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# Efficient Hydrodehalogenation of Aryl Halides by Heterogenized Mcm-Silylamme Palladium (II) Catalyst

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## EFFICIENT HYDRODEHALOGENATION OF ARYL HALIDES BY HETEROGENIZED MCM-SILYLAMINE PALLADIUM (II) CATALYST

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Abstract: Palladium anchored on MCM-41 was used for hydrodehalogenation of aryl halides by molecular hydrogen at atmospheric pressure. The catalyst was reused for several cycles with consistent activity.

Reductive dehalogenation (hydrodehalogenation) of organic halides is a synthetically important and very useful method essentially directed to remove a halogen atom introduced temporarily to block a given position as an activating group or to pursue other synthetic options<sup>1</sup>. Even though various catalysts such as  $KHFe(CO)_4^2$  (generated insitu from  $Fe(CO)_5 / K_2CO_3$ ), borohydride exchanged resin in presence of Ni(OAc)<sub>2</sub><sup>3</sup> etc. have been developed for carrying out this reduction, palladium complexes and heterogenized palladium catalysts have proved to be

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fascinating systems for this organic reaction<sup>4-6</sup>. Sodium formate and sodium methoxide are generally used as a source of hydride ion for the reduction of bromo compounds in the presence of tetrakis (triphenyl phosphine) palladium or palladium on carbon at a temperature of 50-100°C<sup>4-7</sup>. When Cyclodextrin was used as the inverse phase transfer catalyst for the reduction of bromoanisoles using sodium formate and palladium on charcoal at 60°C<sup>8</sup>, dimethoxy biphenyl was the distinct side product. High temperatures, pressures, longer reaction times, formation of undesired side products or low turn-over number preclude the wide use of these catalysts specially for industrial purpose. The recently discovered family of mesoporous materials MCM<sup>9</sup> possesses conceivable industrial application in fine chemical synthesis due to the tunable larger pore size prompted us to design an anchored catalyst using MCM-41 as a support for a variety of organic reactions<sup>10</sup>.

In this communication, we describe the effectiveness of Pd complex anchored on MCM-41 for the hydrodehalogenation of aryl halides by molecular hydrogen at atmospheric pressure. The results are presented in Table1. The reactions were carried out mostly at room temperature using ethanol as the solvent and the catalyst is reused without any loss in activity. 1-Bromo naphthalene gave 76% yield of naphthalene by stirring at room temperature whereas the earlier catalytic methods were carried out at 100-120°C<sup>4,6</sup> in the presence of sodium methoxide as the hydride source. In the case of 1-chloro-4-nitrobenzene, no reaction occurred in ethanol even at reflux temperature. However, when THF was used as a solvent, 62% selectivity to nitroreduction and 38% selectivity to hydrodehalogenation was obtained at room temperature.

S.No	Substrate	Time(h)/Temp <sup>0</sup> C	Product	Yield <sup>a</sup>
1	Bromocyclohexane	10 / RT	Cyclohexane	43
2	Bromobenzene	15 / RT	Benzene	65
3	Chlorobenzene	8 / RT	Benzene	72
4	3-Bromotoluene	10 / RT	Toluene	92, 90 <sup>b</sup>
5	4-Bromoanisole	10 / RT	Anisole	72, 50°
6	Benzylbromide	12 / RT	Toluene	48
7	4-bromo2-methylaniline	13 / 50	2-Methylaniline	36
8	1-Bromonaphthalene	5 / RT	Naphthalene	76 <sup>4</sup> , 65 <sup>e</sup>
9	4-Bromobenzaldehyde	18 / 100	Benzaldehyde	39
10	4-Chloronitrobenzene	6 / RT	4-Chloroaniline (62%) + Aniline (38%)	77 <sup>4. f</sup>

Table1. Hydrodehalogenation of aryl halides

a) Unless otherwise noted, the yields were determined by GC with an internal standard and compared with the authentic samples. Yields are based upon the amounts of aryl halides consumed;
b) with recovered catalyst;
c) with 2-bromoanisole;
d) yield by NMR;
e) isolated yield;
f) in THF

Thus, the advantages of our catalytic system over others are: (1) it is simple, (2) the reaction conditions are mild, (3) reduction of the bulky molecule, bromonaphthalene is with greater ease, and (4) the catalyst is reusable.

#### Experimental

#### **Preparation of the catalyst**

The mesoporous material MCM-41(pure silica) was synthesized as described below following the reported literature procedure<sup>11</sup>. First a solution was prepared by mixing 1 mol of tetraethyl ortho silicate (TEOS) with 6 mol of ethanol and 1 mol of isopropyl alcohol. At the same time, a second solution was obtained by mixing hexadecylamine (0.3 mol) in water (36 mol). The two solutions were then mixed under stirring at room temperature for about 1hr. Then the stirrring was stopped and the product obtained aged at 25°C for 12 hrs under static conditions. The resulting solid was recovered by centrifugation, washed with distilled water 8 to 10 times and filtered. Finally, thus synthesized sample was air dried at room temperature for 24 hrs. 1g of MCM-41 was calcined at 550°C overnight and refluxed with 0.686 mmol of 3-triethoxysilylpropyl amine in dry toluene in inert atmosphere for 48h<sup>10</sup>. This was then complexed with dichlorobis(benzylcyano)palladium (II) in dry benzene under stirring at room temperature. The bright yellow coloured complex thus obtained was filtered, Soxhlet extracted with benzene for 8h and dried under vacuum.

### Hydrodehalogenation reaction: General procedure

The catalyst (30 mg, 0.0056 mmol of Pd) suspended in 4 mL of dry ethanol was treated with molecular hydrogen for 20 min. 1-Bromonaphthalene (entry 8) (1mmol, 0.21 mL) dissolved in 4 mL of ethanol was added to the above mixture dropwise and stirred under hydrogen. The progress of the reaction was monitored by GC. The reaction mixture was filtered and evaporated *in vacuo* and purified by column chromatography over silica gel. Elution with hexane gave pure naphthalene (83 mg,

65%). The product was identified by <sup>1</sup>H NMR which was in consonance with literature data.

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