 mL); T = 120 °C; t = 2 h; P_{CO} = 50 atm. TOF = moles of ester/[(moles of Pd in the solid before reaction)*(reaction time)].