metal was negligible and the catalyst has been efficiently recycle at least for three times. A reaction mechanism has been also proposed and discussed.

2. Experimental

2.1. Reagents

Methanol, cyclohexene, Palladium(II) acetate, triphenylphosphine (PPh$_3$), p-toluenesulfonic acid monohydrate (TsOH), Amberlyst IRC 50, Dowex 1-X8, Amberlyst 15, Cellulose MFC (Type 101), Poly(4-vinylpyridine) average M$_w$ ~60,000, and Poly(4-vinylpyridine-*co*-styrene) powder were purchased from Sigma-Aldrich; Polyketone was synthesized from CO and ethene (supplied by SIAD Company with 'research grade', purity > 99.9 %) as described in literature [58].

2.2. Equipments

The catalyst precursors were weighted on a Sartorious Micro balance (precision 0.001 mg). Gas-chromatographic (GC) analysis was performed on a Hewlett Packard Model 7890, Series II chromatograph fitted with a HP5, 30 m ×0.35 mm ×0.53 μm column (detector: FID; carrier gas: N$_2$, 0.2 ml/min; oven: 45 °C (3 min) to 250 °C at 15 °C/min).

GC/MS analyses were performed on a MS Agilent apparatus 5975C Model, interfaced with an Agilent chromatograph 7890 A Model equipped with a HP5 column (30 m ×0.25 mm ×0.25 μm, oven: 45 °C (3 min) to 250 °C at 15 °C/min).

The ICP-OES (Inductively Coupled Plasma optical emission spectrometry) analyses, to identification and detection of trace metals, were performed by using the PerkinElmer ®Optima 7300 DV ICP-OES instrument.

The specific surface area of the powders was measured by Micromeritics Instrument Inc. USA apparatus, ASAP 2010 model.

2.3. Synthesis of Pd-metal supported pre-catalyst

The palladium metal catalyst was successfully supported on the solid showed in Tables 1 and 2 by using a standard wet impregnation method [59,60]. In a typical procedure, 1 g of support was added, at room temperature and under vigorous stirring, to a solution of 65 mg of Pd(OAc)$_2$ (Pd(II) acetate) in 50 mL of methanol. The Pd(OAc)$_2$ concentration has been eventually arranged to obtain at the end the desired Pd loading (ca. 3 %, w/w). The suspension was refluxed for 2 h under vigorous stirring to assure a complete reduction of Pd(II) to Pd metal. The solid catalyst was separated by filtration (or by using a permanent magnet when Fe$_3$O$_4$ was deposed), washed and dried under vacuum. The amount of Pd-metal deposed on the support was determined through the ICP analysis (confirmed as ca. 3 %, within 1 % of error); the

Table 2
Influence of different heterogeneous catalyst precursors containing magnetite on the methoxycarbonylation of cyclohexene.

entry	Catalyst	Conversion (mol %)	cyclohexane methyl ester detected in solution (mol[a] %)
1	Pd/C (3 %)	83	100
2	Pd/PK, (3 %)	81	100
3	Pd/Amberlyst IRC 50 (3 %)	92	100
4	Pd/Fe$_3$O$_4$, (3 %)	80	8
5	Pd/[C + Fe$_3$O$_4$ 5%], (3 %)	69	30
6	Pd/[C + Fe$_3$O$_4$ 15%], (3 %)	58	16
7	Pd/[C + Fe$_3$O$_4$ 25%], (3 %)	55	12
8	Pd/[PK + Fe$_3$O$_4$ 15%], (3 %)	65	25
9	Pd/[Amberlyst IRC50 + Fe$_3$O$_4$ 15%), (3 %)	77	31

Run conditions: Pd/Support = 50 mg (Pd 3 %, 0.014 mmol); Pd/PPh$_3$/TsOH = 1/50/60; Cyclohexene =19.74 mmol (2 mL), solvent = MeOH (8.0 mL, 197.75 mmol); T=120 °C; t = 2 h; P$_{CO}$ = 50 atm.
[a] [(moles of ester detected)/(moles of cyclohexene converted)]*100.

specific surface area of each solid has measured by using the N$_2$ fisi-sorption-BET technique.

2.4. Synthesis of magnetic supports

The synthesis of magnetic supports was performed by deposition of Fe$_3$O$_4$ nanoparticles on support surface [40] (see Table 2). In a typical procedure, 0.115 g of Fe$_3$O$_4$, suspended in 5 mL of methanol, was added under vigorous stirring to 1 g of support (carbon black or PK) suspended in 20 mL of methanol. The mixture has refluxed for 1 h and then the solid has separated by a permanent magnet, washed with fresh methanol and dried under vacuum. The specific surface area has measured by using the N$_2$ fisi-sorption-BET technique.

2.5. Experimental setup

All the experiments were carried out in a stainless steel batch reactor of *ca.* 50 mL of capacity, provided with a magnetic stirrer and a temperature control system (± 0.5 °C). Carbon monoxide was supplied from a gas reservoir (260 mL) connected to the reactor through a constant pressure regulator.

2.6. Experimental procedure

In a typical experiment, known quantities of the pre-catalyst, PPh$_3$ and TsOH along with 8 mL of methanol and 2 mL of cyclohexene were charged into the reactor. The reactor was purged twice with carbon monoxide at room temperature with stirring, pressurized with a low CO

Table 1
Influence of different heterogeneous catalyst precursors on the methoxycarbonylation of cyclohexene.

entries	Catalyst	Specific area (m^2/g)	Average porous diameter (nm)	Conversion (mol %)	TOF [mol ester/ (molPd[a] * h^{-1})]	Leaching of Pd (w/w %)
1	[Pd(PPh$_3$)$_2$(TsO)$_2$][b]	–	–	93	646	100[b]
2	Pd/Carbon (3 %)	842	6	83	577	6
3	Pd/PK[c](3 %)	40	20	81	563	5
4	Pd/Cellulose	2	20	82	570	6
5	Pd/Amberlyst IRC 50 (3 %)	2	6	92	649	0.3
6	Pd/Amberlyst 15 (3 %)	40	30	91	643	0.1
7	Pd/Dowex 1-X8 (3 %)	0.3	11	42	292	12

Run conditions: Pd/Support = 50 mg (Pd 3 %, 0.014 mmol); Pd/PPh$_3$/TsOH = 1/50/60; Cyclohexene =19.74 mmol (2 mL), solvent = MeOH (8.0 mL, 197.75 mmol); T=120 °C; t = 2 h; P$_{CO}$ = 50 atm.
[a] is the total Pd metal present in the support before the reaction.
[b] homogeneous catalyst Pd/PPh$_3$/TsOH = 1/50/60 (mol/mol/mol) [30,31].
[c] PK = poly(1-oxo trimethylene), named polyketone [61,62].