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$PdAl_2O_4$ spinel type nanoparticle synthesis through sol-gel route: An effective catalyst for Suzuki-Miyaura coupling reaction

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Abstract
Palladium Aluminium spinel type nano particle was synthesized by sol-gel method. It was characterized by SEM, TEM, TG, etc. The catalyst was found to be active for the Suzuki coupling reaction in good to excellent yield. Even less reactive substituted bromo benzenes gave good results in short period of time. The catalyst was found to be active over three cycles.

Keywords: nano spinels, biphenyls, heterogeneous catalysts

Introduction
Bimetallic nanoparticles exhibit better properties than their mono metallic counterpart [1]. Many bimetallic nanoparticles were found to exhibit interesting electronic, optical, chemical and biological properties due to synergic effects [2]. Palladium catalyzed cross-coupling reactions widely used for the formation of C-C bond forming reactions [3-6]. Wide range of catalysts is available for the Suzuki-Miyaura reaction; transition metal catalyzed cross-coupling reactions are useful tool for constructing C-C bonds which finds important industrial applications [7-9]. Palladium-catalysed cross coupling of organo boron derivatives with organic electrophiles is one of the most widely used cross-coupling protocols for carbon-carbon bond formation. Heterogeneous version of palladium catalysts for C-C bond forming reactions are fewer due to difficulty in the synthesis, stability, activity, the cost of ligands, such as bulky tertiary phosphines and difficulties associated with separation of the ligands and their degradation products, phosphine oxides etc. Transition metal aluminates are important class of compound which finds numerous applications in optics and catalysis [10-11]. Transition metal aluminates are generally prepared by solid state method at high temperature (1200 ^oC) [12], hydrothermal methods [13], combustion methods [14] disadvantage of these method includes inhomogeneity, lack of stoichiometry control, high temperature and low surface area. The sol-gel method poses additional advantage of producing ultrafine powders at low temperature.
Transition metal-oxide spinels derived from Mg and Zn when doped with Cr^{3+} ions showed luminescence [15], most of the metal-oxide spinels showed semi conductivity [16], transition metal doped spinels are used as high voltage cathode materials for rechargeable lithium-ion battery [17], as biomarkers for invio imaging [18]. Many metal-oxide spinels in pure and doped form were found wide application in heterogeneous catalysis [19, 21].
In this paper preparation of $PdAl_2O_4$ nano spinel by adapting a procedure of modified Pechini method reported earlier [22], Characterisation of $PdAl_2O_4$ have been done by various instrumental techniques like XRD, FTIR, TG, SEM, HRTEM etc. Catalytic application of the prepared material was investigated for Suzuki coupling reaction.

2. Experimental
2.1 General
All Chemicals were reagent grade and used as purchased. IR spectra were recorded in KBr disks with a SHIMADZU FT-IR Spectrophotmeter. Scanning electron microscopy (SEM) analysis were performed with JEOL JSM-6380LV instrument. Transmission Electron Microscopy (TEM) images were performed with a JEM-2100 instrument. ^1H NMR spectra were recorded with Bruker Avance III 500 analyser. XRD patterns were recorded on a Rigagu D Max C III, X-ray diffractometer using Ni-filtered Cu Kα radiation. Thermo gravimetric analysis (TGA) were carried out using Shimadzu TGA 50H)

2.2 Preparation of the catalyst

1.6mmol $Pd(CH_3COO)_2$ were dissolved in 6mL diethylelene glycol monoethyl ether(DGME) and 2.35mmol anhydrous citric acid was subsequently added the solution is heated to 50°C for 1 h. When the solution becomes uniform 3.14mol Al $(NO_3)_3$. $9H_2O$ in 9mL diethylene glycol monoethyl ether was added. The resulting solution is further heated to 80 °C for 1h Resulting sample is again heated at 130 °C for 1h, the viscous solution so obtained finally became a xerogel. The xerogel obtained is heated at 250 °C for 1 h. The black powder obtained is further heated in the furnaceat 400-800 °C in air and in an Al_2O_3 boat, and then cooled it to room temperature.

2.3 General procedure for Suzuki Coupling reaction

A 10 ml RB flask was charged with aryl halide (1 mmol), aryl boronic acid (1.2 mmol), and K_2CO_3 (3 mmol). The catalyst $PdAl_2O_4$ (100 mg) was added to it followed by 5 ml of dioxan. The reaction mixture was stirred at reflux temperature. The progress of the reaction was monitored by TLC using hexane: ethyl acetate (10:1). After completion of the reaction, the catalyst was filtered and the catalyst was washed with acetone and with small portions of ethyl acetate several times. The combined washings were washed with water in a separating funnel; the organic layer was isolated and dried with 4A° molecular sieves. The pure product was isolated by column chromatography using hexane: ethyl acetate (10:1) as eluent

3. Results and Discussions

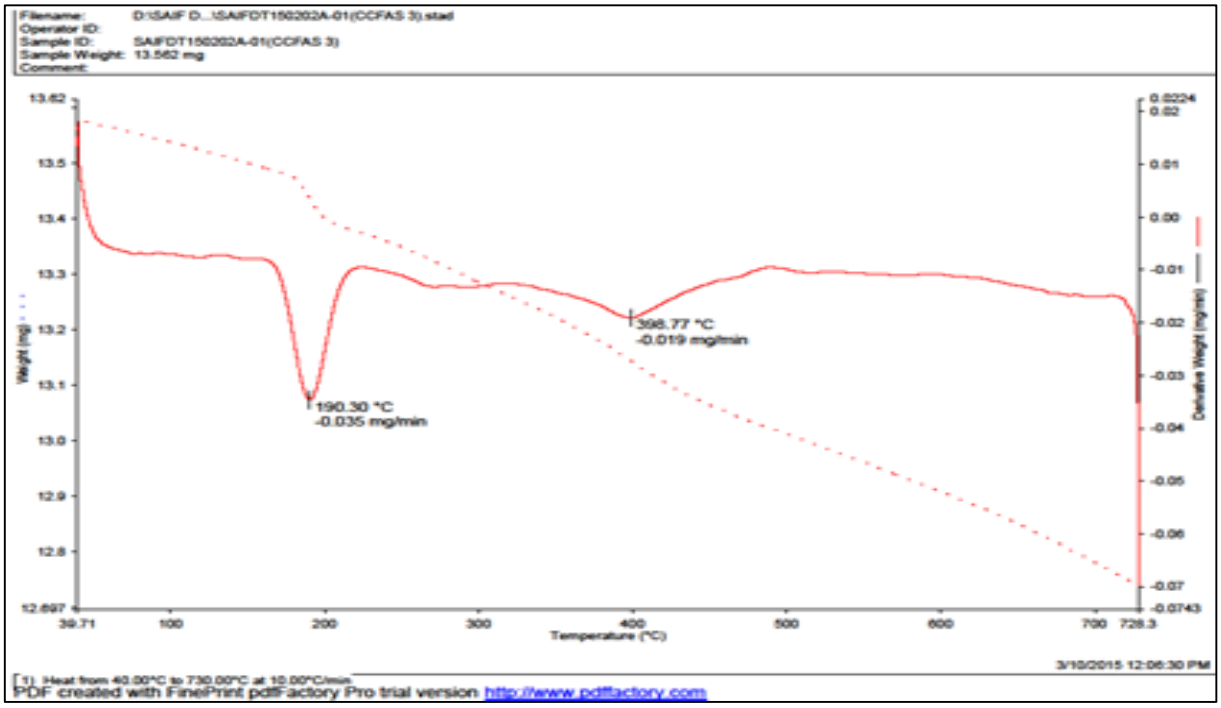


Fig 1: Thermo gravimetric Analysis Curve of $PdAl_2O_4$

In the TGA curve of $PdAl_2O_4$ (Fig. 1) weight loss around 190 °C corresponds to evaporation of adsorbed water, Weight loss around 396 °C may be ascribed to the decomposition of the organic compound. Above 500 °C the catalyst found to be stable indicating the formation of stable oxide, due to spinel-type $PdAl_2O_4$ nanocrystals.

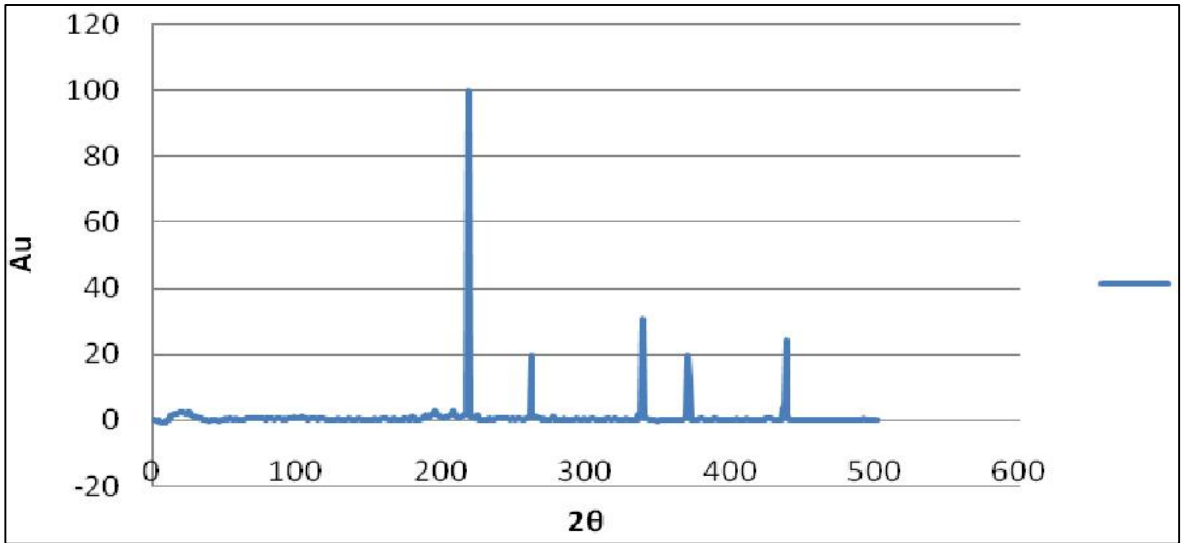


Fig 2: XRD pattern of $PdAl_2O_4$

XRD pattern of the prepared catalyst was analysed, the peaks at 2θ = 33.48º, 41.58º, corresponds to 220 and 111 plane of the spinel from of $PdAl_2O_4$. Characteristic peak of pd(III) plane observed at 41.58º. (99) Fig.2.

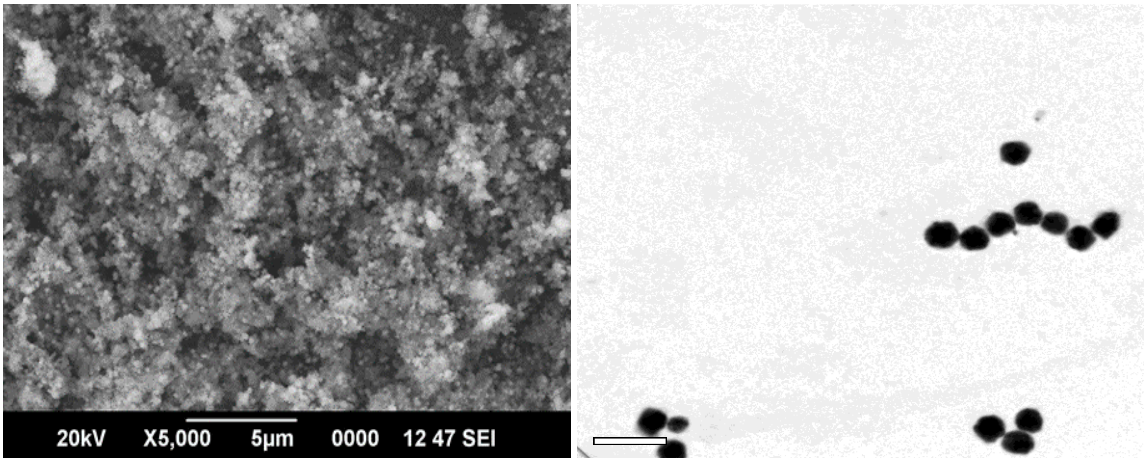


Fig 3. SEM and TEM images of $PdAl_2O_4$ powders calcined at 800ºC

Surface morphology of the prepared catalyst was investigated by scanning electron microscopy (SEM), TEM analysis shows particle size in the range 20-30nm. Fig.3

FTIR analysis is used find the characteristic frequencies of the spinel nano crystals. The peak around 3500-3078cm^{-1} indicates OH longitudinal vibration of the water, a small peak around 1624 cm^{-1} was due to bending vibration of H-O-H in the water molecule. Peaks around 470-836cm^{-1}, associated with vibrations of Pd-O, Al-O and Pd-O-Al bonds (98). Fig 4

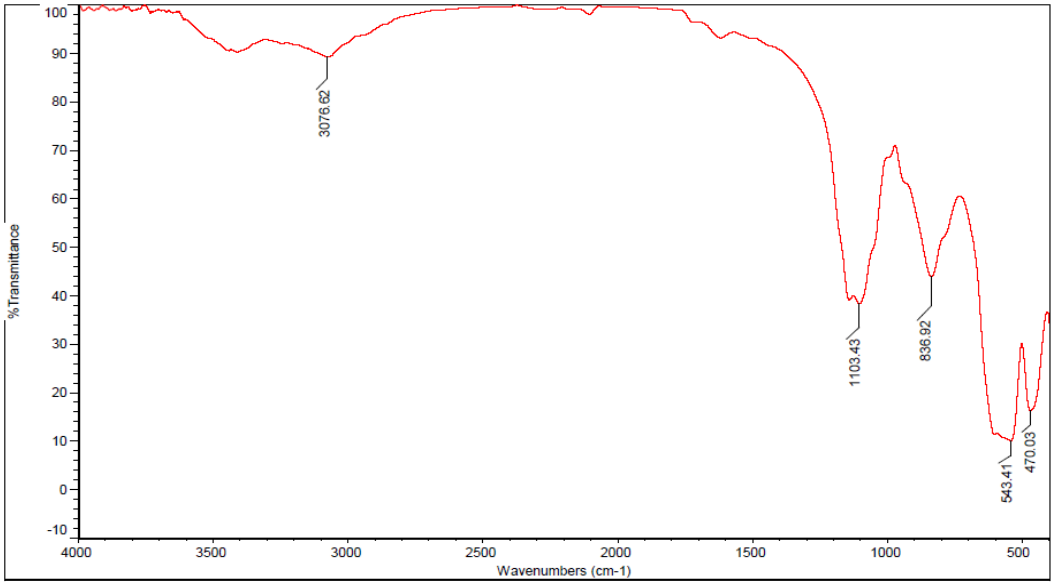


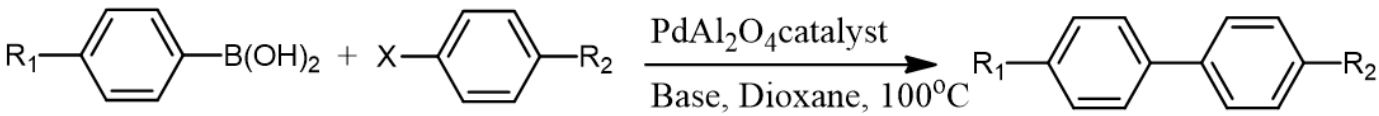
Fig 4. FTIR spectra of $PdAl_2O_4$ nano spinel catalyst

Table 1. Screening of solvent for Suzuki coupling reaction

Entry	Solvent	% Yield
1	Toluene	68
2	Methanol	54
3	Dioxan	89
4	THF	74
5	Acetone	66

Reaction condition: Reaction condition: 4-nitro iodobenzene (1 mmol), benzene boronic acid (1.2 mmol), K_2CO_3 (3 mmol), Reflux temperature. Catalyst 100mg, 5 mL solvent

Scheme 1. $PdAl_2O_4$ spinel type catalyst mediated Suzuki-Coupling reaction



The activity of the catalyst is tested for Suzuki-Coupling reaction by selecting benzene boronic acid and iodobenzene. The catalyst is found to be active towards the reaction with good to excellent yields. various parameters of the reaction has to be optimized, effect of solvent was studied by selecting five different solvents at reflux temperature; better results were obtained for polar solvents as compared to non-polar solvents. This may be due to the smooth interaction of the substrates on the active sites of the catalyst due to easier diffusion effect of solvents as compared to non-polar solvents. The results are summarized in table 1

Different substrates were tried; aryl iodides and bromides gave good results while chlorides gave poor yield even after prolonged reaction under refluxing conditions. The results are summarized in table 2. The electronic factors of substrates had no considerable effect on the reaction.

Table 2: Suzuki coupling reaction of aryl halides with aryl boronic acids.

Entry	R_1	R_2	X	Base	% Yield[a]
1	H	CH_3	I	Na_2CO_3	86
2	H	CH_3	I	Et_3N	81
3	H	CH_3	I	NaOH	84
4	H	H	I	Na_2CO_3	78
5	H	H	I	Et_3N	71
6	H	H	I	NaOH	74
7	H	H	Cl	Na_2CO_3	28
8	H	NO_2	I	Na_2CO_3	89
9	H	NO_2	I	Et_3N	80
10	H	NO_2	I	NaOH	82

Reaction condition: aryl halide (1 mmol), benzene boronic acid (1.2 mmol), Na_2CO_3 (3 mmol), 100 mg catalyst. Solvent: 5ml dioxan at 100ºC, Reaction time: 24h. a. Isolated yield.

Spectral data of products

4-methyl biphenyl(Entry1)^{1}HNMR(400MHz;$CDCl_3$):δ 2.4(s,3H), 7.07(d, 2H J=7.3Hz), 7.2-7.39m,1H), 7.35(t,J=2H,6.36Hz), 7.42(d,2H,J=81.2), 7.46(m,2H)

Biphenyl (Entry 4)^1 HNMR (400MHz; $CDCl_3$):δ7.23-7.34(m, 2H), 7. 36-7.42 (m, 4H), 7.56-7.59(m, 4H)

4-nitrobiphenyl (Entry 8)^1 HNMR (400MHz; $CDCl_3$):δ7.37-7.41(m, 1H), 7.43-7.45(m, 2H), 7. 57 (m, 2H), 7.66 (d, 2H, J=8.80Hz)

3.3 Catalyst reusability

Finally reusability of the catalyst was investigated using 4-nitro Iodobenzene and benzene boronic acid as model substrates. As expected the catalyst showed good reusability with a slight decrease in activity. The results of the recycling studies are shown in

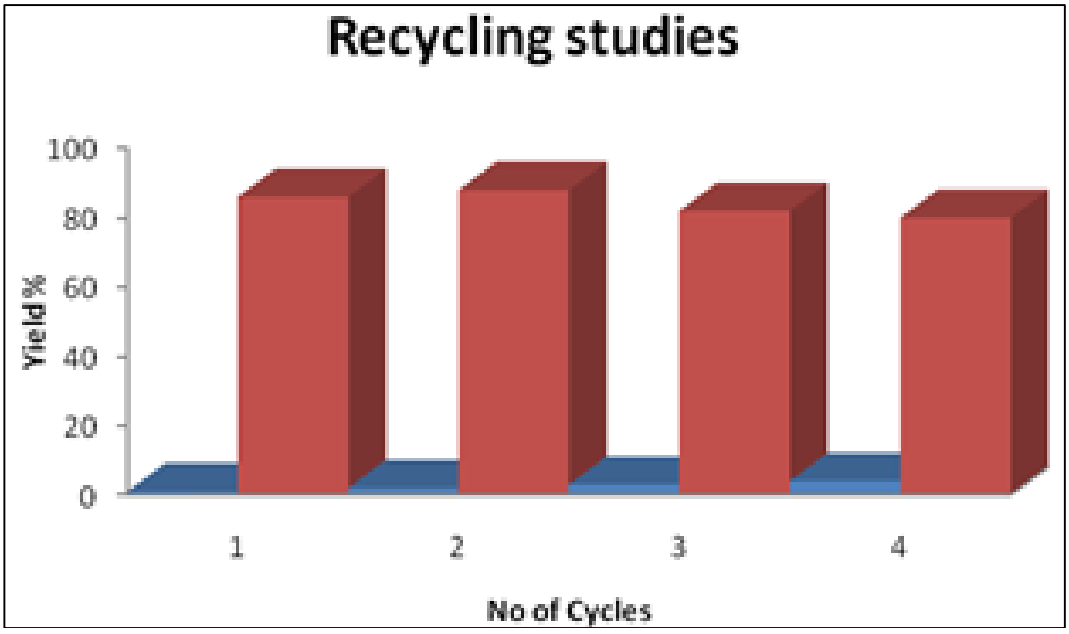


Fig 5

Reaction condition: 4-nitro iodobenzene (1 mmol), benzene boronic acid (1.2 mmol), K_2CO_3 (3 mmol), 100mg catalyst 5ml dioxan at 100 ºC. Reaction time 24h. Isolated yield

Conclusion

In conclusion we have synthesized a $PdAl_2O_4$ spinel type nanocatalyst through sol-gel method. Prepared catalysts were characterized by FTIR, TG, SEM, HRTEM etc. The catalyst is found to be more active towards Suzuki Coupling reaction. The catalyst is recyclable.

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