



Pergamon

Pd-SAPO-31, an efficient, heterogeneous catalyst for Heck reactions of aryl chlorides

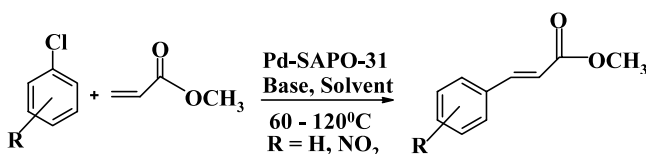
Rajendra Srivastava, N. Venkatathri, D. Srinivas* and Paul Ratnasamy*

Catalysis Division, National Chemical Laboratory, Pune-411 008, India

Received 30 January 2003; revised 3 March 2003; accepted 14 March 2003

Abstract—Pd-SAPO-31 exhibits high activity for Heck reactions of aryl chlorides. These catalysts with activities superior to most known solid catalysts can be recovered and reused with negligible loss in activity. © 2003 Elsevier Science Ltd. All rights reserved.

Palladium catalyzed C–C bond formation (the Heck reaction) is one of the most versatile and useful tools in modern organic chemistry.^{1,2} The recent applications of Heck reactions include the manufacture of Novartis' Prosulfuron™—an agrochemical, octyl-*p*-methoxycinnamate—a sun-screen agent, Albemarle's Naproxen—an antibiotic and Singulair—an anti-asthma drug. To minimize the cost of production, efforts are in progress to (1) replace Pd with less expensive Ni catalysts, (2) replace aryl bromides and iodides with the cheaper chlorides, (3) eliminate the use of phosphine ligands, (4) employ waste-free production methods by using aromatic anhydrides as aryl donors, and (5) utilize heterogeneous, reusable catalysts in place of the present homogeneous systems.³ Metal catalysts on different supports, e.g. carbon, inorganic oxides, molecular sieves, polymeric materials etc. have been explored.^{3–6} Unfortunately, most are efficient for reactions of aryl iodides and bromides but not for chlorides. We have found that palladium-containing silico aluminophosphate-31 (Pd-SAPO-31)^{7,8} is highly active even for the reactions of aryl chlorides (Scheme 1).

**Scheme 1.**

In this work we have prepared 3 wt% of Cu, Ni and Pd containing SAPO-31 materials, characterized them and studied their catalytic activity⁹ in the Heck reactions of aryl halides. Metal incorporation did not alter the crystallinity and framework structure of SAPO-31 (XRD). Cu-SAPO-31 (before reduction with hydrogen) exhibited a weak, broad band at 600–800 nm in the diffuse reflectance UV–vis spectrum that could be assigned to the ${}^2E_g(D) \rightarrow {}^2T_{2g}$ spin allowed, Laporte-forbidden transition of Cu^{2+} in an octahedral geometry (Fig. 1).¹⁰ An intense band due to a ligand-to-metal charge transfer (LMCT) transition was observed at 310 nm. Calcined Ni-SAPO-31 showed characteristic bands at 410 and 700 nm due to ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ and ${}^3A_g \rightarrow {}^3T_{1g}(F)$ transitions, respectively (Fig. 1).¹¹ Pd-SAPO-31 showed a LMCT band at 250–300 nm. This band disappeared and an increased absorbance in the visible region was observed when treated with hydrogen indicating that all the Pd^{2+} ions had been converted to metallic Pd (Fig. 1).¹² EPR spectroscopy revealed that the metal ions are highly dispersed. The Cu^{2+} in Cu-SAPO (before hydrogen reduction) is characterized by signals with spin Hamiltonian parameters, $g_{\parallel} = 2.388$, $g_{\perp} = 2.088$ and $A_{\parallel}^{\text{Cu}} = 118.1$ G. Ni-SAPO-31 showed a perpendicular signal at $g = 2.345$ corresponding to a highly distorted octahedral environment around the Ni^{2+} ions.¹³ Pd-SAPO-31 reduced with hydrogen exhibited a broad signal at $g = 2.12$ characteristic of dispersed metallic Pd.¹⁴

The Ni and Cu catalysts, as expected, exhibited lower activity than the Pd catalyst in the Heck reactions. Complete conversion of iodobenzene in the Heck coupling reaction with methyl acrylate (C–C product selectivity ≈ 97 – 98%) was achieved in 1.5 h with a Pd-SAPO-31 catalyst, DMF solvent and K_2CO_3 base.

* Corresponding authors. Fax: +91-20-589-3761; e-mail: srinivas@catal.ncl.res.in; prs@ems.ncl.res.in

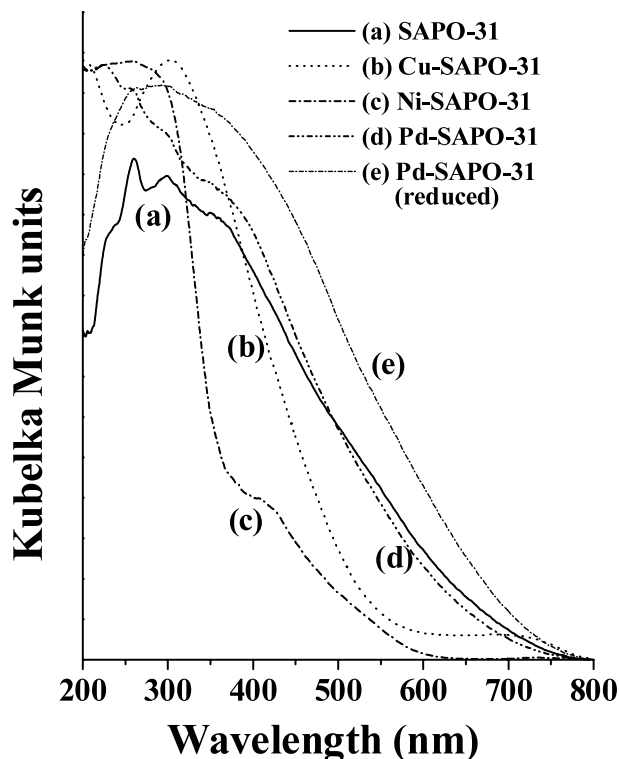


Figure 1. Diffuse reflectance UV-vis spectra of Cu/Ni/Pd-SAPO-31 catalysts.

With the Ni and Cu catalysts, however, the reactions had to be carried out for 24 h. In the case of bromobenzene, about 92% conversion (C–C product selectivity =

96.7%) was achieved in 24 h with Pd-SAPO-31, while only 9.8% conversion was observed with the Ni and Cu catalysts (C–C product selectivity = 89.7 and 97%, respectively). Only the Pd catalyst was active for the reactions of chlorobenzene and its derivatives (Table 1). The catalysts can be used effectively for the arylation of a variety of olefins. In the reaction of iodobenzene and methyl acrylate, the *trans*-product was predominant with selectivity greater than 96%. However, with styrene, α -methylstyrene and ethyl cinnamate both the *cis*- and *trans*-products were detected (Table 1, runs 13–15).

Solvent and base markedly influenced the activity of Pd-SAPO-31 (Table 1). Among the various solvents, *N,N*-dimethyl acetamide (DMA) yielded higher amounts of the C–C product. Among the bases, potassium or cesium carbonate were more effective affording complete conversion of iodobenzene in 1.5 h with 98% selectivity for the C–C product. The reaction is also more facile in the presence of electron withdrawing substituents, such as a nitro group (compare runs 4–6). During the reaction, metal ions leached out of the support (Fig. 2; Pd was estimated by atomic absorption spectroscopy). However, when the reaction was complete (beyond 6 h for iodobenzene) the metal ions could not be detected in the liquid phase indicating that all the leached Pd was apparently redeposited onto the SAPO-31 support. Such a phenomenon of Pd leaching and redeposition has also been observed by others with Pd–C catalysts.¹⁵

As a consequence of this redeposition phenomenon, the Pd-SAPO-31 catalyst could be recovered from the reac-

Table 1. Heck reactions of aryl halides and methyl acrylate over Pd-SAPO-31 at 120°C

Run ^a	Aryl halide	Base	Solvent	Run time (h)	Aryl halide conversion (mol%)	C–C product selectivity (mol%)
1	Chlorobenzene	NEt ₃	DMF	24	29.5	79.9
2	Chlorobenzene	NEt ₃	NMP	24	32.6	98.6
3	Chlorobenzene	NEt ₃	NMP	70	50.3	94.6
4	Chlorobenzene	NEt ₃	DMA	70	70.1	96.7
5	<i>o</i> -Nitrochlorobenzene	NEt ₃	DMA	70	77.5	96.2
6	<i>p</i> -Nitrochlorobenzene	NEt ₃	DMA	70	87.9	97.3
7	Iodobenzene	Na ₂ CO ₃	DMF	6	99.8	97.9
8	Iodobenzene	K ₂ CO ₃	DMF	1.5	100	98.8
9	Iodobenzene	Cs ₂ CO ₃	DMF	1.5	99.8	98.3
10	Iodobenzene	NEt ₃	DMF	2	100	96.8
10a	Iodobenzene	NEt ₃	DMF	2	100	96.3
10b	Iodobenzene	NEt ₃	DMF	2	98.9	97.2
10c	Iodobenzene	NEt ₃	DMF	2	98.3	96.8
11	Iodobenzene	NPr ₃	DMF	3	98.9	84.0
12	Iodobenzene	NBu ₃	DMF	3	99.5	76.8
13 ^b	Iodobenzene	K ₂ CO ₃	DMF	2	99.2	93.7 (14/86) ^c
14 ^c	Iodobenzene	K ₂ CO ₃	DMF	12	96.7	80.0 (36/64) ^c
15 ^d	Iodobenzene	K ₂ CO ₃	DMF	8	99.4	78.1 (29/71) ^e

^a Runs 10a–10c are the 1st, 2nd and 3rd recycles of run 10. DMF = *N,N*-dimethyl formamide, NMP = *N*-methyl-2-pyrrolidinone, DMA = *N,N*-dimethyl acetamide.

^b Styrene was used in place of methyl acrylate.

^c α -Methyl styrene was used in place of methyl acrylate.

^d Ethyl cinnamate was used in place of methyl acrylate.

^e Values in parentheses are distributions of *cis*-/*trans*-isomers.

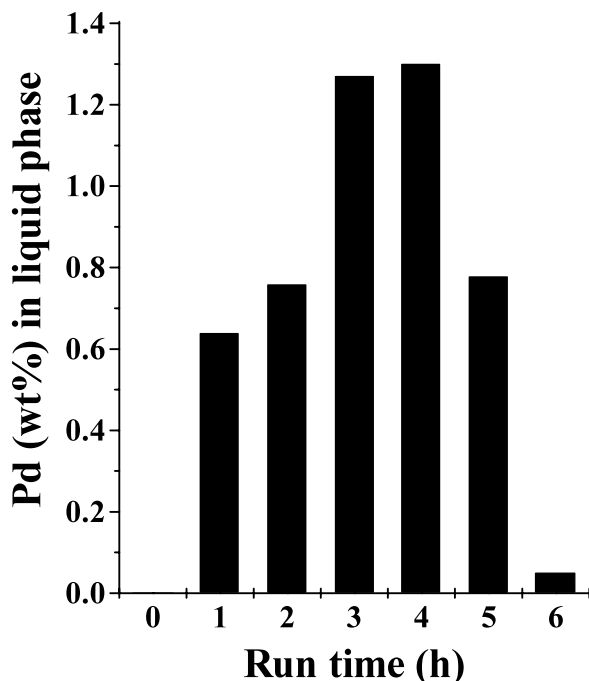


Figure 2. Pd leached into the solution at different reaction times; Heck reaction of iodobenzene and methyl acrylate over Pd-SAPO-31.

tion mixture by filtration and recycled without significant loss in activity or selectivity for a minimum of three cycles (Table 1, runs 10a–10c). The Pd-SAPO-31 is a phosphine-free and easy to prepare catalyst. A comparative study reveals that Pd-SAPO-31 is more active and efficient than other heterogeneous catalysts. The reaction takes place in about 1.5 h as compared to 4–14 h with Pd supported on carbon, graphite, MgO and Al₂O₃ (for carbon–iodobenzene/methyl acrylate/Na₂CO₃; 150°C; 4 h, yield 70%; for MgO–iodobenzene/acrylonitrile/Et₃N; 140°C; 14 h, yield 78%; for Al₂O₃–iodobenzene/acrylonitrile/Et₃N; 140°C; 14 h, yield 72% and for graphite–37 wt%; iodobenzene/styrene/K₂CO₃; 100°C; 95 h, yield 82%).^{3a} The amount of supported Pd is also lower in the SAPO-31 catalysts (3 wt%) as compared to carbon, MgO and Al₂O₃ (5 wt%) and graphite (37 wt%) catalysts.^{3a} Further, the reaction for non-activated aryl halides takes place at relatively lower temperatures (60–120°C) with Pd-SAPO-31 than with the other solid catalyst systems (100–150°C).³

In conclusion, we have demonstrated the superior activity of Pd-SAPO-31 compared to other solid catalysts for the Heck reaction of aryl halides including aryl chlorides.

Acknowledgements

R.S. acknowledges UGC, New Delhi for the award of a Junior Research Fellowship.

References

- (a) Heck, R. F. *Acc. Chem. Res.* **1979**, *12*, 146; (b) Heck, R. F. In *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 4, p. 833.
- de Meijere, A.; Meyer, F. E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2379.
- (a) Biffis, A.; Zecca, M.; Basato, M. *J. Mol. Catal. A: Chem.* **2001**, *173*, 249 and references cited therein; (b) Tucker, C. E.; de Vries, J. G. *Top. Catal.* **2002**, *19*, 111.
- (a) Albert, J. L.; Mau, W.-H.; Strauss, C. R. *Chem. Commun.* **1997**, 1275; (b) Wagner, M.; Köhler, K.; Djakovitch, L.; Weinkauff, S.; Hagen, V.; Muhler, M. *Top. Catal.* **2000**, *13*, 319; (c) Clark, J. H.; Macquarrie, D. J.; Mubofu, E. B. *Green Chem.* **2000**, 53.
- (a) Mehnert, C. P.; Weaver, D. W.; Ying, J. Y. *J. Am. Chem. Soc.* **1998**, *120*, 12289; (b) Djakovitch, L.; Koehler, K. *J. Am. Chem. Soc.* **2001**, *123*, 5990.
- (a) Dell'Anna, M. M.; Mastrorilli, P.; Muscio, F.; Nobile, C. F.; Suranna, G. P. *Eur. J. Inorg. Chem.* **2002**, 1094; (b) Yeung, L. K.; Crooks, R. M. *Nano Lett.* **2001**, *1*, 14.
- SAPO-31 was synthesized hydrothermally, by a procedure similar to that reported for VAPO-31 (see reference 8), using a reactive gel of the following molar composition: Al₂O₃:P₂O₅:1.16 di-*n*-propylamine (DPA):0.3 SiO₂:45 H₂O. The composition of the final product was Al₂O₃: 0.875 P₂O₅: 0.25 SiO₂. SAPO-31 with 3 wt% of Pd was prepared by the ion exchange method using an aqueous solution (10 ml) of (NH₃)₄PdCl₂·H₂O (74.46 mg) and SAPO-31 (1 g). The suspension was stirred for 10 h at 90°C. The solid (Pd-SAPO-31) was calcined at 550°C for 6 h and then reduced at 400°C under hydrogen flow for 6 h. Ni-SAPO-31 and Cu-SAPO-31 were prepared in a similar manner using the nitrate salts of Ni and Cu, respectively.
- Venkatathri, N.; Hegde, S. G.; Sivasanker, S. *J. Chem. Soc., Chem. Commun.* **1995**, 151.
- The Heck reactions were carried out in a glass, round bottom flask (25 ml) fitted with a water-cooled condenser. In a typical reaction, the halobenzene (1 mmol), methyl acrylate (2 mmol), base (1.5 mmol) and catalyst (4 wt% with respect to halobenzene) were taken in 5 g of solvent. The reaction was conducted at 60–120°C under a nitrogen atmosphere. The progress and completion of the reaction was monitored by gas chromatography. The products were identified by GC–MS.
- Velu, S.; Wang, L.; Okazaki, M.; Suzuki, K.; Tomura, S. *Micropor. Mesopor. Mater.* **2002**, *54*, 113.
- Kukovecz, A.; Kónya, Z.; Mönter, D.; Reschetilowski, W.; Kiricsi, L. *J. Mol. Struct.* **2001**, *563–564*, 403.
- Choudary, B. M.; Madhi, S.; Chowdari, N. S.; Kantam, M. L.; Sreedhar, B. *J. Am. Chem. Soc.* **2002**, *124*, 14127.
- Velavan, K.; Rajendiran, T. M.; Venkatesan, R.; Sambasiva Rao, P. *Solid State Commun.* **2002**, *122*, 15.
- Choo, H.; Hong, S. B.; Kevan, L. *J. Phys. Chem. B* **2001**, *105*, 7730.
- (a) Zhao, F.; Shirai, M.; Ikushima, Y.; Arai, M. *J. Mol. Catal. A: Chem.* **2002**, *180*, 211; (b) Zhao, F.; Murakami, K.; Shirai, M.; Arai, M. *J. Catal.* **2000**, *194*, 479.