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Research Article

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Synthesis, characterization and application of eco-friendly and recyclable heterogeneous palladium catalyst

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ABSTRACT

Aluminium supported palladium nanoparticles were prepared by very simple solution reduction method using N-cetyl-N,N,N-trimethyl ammonium bromide (CTAB) as a capping agent and Sodium borohydride as a reducing agent. These synthesized materials are air and moisture stable used in open air. Crystalline nature of the material is characterized by powdered x-ray spectroscopy. The synthesized materials are used as heterogeneous catalyst in Heck coupling reaction with best results. This heterogeneous catalyst are separated from reaction mixture by simply filtration and repeatedly used without loss of activity.

Keywords: Synthesis, Characterization, Catalytic application

INTRODUCTION

The arylation and vinylation of alkene with aryl or vinyl halides was discovered independently by Heck [1] and Mizoroki et al. [2] about 40 year ago. Now a days it is universally known as Heck reaction. Palladium catalyzed Heck reaction between aryl halide and olefins is an important reaction in modern organic synthesis[3,4,5]. The reaction is generally catalyzed by either Pd(0) or Pd(II) complexes in solution [6,7,8]. In order to circumvent the problems, like catalyst recovery and air sensitivity associated with reactions under homogeneous condition, heterogeneous catalytic systems were developed. In recent years, Heck reaction has been catalyzed by palladium metal supported on charcoal[9], mesoporous Carbon[10], magnesium oxide[11], palladium/Nb-MCM-41[12], polymers[13], zeolites[14], polyionic resins.[15] Basic supports such as layered double hydroxide[16], basic zeolites[17], alkaline exchanged sepiolites[18], mixed oxide[19], flourapatite[20] have been used because Pd on these supports shows considerably higher activity towards Heck reaction.

To our knowledge alumina supported palladium nanoparticles has not been prepared by reduction method using CTAB & Sodium borohydride as a reducing agent and has not been used in open air, as a heterogeneous catalyst for the Heck reaction. Herein, we report the synthesis and characterization of air and moisture stable alumina supported palladium nanoparticles and it used as a heterogeneous catalyst for the Heck reaction. The catalyst is air stable, can be stored and handled in air, and after the reaction it can be recovered by simple filtration and reused without significant loss of activity.

EXPERIMENTAL SECTION

The melting point of product determined in open capillary tube are uncorrected. Infrared spectra were recorded using KBr pellets on a FT Perkin Elmer spectrometer. The ^{1}H NMR and ^{13}CNMR spectra were recorded in DMSO/CDCl3 on a Brocker-300 spectrophotometer. **(Scheme No-1)**

Catalyst preparation

Catalyst were prepared as, Solution A: - Aluminum oxide and Sodium borohydride solution were taken in beaker and stirred for 10 min to obtain homogeneous 'Solution A'(details are given in Table 1). Solution B: - CTAB were added in distilled water and stirred for 30 min to obtained clear CTAB solution 'Solution B'

Solution A and Solution B were mixed and $PdCl_2$ was added drop wise in to the mixture of 'Solution A and Solution B' under constant stirring. (Details are given in Table 1) The resulting gel was stirred 1 hr for homogenization and was placed for 3 days. The above clear liquid was decanted and solid particles was washed repeatedly with water & acetone till the filtrate was neutral to litmus and dried.

Table 1. The preparation of Alumina Supported Pallidium Nanoparticles

Sr. No	% of Pd	Solution A in mL		Solution B in mL (CTAB 0.5M)	$PdCl_2$ in mL $1.56 X10^{-3}$ M
		Al_2O_3 in mg	$NaBH_4$ (0.5M)		
1	1	500	50	50	50
2	2	500	100	100	100
3	3	500	150	150	150
4	4	500	200	200	200

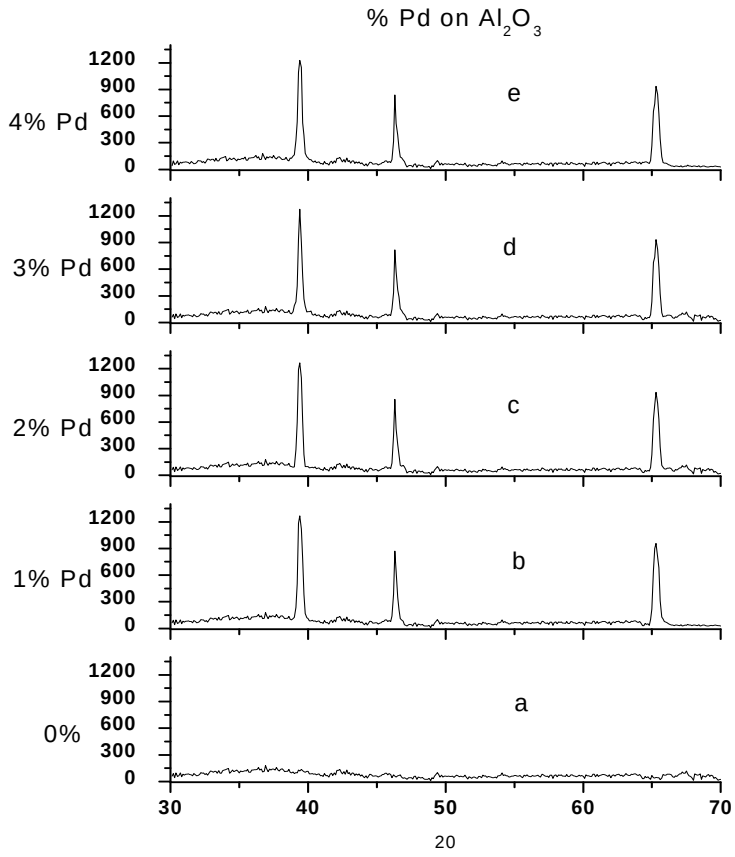


Fig 1. XRD of Pd*/Al_2O_3
** a-Al_2O_3, b-1%Pd/Al_2O_3, c-2%Pd/Al_2O_3, d-3%Pd/Al_2O_3, e-4%Pd/Al_2O_3.*

Catalyst Application

Heck reaction of bromobenzene with styrene was carried out using these catalyst after activation at 200^{o}C for 4 hr (scheme. 1.) A typical reaction was carried out in open air, Bromobenzene 0.42 mL (4 mmol), styrene 0.68 mL(6 mmol), K_2CO_3 1.646 g (12 mmol), solvent DMF 5 mL and Pd/Al_2O_3 5wt% (0.074g)with respect to reactants was taken in 50 mL round bottom flask connected to water condenser and heated in oil bath at 130 °C with constant stirring. The reaction was monitored time to time by TLC. After the 9 hr reaction was quenched with 5 mL of water and the catalyst was filtered. Next 50 mL of water was added to the filtrate and the product was extracted with ether. The product obtained after evaporation of the solvent was purified by column chromatography using silica gel (60-120 mesh) with petroleum ether as eluent. The results of the screening of the catalysts are presented in table 2.

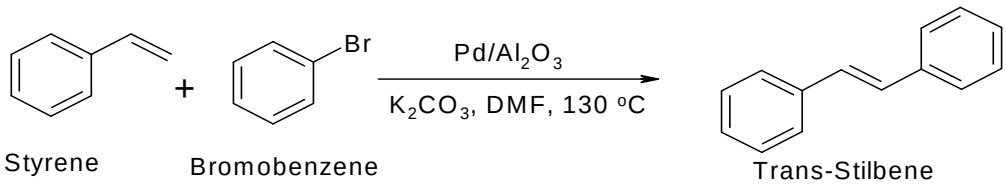
RESULTS AND DISCUSSION

The structure and phase purity of the catalyst were confirmed by analyzing the observed powder X-ray diffraction patterns. Fig 1. All the observed reflections of the Al_2O_3 supported Palladium samples could be assigned to Face Center Cubic indicating their single phase nature. From the X-ray diffraction peaks, average particle size was estimated using Scherrer's formula.

$D = 0.9\lambda/\beta\cos\theta$

Where β is the FWHM of the most intense peak, θ is the Bragg angle for the most intense peak , and λ is the wave length of Cukα = 1.54 A^0. From above equation the average crystalite size of X Pd/Al_2O_3 (X =1% - 4%) was estimated to be 48 nm.

Scheme 1



Trans stilbene

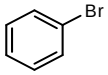
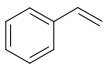
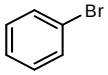
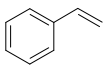
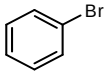
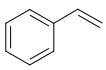
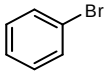
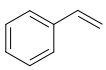
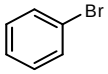
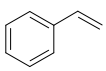
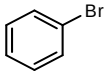
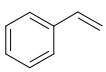
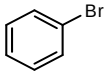
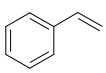
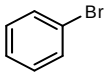
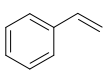
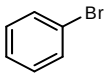
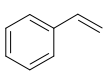
m.p. 124^{o}C; IR (KBr): 2926, 1597, 1451, 962, 764, 692, 525; ^{1}H NMR ($CDCl_3$): δ 7.28 (t, 2H), δ 7.39 (t, 4H), δ 7.55 (d, 2H), δ 7.15 (s, 2H); ^{13}CMR ($CDCl_3$): 78.7, 97.4, 129.6, 137.9.

Pure Al_2O_3 without Pd loading did not produce trans stilbene even after 20 hr. When the reaction was carried out with 0.1 mol% of $PdCl_2$ as the catalyst, the product yield was 37%. Surprisingly, the 2% loading of palladium is sufficient for the Heck reaction. In ethanol solvent no reaction was observed under reflux conditions.

The heterogeneous nature of the reaction over Pd/Al_2O_3 was tested as follows. The catalyst Pd/Al_2O_3, bromobenzene and K_2CO_3 (except the olefin) were mixed in dry DMF and heated at 130^{o}C with constant stirring for 5 hr. The catalyst was filtered out quickly and styrene was added to the reaction mixture followed by 10 % more of the K_2CO_3 base and the reaction was continued for another 5 hr at 130^{o}C. Analysis by GC did not reveal any product formation. This showed that the reaction did not proceed on the removal of the solid catalyst suggesting its heterogeneous nature. The catalyst could be recycled without any treatment, through some loss was noticed in the yield of trans stilbene from the reaction between bromobenzene and styrene using 2 % Pd/ Al_2O_3

In summary, alumina supported palladium nanoparticles has been successfully prepared in a stable form. This catalyst proves to be an excellent catalyst for Heck coupling reaction. A bromobenzene and styrene catalyzed by $PdCl_2$ and the Pd/ Al_2O_3 carried out in air . Excellent conversions and yields make this Pd/ Al_2O_3 catalyst is novel and efficient catalytic system. These reactions take place at low as well as at elevated temperatures although, of course, the reactions require a longer time at a lower temperature.

Table 2 Heck reaction over heterogeneous catalysts: Pd/Al_2O_3

Entry	Alkyl Halide	Olefins	Catalyst	Yield %
1			-	00
2			$PdCl_2$	37[a]
3			1%	90
4			2%	94
5			3%	94
6			4%	94
7			2%	93[b]
8			2%	91[c]
9			2%	90[d]

Reaction Conditions:- Bromobenzene (4mmol), Styrene (6 mmol), K_2CO_3 (12mmol), Pd/Al_2O_3 5wt%, DMF 5 ml Temp 130^{o}C Time 9 Hr. a Yield after first cycle, b Yield after second cycle. c Yield after third cycle, d Yield after fourth cycle

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