

Fig. 2. Influence of TsOH on the catalytic activity of Pd/Amberlyst IRC 50 (3 %).

Run conditions: Pd/Amberlyst IRC 50 = 50 mg (Pd 3 %, w/w); Pd/PPh₃ = 1/50 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)].

According to this, the Fig. 2 shows that the catalyst is not active without acid and linearly increases by increasing the TsOH concentration (constant PPh₃ concentration, PPh₃/Pd = 50/1).

3.3. Influence of temperature on the catalytic activity of Pd/Amberlyst IRC 50 (3 %)

By increasing the temperature, the conversion passes through a maximum at ca. 120 °C (see Fig. 3). At reaction temperatures higher than 120 °C the conversion decreases, suggesting deactivation of the catalyst probably due to decomposition of the active Pd(II) species to form inactive Pd(0) complexes or Pd metal, similarly to what is reported when the homogeneous catalytic system is used [30]. To note that the leaching of metal practically does not change at different temperatures remaining in all the tests below the 3 % w/w.

3.4. Catalyst recycle

The heterogeneous precursor has been recovered at the end of each reaction and recycled (see experimental section). The Fig. 4 shows that

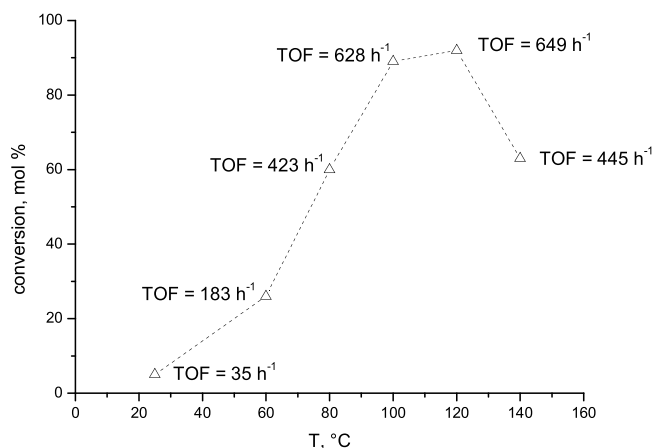


Fig. 3. Influence of temperature on the catalytic activity.

Run conditions: Pd/Amberlyst IRC 50 = 50 mg (Pd 3 %, w/w); Pd/PPh₃/TsOH = 1/50/60 (mol/mol/mol); Cyclohexene = 19.74 mmol (2 mL), solvent = MeOH (8.0 mL); T = 120 °C; t = 2 h; P_{CO} = 50 atm.

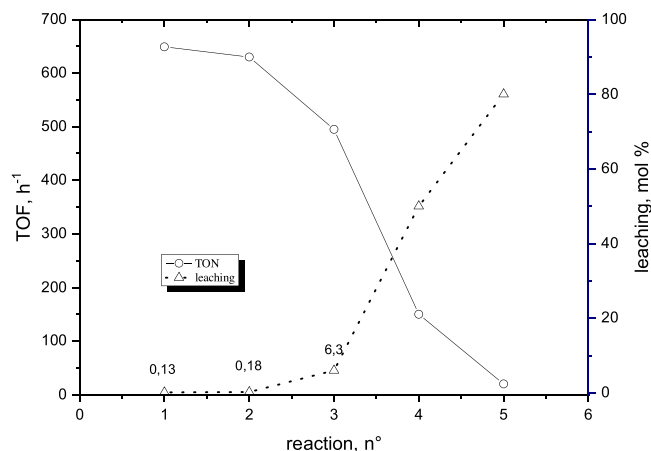


Fig. 4. Influence of catalyst recycling on the catalytic activity and on the leaching of Pd.

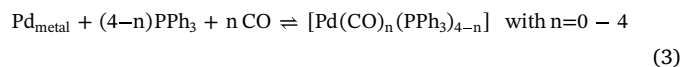
Run conditions: Pd/Amberlyst IRC 50 = 50 mg (Pd 3 %, w/w); Pd/PPh₃/TsOH = 1/50/60 mol/mol/mol; Cyclohexene = 19.74 mmol (2.0 mL), solvent = MeOH (8.0 mL); T = 120 °C; t = 2 h; P_{CO} = 50 atm.

the same precursor can be used at least two times without significant metal losses due to leaching (< 0.2 %). At the third time, however, the catalytic activity decreases whereas the leaching increases up to 6.3 %.

3.5. On the reaction mechanism

The results above discussed suggest that the active species can form in situ by reaction between PPh₃, TsOH and Pd metal, similarly to what is proposed in literature when the reaction is carried out by using the Pd (II) homogeneous catalyst [1–3,26–33]. Consequently, we propose the same reaction mechanism, schematized in the Fig. 5.

According to this, the solvable Pd-hydride species forms in situ from Pd metal deposited on the solid surface and the free CO, PPh₃ and TsOH, present in solution, for instance following the reaction 3 and 4.



As the Pd(0) and/or Pd(II) complexes formed are solvable in the reaction medium, it is plausible to suppose also that they determines the leaching observed. As a matter of fact, the Fig. 1 shows that by using a large excess of PPh₃ (PPh₃/Pd higher than 50/1) the leaching increases, but also decreases the conversion according to the fact that under such conditions is favoured the formation of solvable, but inactive, Pd(0) complexes. Moreover the low leaching generally measured in the experiments reported in Table 1, suggests that the reaction occurs faster

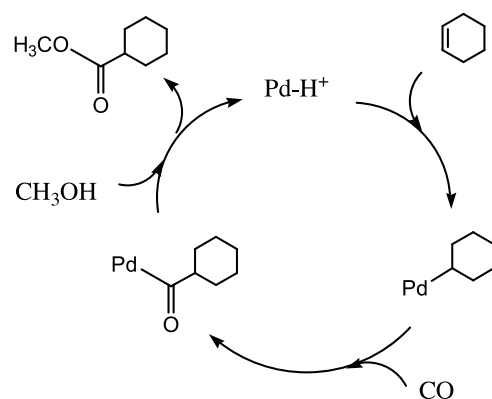


Fig. 5. Scheme of the proposed reaction mechanism.