

Fig. 6. Influence of reaction time on the catalytic activity and on the leaching of Pd.

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

than the diffusion of the solvable Pd(0) (or Pd(II)) species into the bulk and that such species are somehow retained within the solid. It is plausible therefore that the catalysis starts near the surface and, depending by the relative concentration of PPh₃ and TsOH (in particular inside the pores), the solvable Pd-species readily decompose forming Pd metal again (equilibrium 3 moves to the left), which is re-deposited on the surface.

According to this, the Fig. 3 shows that by increasing the temperature (> 110 °C) the conversion decreases suggesting a thermal decomposition of the catalyst with probable formation of Pd_{metal}. However, at each temperatures tested, the leaching of Pd measured was very poor (< 0.12 %), according with the hypothesis that a re-deposition of Pd_{metal} on the surface of the support readily occurs. This is further supported by the finding that the leaching is not influenced by the reaction time (Fig. 6 shows that at 7 h it is very low, < 0.12 %) but only by the PPh₃ and TsOH concentrations (Figs. 1 and 2).

A further influence on the amount of leaching measured should be due to the nature of the support. In fact, the Table 1 shows that when a cations exchange support was used the leaching was very poor (entries 5 and 6). As a matter of facts, the carboxylate groups present in the Amberlyst IRC 50 (sulfonate in Amberlyst 15) could interact with the cationic Pd(II) species readily formed in situ. Such interaction could

Table 3
Effect of addition of a pyridine based metal scavenger.

Experiment (entry)	scavenger	catalyst	Conversion (mol %)	TOF (h ⁻¹)
1		^a Pd/IRC 50	92	649
2		Pd/IRC 50 recycled from exp. 1	89	627
3	^b PVPy	Pd/IRC 50	3	21
4	^c PVPy- co-Sty	Pd/IRC 50	5	35
5		Pd/IRC 50 recycled from exp. 3	n.d.	-

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

^a Pd/IRC 50 = Pd/Amberlyst IRC 50 (3 %).

^b PVPy = Poly(4-vinylpyridine) average M_w ~ 60,000 = 150 mg.

^c PVPy- co-Sty = Poly(4-vinylpyridine-co-styrene) powder = 150 mg.

allow to the metal to remain inside the solid phase avoiding the leaching. It is therefore plausible to suppose that the functional groups of the support act as “heterogeneous” coordinating ligands (Fig. 7, path a) and/or as cations exchanging resin between H⁺ and the [Pd(II)]⁺ cationic species which form during the catalytic cycle (Fig. 7, path b).

With the aim to test the homogeneity/heterogeneity of the catalytic system, a metal scavenger has added to the reaction mixture [63–70]. In particular it has been added a polymer containing pyridine ligand (see Table 3) which is referred as effective scavengers for soluble Pd complexes or salts, due to the ability of the pyridine moiety to bind Pd species [68–70].

The Table 3 shows that the addition of such metal scavenger causes a decrease of catalytic activity (entries 3, 4), supporting the hypothesis that the catalysis was due to the formation of solvable Pd-species into the pores. According to this, in the experiment in which the Pd/Amberlyst IRC 50 has been recycled (entry 5) the ester has not detected.

4. Conclusions

The methoxycarbonylation of cyclohexene can be efficiently carried out in methanol by using palladium metal deposited over an unsolvable support as catalyst precursor. Although the catalytic activity depends on the PPh₃ and TsOH concentration and on the temperature, the best results both in terms of productivity and leaching have been obtained by using cations exchange supports.

Such heterogeneous system is proposed as a more sustainable catalytic pathway for the alkoxy carbonylation of olefin in comparison to

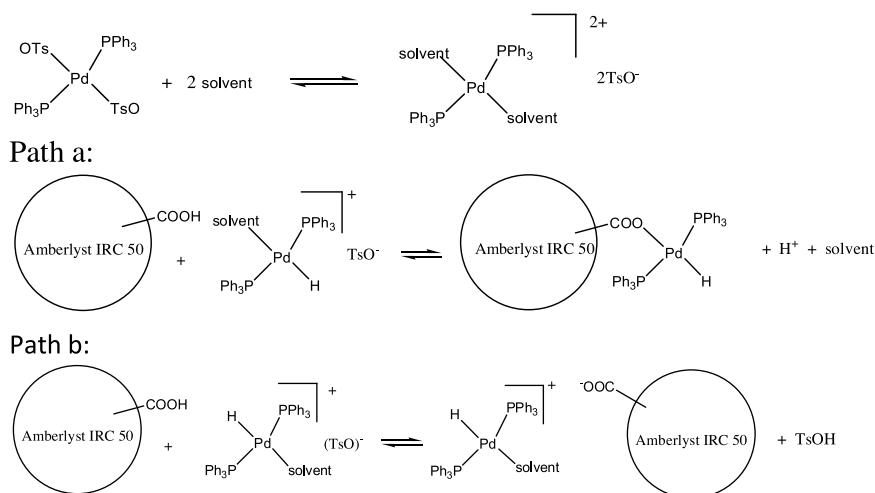


Fig. 7. Scheme of the possible interactions of the Pd(II) complexes and the functional groups of the support. Path a: coordination to the metal center; Path b: cations exchanging.