

Heterogeneous palladium catalysts for the Heck reaction

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Abstract

The vinylation of iodobenzene with methyl acrylate was studied using palladium-based heterogeneous catalysts. Methyl cinnamate was formed as vinylation product and benzene as side product. All catalysts were of the type $\text{SiO}_2\text{-X-(NH)}_2\text{-Pd-L}_2$, where $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$ or $\text{C}_6\text{H}_5\text{CN}$ and $\text{X} = \text{Sn, Al or Ti}$. The catalysts were stable and could be reused several times in normal atmosphere without suffering appreciable loss in catalytic activity. The activity of the catalysts was good even at low temperature, and selectivities were very high. Strong interaction indicating the existence of chemical bonding was found between the modified silica support and palladium complex. A model of the active surface compound is proposed and confirmed.

Keywords: Heck reaction; Iodobenzene; Methyl acrylate; Palladium; Silica; Supported catalysts; Vinylation

1. Introduction

The usefulness of metal complex promoted reactions in organic synthesis is well documented. One of the most important homogeneously catalysed reactions for carbon–carbon bond formation is the Heck reaction (arylation of olefins). Under suitable laboratory conditions the reaction is relatively fast in most cases. Palladium compounds are particularly useful reagents for the Heck reaction. However, the presence of such catalytically active species in a reaction mixture may present problems associated with the separation, recovery and regeneration of the metal complex [1]. The use of even 1 mol% of palladium complex is prohibitively expensive for the commercial synthesis of most chemicals, even if recovery is reasonably

efficient [2]. Such problems can be avoided by the use of heterogeneous catalysts for these reactions. So far, only a few reports have been published on the use of heterogeneous catalysts to promote the formation of C–C bond [3]. The main goal of our study was to develop active, selective and stable heterogeneous catalysts that could be reused in Heck reaction with no appreciable deterioration in catalyst performance.

2. Experimental

2.1. Preparation of catalysts

The modified silica supports; silica supported polyalumazane [4], polytitanazane and polystannazane [5] were prepared by a published method. The modified silica support was impregnated with $\text{Pd}(\text{P}(\text{C}_6\text{H}_5)_3)_2\text{Cl}_2$, $\text{Pd}(\text{C}_6\text{H}_5\text{CN})_2\text{Cl}_2$ or

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$\text{Pd}(\text{OAc})_2$ as precursor in CH_2Cl_2 or benzene solution to give a palladium load of about 1 wt.%. After impregnation, the catalyst was washed with an excess of solvent to remove the part of the complex that was only physically adsorbed. After filtering, the catalyst was dried in normal atmosphere in an oven at 60°C for 12 h. Part of the catalyst was also reduced in a H_2 flow (60 ml/min) at 450°C for 3 h and used as catalyst in a hydrogenation reaction.

2.2. Reaction tests

Vinylation experiments were carried out in a 100-ml three-necked flask with magnetic stirrer and condenser. In a typical vinylation experiment, iodobenzene (3 mmol), methyl acrylate (3.75 mmol), Et_3N (3.75 mmol), catalyst ($\text{Pd}=0.03$ mmol) and 1,3-dimethyl-2-imidazoline (DMI) as solvent (40 ml) were introduced to the reactor. Air was removed by flowing nitrogen and the reactor was heated to 50°C or 90°C. The reaction was started by switching on the stirrer. The reaction continued for 12 h, after which the reactor was cooled to room temperature. The catalyst was separated from the reaction mixture by filtration, washed several times with excess CH_2Cl_2 to remove the starting material, products and possible Et_3NHI salt and then oven-dried at 60°C for 4 h. The catalyst was used again in vinylation or in hydrogenation reaction. The reaction mixture was analysed periodically with Shimadzu GC 14 A gas chromatograph with FID and helium as carrier gas. The GC capillary column was FS-WCOT Bonded, 30 m \times 0.25 mm \times 0.34 μm .

Hydrogenation reactions were run in a 100-ml three-necked flask fitted with condenser, magnetic stirrer, thermometer and gas burette. The catalyst ($\text{Pd}=0.027$ mmol) and 1.5-cyclooctadiene (14 mmol) in 40 ml solution in ethanol were added to the flask. The reactor was purged with flowing hydrogen and the atmospheric pressure of hydrogen was maintained in the apparatus during the reaction. The reaction temperature was maintained at 30°C with stirring. The degree of conversion and the selectivity were measured by

taking a 1 ml sample periodically. Samples were analysed using the Shimadzu GC 14 A gas chromatograph with FID and a capillary column, TC-WAX, 30 m \times 0.25 mm \times 0.25 μm .

2.3. Characterization of catalysts

ESCA measurements were carried out using a Perkin Elmer PHI 5500 ESCA system, with monochromated Al $\text{K}\alpha$ X-ray radiation (1487 eV). The flood gun was used to compensate the charging effect. The binding energies of the supported catalysts were corrected from the value of Si (2s) = 103.4 eV. The palladium complexes supported on modified silica support were formed into tablets and kept in vacuo for two days before the measurements.

FT-IR spectra were measured with a Perkin Elmer 1720X FT-IR spectrometer with MCT detector. Scan number 100 and 2 cm^{-1} resolution and reflectance method were used.

The palladium content of the catalysts was measured with a SEA 2010 X-ray fluorescence spectrometer.

3. Results and discussion

Our new heterogeneous catalysts catalysed the vinylation of iodobenzene with methyl acrylate to methyl cinnamate with high activity and selectivity at 90°C, as shown in Table 1. The main product was methyl cinnamate and the minor product benzene; no biphenyl was produced during the reaction. All the catalysts exhibited almost the same activity in second use after recycling as in the first use and in every case the selectivity was better. A small part of the palladium was released from the surface of the catalysts during the first reaction, and this part had a high capability to catalyse the hydrogenation reaction and produce benzene, and so to decrease the selectivity for methyl cinnamate. In the second use, when the detached palladium was no longer in situ and the catalyst was totally heterogeneous, only the vinylation reaction proceeded and selectivity was vir-

Table 1

Results of the vinylation of iodobenzene with methyl acrylate at 90°C

Catalyst	Reaction (I)		Reaction (II)	
	Conversion (mol%)	Selectivity for methyl cinnamate (mol%)	Conversion (mol%)	Selectivity for methyl cinnamate (mol%)
$\text{Pd}(\text{P}(\text{C}_6\text{H}_5)_3)_2/\text{SiO}_2\text{-Sn-(NH)}_2$	80.1	93.1	69.1	100
$\text{Pd}(\text{P}(\text{C}_6\text{H}_5)_3)_2/\text{SiO}_2\text{-Al-(NH)}_2$	91.6	99.5	91.2	99.6
$\text{Pd}(\text{P}(\text{C}_6\text{H}_5)_3)_2/\text{SiO}_2\text{-Ti-(NH)}_2$	81.2	100	83.3	100
$\text{Pd}(\text{C}_6\text{H}_5\text{CN})_2/\text{SiO}_2\text{-Al-(NH)}_2$	88.2	94.5	70.8	99.5
$\text{PdC}_6\text{H}_5\text{CN})_2/\text{SiO}_2\text{-Ti-(NH)}_2$	83.3	96.2	75.1	100
$\text{Pd}(\text{OAc})_2/\text{SiO}_2\text{-Ti-(NH)}_2$	82.8	99.5	69.3	100

The main product is methyl cinnamate and the minor product is benzene. The reaction conditions are described in the Experimental part.

(I) = fresh catalyst used.

(II) = the catalyst of reaction (I) filtered, washed, dried and reused.

Table 2

Palladium content of the catalysts before and after vinylation

Catalyst	Pd (wt.-%) before vinylation	Pd (wt.-%) after vinylation
$\text{Pd}(\text{P}(\text{C}_6\text{H}_5)_3)_2/\text{SiO}_2\text{-Sn-(NH)}_2$	0.7	0.5
$\text{Pd}(\text{P}(\text{C}_6\text{H}_5)_3)_2/\text{SiO}_2\text{-Al-(NH)}_2$	0.6	0.6
$\text{Pd}(\text{P}(\text{C}_6\text{H}_5)_3)_2/\text{SiO}_2\text{-Ti-(NH)}_2$	0.9	0.9
$\text{Pd}(\text{C}_6\text{H}_5\text{CN})_2/\text{SiO}_2\text{-Al-(NH)}_2$	0.9	0.7
$\text{Pd}(\text{C}_6\text{H}_5\text{CN})_2/\text{SiO}_2\text{-Ti-(NH)}_2$	0.8	0.6
$\text{Pd}(\text{OAc})_2/\text{SiO}_2\text{-Ti-(NH)}_2$	0.7	0.6

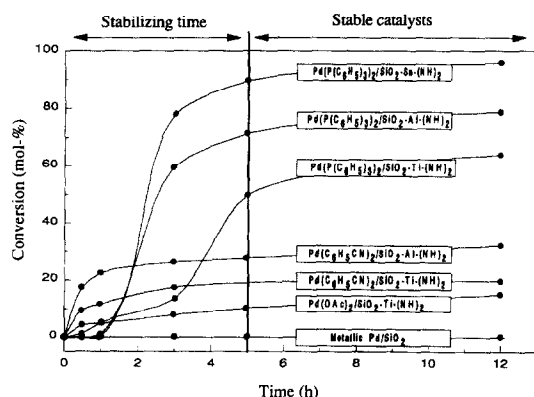


Fig. 1. The yield of methyl cinnamate vs. time at 50°C.

tually 100%. The palladium content of all the catalysts was changed very little during the first reaction, as shown in Table 2, which demonstrates that the real performance of the catalysts was heterogeneous. The catalysts did not seem to be air-sensitive, which made their use and recycling very easy.

The typical reaction temperature of the vinylation of iodobenzene is about 100°C [6], but some of our catalysts were very active at as low a temperature as 50°C. As shown in Fig. 1, a more conventional catalyst, metallic palladium on silica, had no activity at that temperature, while the conversion for our most active heterogeneous catalyst was 92% and for the least active 15%. Selectivities were virtually 100% in every case.

At 90°C the performance of all catalysts was more or less the same; the precursor and the support had little or no influence on the activity and selectivity. At 50°C, the activity of the catalysts initially depended strongly on the precursor and support. During the first five hours the most active precursor was $\text{Pd}(\text{P}(\text{C}_6\text{H}_5)_3)_2\text{Cl}_2$ and the least active $\text{Pd}(\text{OAc})_2$, but they had the same selectivity. The most active precursor on silica-supported polytitanaze gave about four times as high a

Table 3

Influence of the base on vinylation at 50°C for 12 h

Catalyst	Et ₃ N		2,3-Dihydroindole	
	Conversion (mol%)	Selectivity for methyl cinnamate (mol%)	Conversion (mol%)	Selectivity for methyl cinnamate (mol%)
Pd(OAc) ₂ /SiO ₂ -Ti-(NH) ₂	15.3	100	32.5	100
Pd(C ₆ H ₅ CN) ₂ /SiO ₂ -Al-(NH) ₂	31.9	100	43.8	100
Metallic Pd/SiO ₂	0	0	7.1	100

The reaction conditions are described in the Experimental part.

conversion as the least active precursor on the same support. Selectivity for the main product was 100% in both cases. In addition, the behaviour of Pd(P(C₆H₅)₃)₂Cl₂ differed from that of the other catalysts in having a long activation time of about one hour at the beginning of the reaction. The support too, had some effect on the initial performance of the catalysts, and the difference between the most and the least effective was very clear. Supports enhanced the activity of the catalyst in the order SiO₂-Sn-(NH)₂ > SiO₂-Al-(NH)₂ > SiO₂-Ti-(NH)₂.

With time the activities of the all catalysts grew more similar and after 5 h the reaction rates were almost the same. This shows very clearly that the final active surface species were shaped during the first five hours and were almost identical in every case, even though the supports were different. Exceptionally, because of its slightly higher metal content, the Pd(P(C₆H₅)₃)₂/SiO₂-Ti-(NH)₂ catalyst showed slightly more activity after stabilizing period. In every case the active surface species were also very stable in normal atmosphere, and catalysts did not lose any activity during filtering, washing and drying.

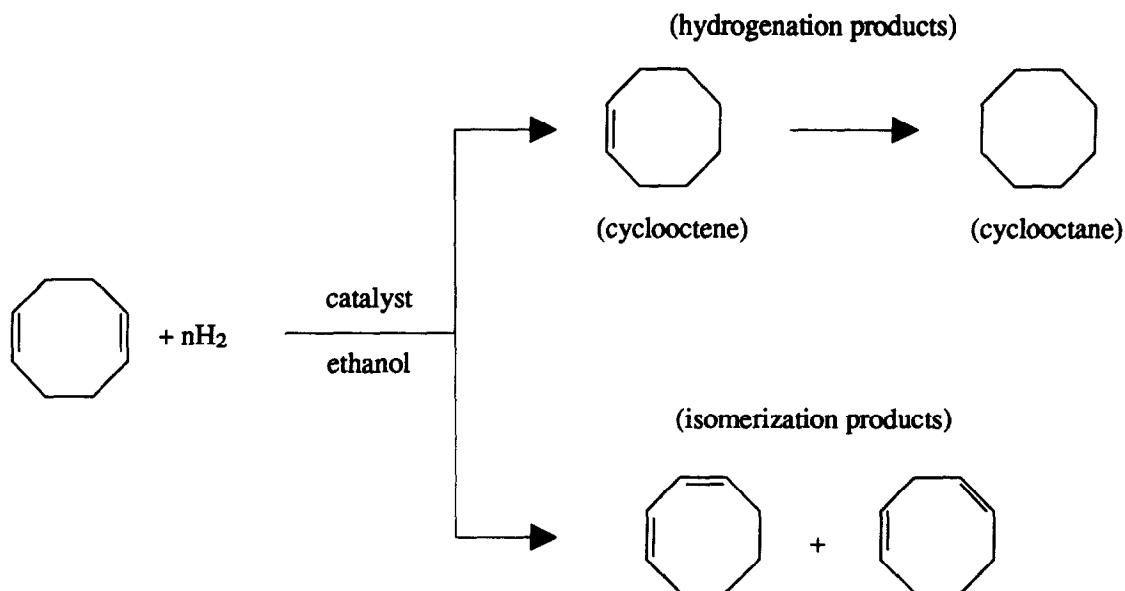
Some organic bases act as a source of hydride and promote the hydrogenation of aromatic compounds. Because of this there usually is competition between vinylation and hydrogenation in the Heck reaction and the selectivity pattern will be influenced by the type of base used. Selectivity for a vinylation product like methyl cinnamate is high when Et₃N is the base, while selectivity for

a hydrogenation product like benzene tends to be high in the case of indoline [7].

With our catalysts, by contrast, the base had no influence on the selectivity. Only methyl cinnamate was formed, regardless of the base used, as shown in Table 3. Conversion with indoline was higher than with Et₃N. The reason for this was the greater capability of indoline than Et₃N to remove HI and promote the reaction rate.

The main purpose of our hydrogenation of 1,5-cyclooctadiene (Scheme SCHEME) was to prove the different nature of metallic palladium and the active surface complex of the heterogeneous catalysts. The hydrogenation of 1,5-cyclooctadiene catalysed by metallic palladium/support catalysts proceeded very well at 30°C and atmospheric pressure of hydrogen as shown in Table 4 (reactions 1–3). After the vinylation reaction and under the same reaction conditions the heterogeneous palladium catalysts exhibited no or only very moderate activity in the hydrogenation of 1,5-cyclooctadiene (reactions 5–7), whereas metallic Pd/SiO₂ catalyst still had good activity (reaction 4). The results indicate very clearly that the palladium of our new catalyst did not reduce to metallic form even though the surface complex was modified during the vinylation reaction.

During the vinylation reaction the surface of all catalysts became covered with a deposit, which lowered the rate of the hydrogenation of cyclooctene but had no influence on the rate of hydrogenation of 1,5-cyclooctadiene. The hydrogenation reaction catalysed by fresh metallic palladium/



Scheme 1. The hydrogenation of 1,5-cyclooctadiene.

support catalysts proceeded very well and the final product was cyclooctane. After vinylation, however, the metallic Pd/SiO₂ catalyst had a high hydrogenation rate for 1,5-cyclooctadiene but negligible for cyclooctene; in practice, the reaction stopped in the intermediate stage and almost no further cyclooctane formed during the next two hours. Possibly the deposit was iodine, which often has been used as a poison in the selective hydrogenation of cyclodienes.

The ESCA data for supports, precursors and fresh catalysts in Table 5 point to the existence

of a strong interaction between the support and palladium. Large differences in the binding energies of nitrogen (1s) and palladium (3d_{5/2}) in catalysts compared with the corresponding energies in supports and precursors suggest that a chemical bond was formed between nitrogen and palladium. Such a chemical bond between nitrogen and Pd, Rh or Pt in heterogeneous catalysts has been reported earlier [4,5,8].

Vinylation of iodobenzene had a modifying effect on the surface species of the fresh catalysts as already seen in Fig. 1. ESCA provided addi-

Table 4
Results of the hydrogenation of 1,5-cyclooctadiene for 4 h

No.	Catalyst	Conversion (mol %)	Selectivity for cyclooctane (mol %)	Selectivity for cyclooctene (mol %)	Selectivity for 1,3-cyclooctadiene (mol %)	Selectivity for 1,4-cyclooctadiene (mol %)
1	Pd/SiO ₂ ^a	100	44.7	55.3	0	0
2	Pd/SiO ₂ -Al-(NH) ₂ ^b	100	62.5	37.5	0	0
3	Pd/SiO ₂ -Ti-(NH) ₂ ^a	100	42.1	57.9	0	0
4	Pd/SiO ₂ ^a	100	1.5	98.5	0	0
5	Pd/SiO ₂ -Al-(NH) ₂ ^b	17	0	27.5	55.8	16.7
6	Pd/SiO ₂ -Ti-(NH) ₂ ^a	0	0	0	0	0
7	Pd/SiO ₂ -Sn-(NH) ₂ ^a	0	0	0	0	0

The reaction conditions are described in the Experimental part. Nos. 1–4: The catalyst was reduced in a H₂ flow at 450°C for 3 h. Nos. 4–7: The catalyst was first used in the vinylation of iodobenzene with methyl acrylate.

^a Pd(P(C₆H₅)₃)₂Cl₂ was used as precursor.

^b Pd(C₆H₅CN)₃Cl₂ was used as precursor.

Table 5
ESCA data for supports, precursors and fresh catalysts

Catalyst No.	Component	N (eV)	ΔN (eV)	Pd (eV)	ΔPd (eV)
1	SiO ₂ -Sn-(NH) ₂	400.0	—	—	—
	Pd(P(C ₆ H ₅) ₃) ₂ Cl ₂	—	—	337.3	—
	Catalyst	398.9	-1.1	336.5	-0.8
2	SiO ₂ -Al-(NH) ₂	400.9	—	—	—
	Pd(P(C ₆ H ₅) ₃) ₂ Cl ₂	—	—	337.3	—
	Catalyst	400.1	-0.8	337.2	-0.1
3	SiO ₂ -Ti-(NH) ₂	399.8	—	—	—
	Pd(P(C ₆ H ₅) ₃) ₂ Cl ₂	—	—	337.3	—
	Catalyst	399.6	-0.2	336.7	-0.6
4	SiO ₂ -Al-(NH) ₂	400.9	—	—	—
	Pd(C ₆ H ₅ CN) ₂ Cl ₂	—	—	337.3	—
	Catalyst	400.5	-0.4	337.9	+0.6
5	SiO ₂ -Ti-(NH) ₂	399.8	—	—	—
	Pd(C ₆ H ₅ CN) ₂ Cl ₂	—	—	337.3	—
	Catalyst	399.5	-0.3	337.6	+0.3
6	SiO ₂ -Ti-(NH) ₂	399.8	—	—	—
	Pd(OAc) ₂	—	—	337.1	—
	Catalyst	399.5	-0.3	337.4	+0.3

The measurements are described in the Experimental part.

Table 6
Influence of the vinylation reaction of the binding energies of the catalysts measured by ESCA

Catalyst No.	Catalyst	ΔN (eV)	ΔPd (eV)
1	Pd(P(C ₆ H ₅) ₃) ₂ /SiO ₂ -Sn-(NH) ₂	+0.1	-2.4
2	Pd(P(C ₆ H ₅) ₃) ₂ /SiO ₂ -Al-(NH) ₂	-0.2	-1.5
3	Pd(P(C ₆ H ₅) ₃) ₂ /SiO ₂ -Ti-(NH) ₂	+0.2	-2.7
4	Pd(C ₆ H ₅ CN) ₂ /SiO ₂ -Al-(NH) ₂	-0.6	-1.5
5	Pd(C ₆ H ₅ CN) ₂ /SiO ₂ -Ti-(NH) ₂	+0.3	-2.7
6	Pd(OAc) ₂ /SiO ₂ -Ti-(NH) ₂	+0.3	-2.6

tional evidence for this. The change in the surface species was easily seen in the binding energies of nitrogen and especially the binding energies of palladium before and after the reaction (Table 6). Evidently in the fresh catalysts ligands were joined to the palladium, but during the vinylation reaction when the final active surface compounds were formed they disengaged. FT-IR provided support for this because, characteristics peaks of ligand L, such as Pd(P(C₆H₅)₃)₂Cl₂,

could be seen before but not after the vinylation reaction (Fig. 2.)

A modification scheme for the surface complex is proposed in Fig. 3. In the case of complex (I),

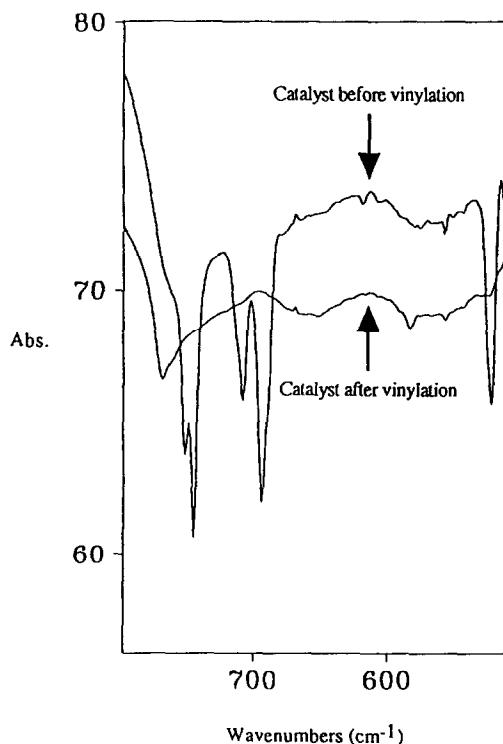


Fig. 2. IR spectra of Pd(P(C₆H₅)₃)₂/SiO₂-Sn-(NH)₂ catalyst before and after vinylation reaction.

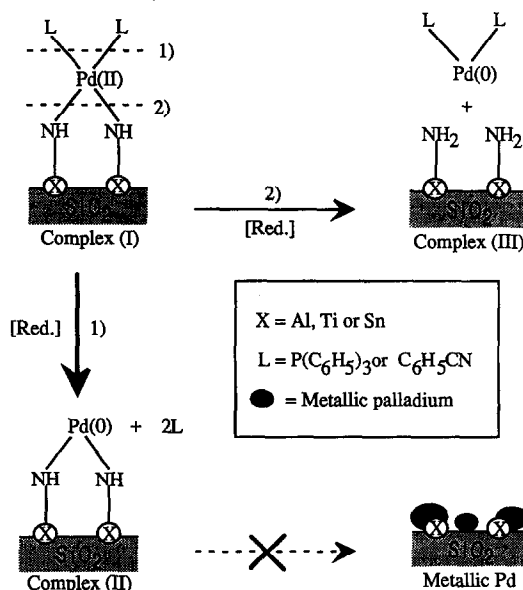


Fig. 3. Proposed modification scheme for the surface complex during vinylation reaction.

palladium has coordination number 4 and is not active because of steric hindrance. When two Pd–L bonds (route 1) were severed, both steric hindrance and coordination number decrease and the active complex (II) is formed. Both ESCA and FT-IR results give support to the formation of the surface complex (II), and the results of the hydrogenation of 1,5-cyclooctadiene exclude the possibility of metallic palladium on the support because, as shown in Table 4, complex behaves very differently in hydrogenation from the real metallic catalyst. When Pd–N bonds (route 2) are broken, the homogeneous complex (III) is formed. The results of the vinylation at 90°C (Table 1) and palladium content of the catalysts (Table 2) show that the modification route 2 is uncommon but might nevertheless occur. The presence of the homogeneous active complex (III) presumably decrease selectivities in the first vinylation reaction, and in the second use, when complex (III) no longer existed in the reaction mixture, selectivities increased in practice up to 100%.

4. Conclusions

The primary goal of this research was to develop an active, selective and stable catalyst that could be reused in the Heck reaction with no appreciable change in performance. This goal was

achieved very well. Our new heterogeneous catalysts exhibited high activity and selectivity. Also the stability was good: catalysts could be reused and stored in air for various periods of time with no loss of catalytic activity. The results showed that this new type of supported palladium catalyst is useful for reactions such as the Heck reaction and should be considered as a viable alternative to the commonly used homogeneous catalysts.

Use in the hydrogenation of 1,5-cyclooctadiene of metallic palladium/SiO₂ catalyst previously used in the vinylation of iodobenzene gave the very interesting result that hydrogenation virtually stopped at the level of cyclooctene. It seems that iodine deposited on the surface played an important inhibitory role in the hydrogenation of cyclooctene

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