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Heck Reaction over Pd-Loaded ETS-10 Molecular Sieve

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A palladium-loaded ETS-10 molecular sieve has been used as a catalyst in Heck reaction. The catalyst exhibits high activity and selectivity towards the carbon–carbon coupling of aryl halides with olefins, even at low concentrations of Pd (0.009 to 1.4 mol% with respect to the substrate). In the case of the coupling of ethyl acrylate with iodobenzene, 96% conversion of iodobenzene with greater than 98% selectivity could be obtained within 1 h over a 0.2 wt % Pd-loaded catalyst. The catalyst activates aryl bromide and chloride substrates, and appears to be heterogeneous. The reaction has been investigated with different alkyl halides, olefins and bases.

The palladium catalyzed carbon–carbon bond forming reaction of aryl halides with olefins (the Heck reaction) in a single step has become an excellent tool for the synthesis of numerous styrene derivatives due to its tolerance for a wide variety of functional groups on both reactants.[1] The use of homogeneous Pd catalysts to promote this reaction is well established.[1,2] For economic reasons, industrial applications of homogeneous Heck reactions are limited.[3] In order to overcome the problems arising from the separation, recovery and reuse of Pd complexes, a variety of heterogeneous catalysts have been developed for the Heck reaction.[4–6] These include Pd supported on carbon, different metal oxides,[7,8] clays, mesoporous silica, zeolites[9,10] and Pd nanoparticles.[11] The use of Cu, Ni, Co, and Mn heterogeneous catalysts for Heck reactions is also known.[12] However, only a few reports are available on the use of metal supported basic catalysts for the Heck reaction.[10,13]

ETS-10 molecular sieve has been used as a catalyst in the shape-selective photo catalytic decomposition of aromatic molecules,[14] Aldol-type condensations,[15] aniline oxidation,[16] acylation reactions[17] and alcohol dehydrogenation.[18] The carbon–carbon coupling of different aryl halides with ethyl acrylate over Pd-loaded ETS-10 is reported in this paper. The influences of the Pd content, nature of the base and reactivity of the different substrates and reactants on the coupling reaction are presented.

Experimental

Preparation of Pd-ETS-10. The hydrothermal synthesis of ETS-10 using $TiCl_4$ was carried out following a published procedure[19] with a gel of molar composition: 3.70 Na_2O:0.95 K_2O:1.0 TiO_2:5.70 SiO_2:171 H_2O. After crystallization, the product was filtered, washed, dried at 110 °C for 10 h and calcined at 450 °C in dry air for 6 h. Pd (0.2 to 6 wt %) was loaded on the molecular sieve using a solution of $[Pd(NH_3)_4]Cl_2$ at 80 °C. The procedure involved the stirring of ETS-10 powder with a solution of the salt (10 mL/g of ETS-10) at 80 °C for 2 h, and then slowly evaporating the mixture on a water bath to dryness. This procedure enabled loading of the required amount of Pd. The Pd is expected to be partly exchanged and partly deposited. Pd-loaded samples were dried at 110 °C (6 h), calcined at 400 °C (6 h) in air, reduced at 350 °C in H_2 for 6 h and stored under nitrogen. Though metal dispersion was not measured on the samples, based on one earlier our study concerning similarly prepared Pt-ETS-10 samples,[20] the dispersions are expected to be moderate in the range of 0.5–0.8 for samples containing 0.2–2% Pd. The ETS-10 molecular sieve used in this study had the chemical composition $[Na_{16.60}K_{14.40}(Ti_{16.21}Si_{79.74}O_{208})]$ (by atomic absorption spectroscopy) and a N_2 adsorption surface area of 460 m^2/g.

Reaction Procedure. The reactions were carried out in the liquid phase in a 50 mL two neck round-bottomed flask fitted with a reflux condenser. The flask was charged with the substrate (1 mmol), olefin (5 mmol), base (typically, tributylamine (TBA); 2 mmol), solvent (dimethylformamide (DMF); 5 g) and the catalyst (0.025 g), and placed in an oil bath kept at 130 °C. The progress of the reaction was monitored by a gas chromatograph (Varian CX) using a capillary column, CP Sil 5CB, (i.d. 0.53 mm and 30 m long). Conversions were calculated on the basis of the substrate (aryl halide).

Results and Discussion

ETS-10 is a large pore titanosilicate molecular sieve, first synthesized at Engelhard.[21] The framework structure of ETS-10 consists of corner shared oxygen ions of $[TiO_6]^{2-}$ octahedra and $[SiO_4]$ tetrahedra. ETS-10 possesses a three-dimensional pore system made up of 12-membered ring (12-MR) channels with a pore diameter of 7.6 Å.

Pd-loaded ETS-10 samples with different Pd contents (0.2 to 6 wt %) were used in the studies. The reaction of iodobenzene with ethyl acrylate was chosen as the model reaction to test the catalytic activity of different samples. The catalytic activities of different Pd-ETS-10 samples are plotted as a function of the duration of the run in Fig. 1. The general observation is that the catalytic activity increases with increasing Pd loading. The selectivity for Heck products was >98% over all the catalysts.

The results of studies on the coupling of ethyl acrylate and iodobenzene carried out over 1 wt % Pd-ETS-10 are presented in Table 1. A conversion of about 97% was obtained in about

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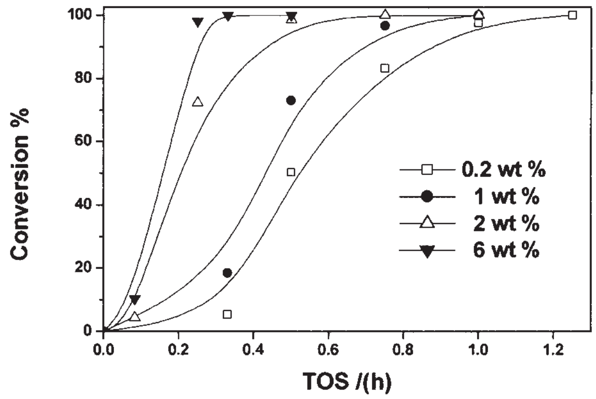

Fig. 1. Conversion of the substrate over different Pd-ETS-10 molecular sieves (Reaction conditions: catalyst = 25 mg, temperature = 130 °C, substrate = 1 mmol iodobenzene, reactant = 5 mmol ethyl acrylate, base = 2 mmol TBA, and solvent = 5 g DMF).

0.75 h of run duration. The catalyst was found to be recyclable without any loss of activity, the TOF values being 549 for a fresh catalyst and 572 after one recycle (Table 1; entries 1 and 2). Experiments carried out on the 0.2 wt % Pd catalyst are also reported in Table 1 (entry 4). The catalyst is quite active in spite of the low (0.2 wt %) Pd-loading; a TOF of about 10000 was achieved when 5 mmol of iodobenzene was used (Table 1; entry 5). The 0.2 wt % catalyst is also recyclable (Table 1; entry 6).

Leaching studies were carried out to verify the heterogeneous nature of the reaction. The tests were performed on both 0.2 and 1 wt % Pd catalysts (Table 1; entries 7 and 3). As the catalysts were reduced in H_2 at 350 °C, the Pd is expected to be present mainly as the Pd^0 species, which are not soluble in organic solvents. However, Pd^0 may slowly react with a polar solvent (DMF) and/or an organic base, and form complexes that can be leached into the solution, as reported by Arai and others.[22]

In a typical leaching experiment, the catalyst was refluxed with iodobenzene at 130 °C for 15 min, and separated from the organic layer by centrifuging under hot condition. Ethyl acrylate was then added to the organic layer. The composition of the clear filtrate was determined by GC. This homogeneous reaction mixture was heated at 130 °C, and the progress of the reaction was monitored by GC by following the iodobenzene conversion. Conversions of 8.1% and 14.6% were observed in the case of 0.2% and 1 wt % Pd catalysts, after 2 h (Table 1; entries 7 and 3). A similar experiment was conducted with 1-bromo-4-nitrobenzene, and no conversion was observed in the homogeneous reaction mixture (Table 1; entry 9). The conclusion of these leaching experiments is that some leaching of Pd occurs in iodobenzene and not in 1-bromo-4-nitrobenzene, and the leached Pd is less active than the heterogeneous Pd (in ETS-10).

The Heck reaction was also carried out using the Pd salts, $[(NH_3)_4Pd]Cl_2 \cdot H_2O$ and $Pd(OAc)_2$. In these experiments, the amount of Pd used was equivalent to the Pd present when 1 wt % Pd-ETS-10 was used as the catalyst. These complexes were less active compared to the (1 wt %) Pd-loaded ETS-10 (Table 1). Pd-ETS-10 catalyst is phosphine free, and easy to prepare compare to homogeneous catalysts. A comparison of the results of the present study with those published in the literature concerning Pd supported over other supports reveals that Pd-ETS-10 is more active and efficient than the other catalysts. The reaction takes place in about 1 h over ETS-10, as compared to 2–14 h over Pd supported on Al_2O_3, MOR and SAPO-31 (over Al_2O_3–iodobenzene/acrylonitrile/Et_3N, 140 °C, 14 h: yield = 72%; over Pd-MOR and SAPO-31–iodobenzene/$Bu^n{}_3N$, 130 °C, 2 h: conversion = 97%; with promoter $Bu^n{}_4Br$ (0.413 mmol) and Pd-SAPO-31–iodobenzene/$Bu^n{}_3N$, 120 °C, 3 h: conversion = 99.5%). The amount of supported Pd is also lower in the Pd-ETS-10 catalysts (0.2 wt %), as compared to published reports, e.g. Al_2O_3 (5 wt %), MOR (4 wt %) and SAPO-31 (3 wt %).[23]

The influence of different bases on the conversion and selectivity was investigated (Table 2). The reaction was faster when tributylamine and triethylamine were used in the case of both iodobenzene and 1-bromo-4-nitrobenzene (Table 2). The reactivities of different olefins (different acrylates and styrene) are compared in Table 3. Ethyl acrylate is found to be the most reactive and selective among the acrylates (96.5% in 0.75 h). The reactivities of the acrylates are in the order, ethyl acrylate > *t*-butyl acrylate > methyl acrylate > butyl meth-

Table 1. Studies on Heck Reaction Using Pd-ETS-10 and Pd-salts

No.	Substrate	Catalyst[a]	TOS/h	Sel./%	Conv./%	TOF[b]	Pd[c]/$\times 10^{-3}$ g
1	Iodobenzene	Pd-ETS-10 (1.0)	0.75	98.2	96.7	549	0.250
2	Iodobenzene[d]	Pd-ETS-10 (1.0)	0.75	99.1	95.9	572	0.240
3	Iodobenzene[e]	Pd-ETS-10 (1.0)	2.00	99.2	14.6	170	0.012
4	Iodobenzene	Pd-ETS-10 (0.2)	1.00	98.0	95.7	2037	0.050
5	Iodobenzene[f]	Pd-ETS-10 (0.2)	1.00	99.1	95.7	10023	0.050
6	Iodobenzene[d,f]	Pd-ETS-10 (0.2)	1.00	98.3	92.1	9799	0.050
7	Iodobenzene[e]	Pd-ETS-10 (0.2)	2.00	98.2	8.1	287	0.001
8	1-Bromo-4-nitrobenzene	Pd-ETS-10 (1.0)	9.00	100	84.3	40	0.250
9	1-Bromo-4-nitrobenzene[e]	Pd-ETS-10 (1.0)	6.00	—	—	—	0.001
11	Iodobenzene	$[(NH_3)_4Pd]Cl_2$ (1.0)	6.00	72.7	16.1	11	0.250
12	Iodobenzene	$Pd(OAc)_2$ (1.0)	6.00	69.0	6.9	5	0.250

Reaction conditions: catalyst = 0.025 g; temperature = 130 °C; substrate = 1 mmol iodobenzene; reactant = 5 mmol ethyl acrylate; base = 2 mmol tributylamine (TBA); solvent = 5 g dimethylformamide (DMF). a) wt % of Pd in the catalyst is given in brackets. b) TOF = [(mole of iodobenzene converted/mole of Pd)/h]. c) Pd present in the reaction mixture, in catalyst/in solution. d) First recycle. e) Leaching test. f) 5 mmol iodobenzene, 25 mmol TBA, 20 g DMF.

Table 2. Influence of Different Bases on the Catalytic Activity of Pd-ETS-10

No.	Base	TOS /h	Sel. /%	Others /%	Conv. /%
1	Triethylamine	1.00	100	—	95.3
2	Tributylamine	0.75	98.2	1.8	96.7
3	K_2CO_3	2.00	100	—	96.7
4	NaOAc	12.00	97.3	2.7	77.2
5	$K_2CO_3$$^{a)}$	12.00	100	—	24.5
6	Triethylamine$^{a)}$	9.00	98.1	1.9	84.3

Reaction conditions: catalyst = 0.025 g (1 wt % Pd); temperature = 130 °C; substrate = 1 mmol iodobenzene; reactant = 5 mmol ethyl acrylate; base = 2 mmol TBA; solvent = 5 g DMF. a) 1-Bromo-4-nitrobenzene.

Table 3. Reactivities of Different Olefins in the Heck Reaction Catalyzed by Pd-ETS-10

No.	Olefin	TOS /h	Sel. /%	Others /%	Conv. /%
1	Methyl acrylate	1.50	100	—	99.7
2	Ethyl acrylate	0.75	98.2	1.8	96.7
3	Methyl methacrylate	2.00	100	—	95.2
4	Butyl methacrylate	2.00	76.5	23.5	77.5
5	*t*-Butyl acrylate	1.00	100	—	100
6	Styrene$^{a)}$	3.00	80.2	19.8	96.7

Reaction conditions: catalyst = 0.025 g (1 wt % Pd); temperature = 130 °C; substrate = 1 mmol iodobenzene; reactant = 5 mmol ethyl acrylate; base = 2 mmol TBA; solvent = 5 g DMF. a) 2 mmol iodobenzene used.

acrylate > methyl methacrylate. Styrene is also quite reactive (conv. = 96.7% and sel. = 80.2%).

Another important issue concerning a heterogeneously catalyzed Heck reaction is the possibility to activate the industrially more interesting aryl bromides and chlorides. A comparison of the reactivities of different halobenzenes is presented in Table 4. As expected, the results reported in Table 4 (entries 1, 2 and 3) show that aryl chloride is less active than aryl bromide and aryl iodide. A similar trend is also observed for the aryl chloride derivative (Table 4; entries 4, 5 and 6). The reactivities of different halobenzenes are in the following order: iodobenzene > bromobenzene > chlorobenzene (Table 4). In the case of 1-halo-4-nitrobenzenes, the conversion and selectivity decrease in the following order: 1-iodo-4-nitrobenzene > 1-bromo-4-nitrobenzene > 1-chloro-4-nitrobenzene. In general, it is noticed that electron-withdrawing substituents increase the conversion.

Table 4. Reactivities of Different Substrates in the Heck Reaction Catalyzed by Pd-ETS-10

No.	Substrate	TOS /h	Sel. %	Conv. %
1	Iodobenzene	0.75	98.2	96.7
2	Bromobenzene	24	77.6	50.1
3	Chlorobenzene	24	43.8	35.7
4	1-Iodo-4-nitrobenzene	0.5	100	100
5	1-Bromo-4-nitrobenzene	9	99.1	84.3
6	1-Chloro-4-nitrobenzene	12	44.5	40.2
7	4-Iodophenyl methyl ketone	2	100	87.1
8	4-Bromophenyl methyl ketone	6	98.2	45.9
9	1-Choro-4-iodobenzene	9	98.2	98.5
10	4-Iodoanisole	3	99.3	64.1

Reaction conditions: catalyst = 25 mg (1 wt % Pd); temperature = 130 °C; substrate = 1 mmol; reactant = 5 mmol ethyl acrylate; base = 2 mmol TBA; solvent = 5 g DMF.

The mechanism of the Heck vinylation of iodobenzene with supported palladium catalyst in a polar solvent (NMP) and an organic base (Et_3N) or Na_2CO_3 bases has been proposed.[24] As the first step, palladium complexes are formed by coordination with the polar solvent and/or the organic base, and these are the catalytically active species. The superior activity of Pd-ETS-10 could be a result of the support influencing the electronic property of the Pd metal enhancing its ability to coordinate with the basic ligand, and probably also to form a more active surface complex. It is also likely that the support, itself, acts as a basic ligand, making the supported Pd metal very active.

Conclusions

Pd-ETS-10 (reduced in H_2) exhibits a high activity towards the Heck coupling of aryl iodides with acrylates under the typical reaction conditions. A TON value of ~10000 is achieved for a 0.2 wt % Pd-ETS-10 catalyst for iodobenzene. Though a small amount of Pd leaches out into solution when iodobenzene is used as the substrate and DMF as a solvent, the reaction is found to proceed mainly by a heterogeneous route. When 1-bromo-4-nitrobenzene is used as the substrate, the reaction is totally heterogeneous. Aryl bromide, chloride and their derivatives exhibit moderate activity with ethyl acrylates. Organic bases lead to higher catalytic activity than inorganic bases. The catalysts can be reused and reactivated by washing with a moderate decrease in activity. The substrate reactivity increases with electron-withdrawing substituents.

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