

Structure-activity relationship between some novel silica supported palladium catalysts: a study of the Suzuki reaction

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Received 17 November 2003; accepted 24 December 2003

Abstract

A series of novel silica supported palladium catalysts bearing N–N, N–S and N–O chelating ligands have been prepared by the following reactions—(a) synthesis of 3-aminopropylsilica from activated silica and 3-aminopropyl(trimethoxy)silane; (b) synthesis of Schiff-bases from 3-aminopropylsilica and 2-acetylpyridine, 2-pyridinecarboxaldehyde, 2-thiophenecarboxaldehyde, 2-furancarboxaldehyde, 2-acetylfuran, 2-hydroxyacetophenone, 2-aminoacetophenone and 2-pyrrolicarboxaldehyde; (c) reaction of Schiff-bases with palladium acetate to obtain silica supported palladium catalysts. The catalysts were characterized by STA, BET, DRIFT and X-ray photoelectron spectroscopy (XPS). X-ray photoelectron spectroscopy has been found to be a useful tool for establishing the structure-activity relationship between supported palladium catalysts with different chelating atoms using Suzuki reaction as an example. The catalysts with lower binding energy for palladium in comparison to palladium acetate are more active than those with higher binding energies. The activity of the catalysts was compared on the basis of rate constants in the Suzuki reaction between bromobenzene and benzenboronic acid using anhydrous potassium carbonate as base and *o*-xylene as solvent.

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Keywords: Structure-activity relationship; Heterogeneous catalysis; Silica supported palladium catalysts; Suzuki coupling; X-ray photoelectron spectroscopy

1. Introduction

Heterogeneous catalysts for environmental related applications have progressively occupied a significant part of catalytic chemistry [1,2]. From the standpoint of environmentally benign organic synthesis, development of immobilized and insoluble metal catalysts is challenging and important (For reviews of immobilized metal catalysts, see: [3–6]). In an ideal system, they can be recovered from the reaction mixture by simple filtration and re-used infinitely, and contamination of products by metallic species is prevented. Among various transition metals, use of immobilized palladium on the surface of silica gel, aluminium oxide, polymers, metal oxides etc is well documented [7–10]. Recently palladium immobilized on the surface of silica gel was used for Suzuki [7,11], Heck, carbonylation [7,12,13] and other reactions. Keeping in view the application and

interest of heterogeneous palladium catalysts in academia and industry, there is a need to design and develop stable, re-usable and easily recoverable chemically supported heterogeneous palladium catalysts. In this study our aim is to prepare novel heterogeneous palladium catalysts with different chelating ligands so as to study the structure-activity relationship between them. This will help the chemists working in the area of heterogeneous catalysis to choose appropriate catalytic systems for their own systems.

2. Experimental

2.1. Catalyst preparation

The silica supported palladium catalysts were prepared by the following steps:

- synthesis of 3-aminopropylsilica from activated silica and 3-aminopropyl(trimethoxy)silane;
- synthesis of Schiff-bases from 3-aminopropylsilica and 2-acetylpyridine, 2-pyridinecarboxaldehyde, 2-thiophe-

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reaction was stirred at 100 °C and 600 rpm for the appropriate time. The samples were withdrawn at regular interval and analyzed by GC. The reaction was carried out under nitrogen to ensure that there is no change in the ligand structure during the reaction. The yields were calculated on the basis of bromobenzene using *n*-dodecane as internal standard.

2.3. Characterization of catalysts

Catalyst characterization was performed using thermal analysis, surface analysis, DRIFT and X-ray photoelectron spectroscopy (XPS). The thermal analysis was performed using a Netzsch 409 STA with a temperature range of 10 °C/min. The presence of C–H and C=N bonds was confirmed by DRIFTS using a Bruker Equinox 55 FTIR spectrometer. The binding energy of palladium in the catalysts was determined by XPS using a Kratos AXIS HIS instrument equipped with a charge neutraliser and Mg K α X-ray source. The pore size distribution and BET surface area were determined by using a Beckman Coulter SA 3100 porosimeter with dinitrogen as an adsorbate. The amount of palladium loaded on the surface of silica was determined by atomic absorption spectroscopy.

3. Results and discussion

3.1. Structure-activity relationship

Following catalyst preparation, efforts have been made to prepare the catalysts with similar physical characteristics. The thermal analysis of catalysts shows the loss of residual solvent at 80 °C. The decomposition of bound organics starts from 187 to 256 °C for the eight catalysts studied here.

Table 1

BET surface area, total pore volume and amount of Pd loaded on the surface of silica

Catalyst	BET surface area (m ² /g)	Total pore volume (ml/g)	Amount of Pd by AAS (mmole/g)
Cat 1	249.40	0.7130	0.100
Cat 2	266.36	0.7236	0.095
Cat 3	255.71	0.6630	0.092
Cat 4	266.03	0.7031	0.093
Cat 5	281.79	0.7405	0.197
Cat 6	260.89	0.7237	0.080
Cat 7	261.41	0.7254	0.088
Cat 8	293.37	0.7635	0.090

The major weight loss at high temperature is characteristic of chemisorbed material and confirms that the aminopropyl group is chemically bound on the surface of silica. From STA results it is clear that 100 °C is a safe temperature to carry out the reaction without any chance of decomposition of catalysts. The BET surface area, total pore volume and the amount of palladium loaded on the surface of silica gel is as shown in Table 1. There is not much difference in the surface area of the various catalysts with values between ca. 250 and 290 m²/g. Different surface area and pore volume can contribute to different activities of porous solid catalysts but we assume that there is no contribution due to different BET surface areas and pore volumes in our study towards establishing the structure-activity relationship. The amount of Pd loaded on the surface of silica gel was determined by AAS. All the reactions were carried out with catalysts containing 0.02 mmol of Pd. Fig. 1 shows the DRIFTS of modified silica and supported palladium catalyst (Cat 1). The DRIFTS of 3-aminopropyl silica displays characteristic CH₂ stretching bands at 2936 and 2865 cm⁻¹ and aliphatic deformation bands at 1469 and 1445 cm⁻¹. The DRIFTS of chemically

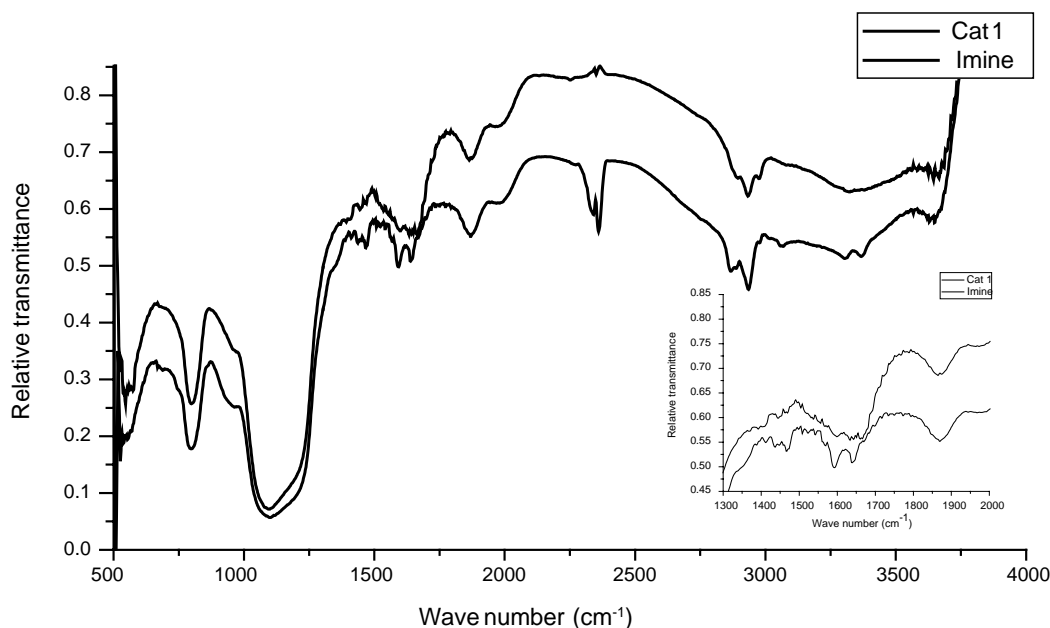


Fig. 1. DRIFT of Cat 1 and modified silica (imine) (inset shows the imine peak at 1639 shifted to 1599 cm⁻¹).

Table 2
Approximate C=N peak values for catalysts and their corresponding imines in DRIFTS

Catalyst	C=N (cm ⁻¹) in imine	C=N (cm ⁻¹) catalyst	Shift of C=N peak (cm ⁻¹)
Cat 1	1639	1599	40
Cat 2	1648	1594	54
Cat 3	1637	1631	6
Cat 4	1646	1637	9
Cat 5	1630	1615	15
Cat 6	1616	1601	15
Cat 7	1596	1588	8
Cat 8	1639	1594	45

modified silica (imine) shows sharp peak due to C=N, which on complexation with Pd disappears and appears as a band at lower value. The lowering in frequencies of the C=N peak is indicative of the formation of metal–ligand bonds. The difference in the values of the C=N stretching band before and after complexation for all catalysts is shown in Table 2. The larger shifts of the C=N peak indicate stronger bonding of Pd with the ligands. On the basis of this, we tried to correlate the activity of the catalysts with the shift of the C=N peak. If we consider the C=N bond shift values before and after complexation as a measure of activity of catalysts, then Cat 2 with shift of 54 cm⁻¹ would be most active and Cat 3 with a small shift of 6 cm⁻¹ would be the least active. But actually this is not the case when we consider the rate constant values (Table 3). Rate constants are in the order Cat 1 ($\Delta\nu_{\text{C=N}} = 40 \text{ cm}^{-1}$) > Cat 7 (8 cm⁻¹) > Cat 6 (15 cm⁻¹) > Cat 5 (15 cm⁻¹) > Cat 3 (6 cm⁻¹) = Cat 4 (9 cm⁻¹) > Cat 2 (54 cm⁻¹) > Cat 8 (45 cm⁻¹). Unfortunately, we were unable to find any correlation between structure and activity of catalysts on the basis of DRIFTS data. This may be because the value of C=N peak before complexation is not a true value as in the cases of Cat 6 & 7, there is a hydrogen bonding between the H of -OH & -NH₂ with the nitrogen of C=N bond, thus lowering the value of the C=N peak. We should also note the breadth of some of the C=N stretching band making assignment of frequencies difficult.

X-ray photoelectron spectroscopic data gives the binding energies of Pd with different chelating ligands. The different

Table 3
Binding energies (eV) of Pd in catalysts and Pd(OAc)₂ and rate constants in the Suzuki cross-coupling reaction between bromobenzene and benzenboronic acid using K₂CO₃ as base and *o*-xylene as solvent

Catalyst	Binding energy (eV)	Rate constant
Pd(OAc) ₂	336.25	–
Cat 1	333.45	0.0364
Cat 2	335.95	0.00198
Cat 3	334.95	0.00601
Cat 4	335.15	0.00601
Cat 5	334.05	0.00755
Cat 6	334.05	0.00943
Cat 7	334.35	0.01403
Cat 8	336.35	0.00167

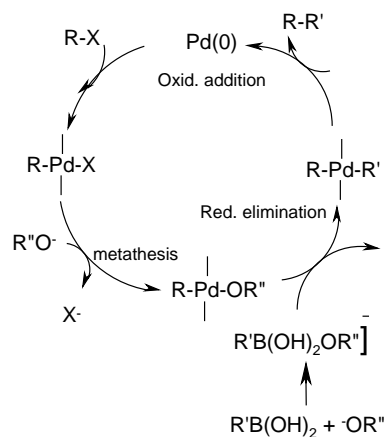


Fig. 2. Proposed mechanism for Suzuki cross-coupling reaction.

values of binding energies for Pd in each catalyst suggests a different environment around the palladium. If we look at the proposed mechanism of the Suzuki cross coupling reaction (Fig. 2), it appears that a more electron rich environment around the palladium make it easy to insert it into the R–X bond. But if we consider the XPS data, a more electron rich environment around the palladium leads to lower binding energy values. Thus, the lower the binding energy for Pd, the more easy the insertion of Pd in the R–X bond can take place and hence the faster is the reaction. The binding energy values for Pd and the rate constants in the Suzuki cross-coupling reaction for each catalyst is shown in Table 3. From Table 3, it is clear that the lower the binding energy of Pd in the catalysts, the greater their activity in the Suzuki reaction. There is a clear but not linear relationship between binding energies and rate constants. The presence of the methyl group on the carbon of the C=N group dramatically increases the rate of the reaction (cf. Cat 1 and Cat 2). This may be due to the electronic effect of a methyl group, which ultimately increases the electronic environment around the palladium. But if a methyl group is present on the carbon of the C=N group, where one chelating atom is oxygen (Cat 5), there is no significant difference in the rate of the reaction (cf. Cat 4 & Cat 5). The reason for this is not clear. Thus, on the basis of XPS data, we can say that groups which increase the electronic environment around the palladium make the catalyst more active for the Suzuki cross-coupling reaction (e.g. Cat 1, 5–7, presence of methyl group on the carbon of the C=N group). The reaction was also carried out with 4-bromoanisole and 4-bromobenzonitrile in the presence of Cat 1 to determine the electronic effects of the substituents on the bromobenzene. The rate constants were found to be 0.02479 for 4-bromoanisole and 0.05957 for 4-bromobenzonitrile in comparison to 0.03674 for bromobenzene. This suggests that different electronic effect of the substituents on bromobenzene affect the rate of the reaction significantly.

Re-usability of Cat 1 was checked by performing the reaction after washing the catalyst with methylene chloride

followed by excess of water. The catalyst was dried at 95 °C for 5 h in air prior to use. Up to the seventh use (1st use: 100% after 100 min; fourth use: 95% after 150 min; seventh use: 97% after 180 min), of the catalyst leads to no significant drop in activity. Hence the catalyst can be used several times without any loss of activity. Although no significant change in the activity of the catalyst was observed, we have performed surface analysis and simultaneous thermal analysis of catalyst 1 after the seventh use in order to determine any changes in the catalyst. The surface analysis shows that there is no significant change in the surface area (from 249.40 to 246.28 m²/g) and a slight increase in the total pore volume from 0.7130 to 0.7385 ml/g. The simultaneous thermal analysis also shows the same weight loss after the seventh use as for the fresh catalyst. Clearly no significant restructuring of the catalyst has taken place on multiple use.

4. Conclusion

In conclusion, we have for the first time demonstrated a structure-activity relationship for supported Pd catalysts in the Suzuki reaction based on Pd binding energies (as measured by XPS) and initial rate of the reaction. A surprisingly positive effect due to the alkyl substituent on the ligand provides the possibility for designing new ligand structures to examine the activity of the catalysts and this is currently being pursued in research in our laboratory.

Acknowledgements

We gratefully acknowledge the support of the department of Science and Technology, New Delhi, Govt. of India for

a BOYSCAST fellowship to S.P. and the constant support and advice of the York Green Chemistry group.

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