The Imprinted MCM-41 Palladium(II) Salen Complex: Its Synthesis, Characterisation and Catalytic Activity for the Suzuki-Miyaura Reaction

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Abstract: *The symmetric palladium(II)(4-OH)$_2$salen complex ((4-OH)$_2$salen=N,N'-bis(4-hydroxysalicylidene)ethylenediimine) has been immobilised on MCM-41, resulting in an efficient and highly recyclable heterogeneous catalyst for the Suzuki-Miyaura reaction. The catalyst afforded a fast and high percent conversion of bromobenzene at a catalyst loading of 0.05 g, 0.184 mol% Pd. Transmission electron micrographs (TEM) and surface area measurements clearly demonstrate that the immobilisation of the Pd(II)(4-OH)$_2$salen complex on mesoporous silica has a significant effect on the pore structure of the catalyst. Nevertheless, after immobilisation of the palladium complex, the meso-porosity of the material is retained, as evidenced by nitrogen sorption measurements. The scanning electron microscope (SEM) images show that both MCM-41 and the MCMSalenPd catalyst have similar types of external surface morphology; however, the catalyst was less ordered.*

1. INTRODUCTION

The favourable properties of supported metal complexes as heterogeneous catalysts have been widely used in various chemical industries.[1] Some of those important complexes are transition metal-salen complexes, which have been successfully employed in several heterogeneous catalytic reactions.[2–8] Salen(N,N′-ethylenebis(salicylimine)) is a tetra dentate symmetric ligand system, which provides a square planar or an octahedral geometry around the coordinated central metal, and can be easily prepared in a one-step condensation reaction of two equivalents of an inexpensive salicylaldehyde derivative or a ketone with 1,2-diaminoethane. These ligands are able to stabilise different metals in various oxidation states.[9] Although the palladium(II) salen complex was first isolated in 1963, the tetra dentate Schiff base complexes of this metal ion are still important reagents due to their stability and ease of handling. Recently, these ligands have been widely studied and developed into various designer catalyst systems for many organic syntheses such as hydrogenation, oxidation and C–C cross-

coupling reactions, including Suzuki-Miyaura and Mizoroki-Heck reactions. Moreover, these catalytic complexes can be supported on different materials, resulting in efficient heterogeneous catalysts such as those grafted on polymers,[10–12] anchored on activated carbon or carbon nanotubes[13,14] encapsulated into zeolites[15,16] or immobilised on silica.[17,18]

The immobilisation of metal complexes onto silica support can usually be achieved using organosilanes, such as trialkoxy silanes, with a suitable functional group (e.g., –Cl, –NH$_2$, –SH). These functional groups operate as a linking agent between the different silanol (Si-OH) groups[19] present on the silica surface and the terminal groups of the metal complexes or the central metal itself.[20–26] This immobilisation provides the catalyst with heterogeneous properties and improves the stability of the catalytic metal complexes.

In this work, mesoporous MCM-41 silica was prepared from rice husk ash (RHA) for use as a support, and chloropropyltriethoxysilane was employed to functionalise the surface of MCM-41. Symmetric palladium(II) (4-OH)$_2$salen complex was then immobilised on the silica surface. Herein, the authors report the successful preparation of an efficient heterogeneous catalyst for the Suzuki-Miyaura reaction between various halobenzene compounds and phenylboronic acid. This work describes the preparation, characterisation and application of the MCMSalenPd catalyst.

2. EXPERIMENTAL

2.1. Materials

RHA was chosen as a natural source of silica because it was abundantly available in Malaysia. Cetyltrimethylammonium bromide (CTAB), 1,2-diaminoethane, palladium acetate (Pd(OAc)$_2$), iodobenzene, bromobenzene, phenylboronic acid and dimethylformamide(DMF) solvent were purchased from Merck, and 3-chloropropyltriethoxysilane (CPTES), triethylamine (Et$_3$N), and chlorobenzene were purchased from Aldrich. 4-Hydroxysalicylaldehyde was obtained from Fluka, and toluene, methanol and ethanol were supplied by QRëC. All chemicals and solvents were used without further purification.

2.2 Catalyst Preparation

2.2.1 Preparation of RHA

RHA, which consists of 87%–97% amorphous silica, was chosen as the source of silica[27,28] and was extracted from rice husks (RH) using a previously reported

method.[29] Briefly, the rice husks were washed thoroughly with tap water to remove any soil, tiny stones or other unwanted particles adhering to the husks. Then, the husks were rinsed with distilled water three times and dried at room temperature. The rice husks were collected and stirred with 1.0 M nitric acid at room temperature for 24 h to remove all metals. The resulting RH was calcined at 800°C for 24 h in a muffle furnace (Carbolite, UK, Model AAF 11/7). The obtained white ash RHA was washed with distilled water and used as a source of silica.

2.2.2   Synthesis of silica MCM-41

The mesoporous silica MCM-41 was prepared by modifying a previously reported method.[30,31] Sodium silicate was obtained by refluxing 4 g of RHA in 200 ml of 2 M NaOH at 70°C for 24 h. The solution was filtered and added dropwise under stirring to a solution of CTAB (4.6 g), which was dissolved in 25 ml of H_2O, at room temperature. The pH was adjusted to 10 by adding 1 M acetic acid. The pH was monitored by a pH metre (Metrohm Ion analysis model 827). The mixture was heated at 100°C for 96 h, and the pH was readjusted to 10 by adding 1.0 M acetic acid dropwise. The mixture was aged for 24 h at room temperature. The resulting gel/solid was separated by centrifugation (Rotina 38 Hettich Zenterifugen model D-78532 Tuttlingen), washed with distilled water and dried at 100°C for 24 h. Finally, the product was washed with an ethanol-HCl mixture, dried again and calcined in air at 450°C for 24 h.

2.2.3   Insertion of the linking agent (functionalization of MCM-41 with 3-chloropropyltriethoxysilane)

The functionalised silica Cl-MCM-41 was prepared according to a previously published procedure.[32] The silica MCM-41 (1 g) support was dehydrated at 110°C for 3 h to remove any physisorbed water and was added to a solution of CPTES (1 ml) using dry toluene (30 ml) as a solvent. The mixture was refluxed with stirring under a dry argon atmosphere for 24 h. The resulting MCM-41-$(SiCH_2CH_2CH_2Cl)_x$ was filtered, washed with dry toluene, washed with ethanol and dried in air at 70°C overnight, resulting in a white solid Cl-MCM-41 (1.13 g).

2.2.4   Synthesis of Palladium(II)(4-OH)$_2$salen complex

The N,N′-bis(4-hydroxysalicylidene)ethylenediaminepalladium(II) complex was prepared with a one-pot method, which has been previously reported.[33] 4-Hydroxysalicylaldehyde (1 g, 7.24 mmol) in dichloromethane (30 ml) was added dropwise to a solution of 1,2-diaminoethane (0.217 g, 3.62 mmol) in 20 ml of dichloromethane. The mixture was stirred for 30 min at room temperature. A

yellow precipitate was produced. Pd(OAc)$_2$ (0.812 g, 3.62 mmol) in 30 ml of pure methanol was added to the mixture during stirring, after which the stirring was continued overnight at room temperature. The resulting yellowish green precipitate was allowed to cool; the precipitate was collected, filtered and recrystallised from hot dichloromethane at a yield of 1.44 g, 98% and characterised as follows: m.p., decomp. > 230°C; IR (KBr, cm^{-1}) bands at, 3282, 1611, 1534, 1442, 1338, 1221, 1174, 1132, 987, 846, 790, 659, 465; ^{1}H NMR (500 MHz, d$_6$-DMSO, ppm) δ 3.70 (s, CH$_2$-N, 4H); 6.085-6.106 (d d, J = 2.0 and 2.0 Hz, Ar-CH, 2H); 6.195-6.199 (d, J = 1.75 Hz, Ar-CH, 2H); 7.181-7.198 (d, J = 8.65 Hz, Ar-CH, 2H); 7.923 (s, CH = N, 2H); 9.973 (s, OH, 2H); ^{13}C NMR (500 MHz, d$_6$-DMSO, ppm), δ 60.1, 105.0, 106.4, 115.4, 136.8, 159.6, 164.3, 167.4. All obtained data agreed with published results.[34]

2.2.5 Immobilisation of palladium complex

The catalyst was prepared by immobilising the N,N′-bis(4-hydroxysalicylidene)ethylenediiminepalladium(II) complex on functionalised silica Cl-MCM-41 (see Scheme 1) by adding 1 g (2.47 mmol) of the Pd(II)(4-OH)$_2$salen complex to a suspension of 1 g of functionalised silica Cl-MCM-41 and 0.5 g (4.94 mmol) of Et$_3$N in 30 ml of dry toluene. The resultant mixture was refluxed for 48 h. Then, the product was filtered, washed with dry toluene, dried in air and kept in a desiccator. The resulting catalyst was labelled as MCMSalenPd, with a yield of 1.64 g.
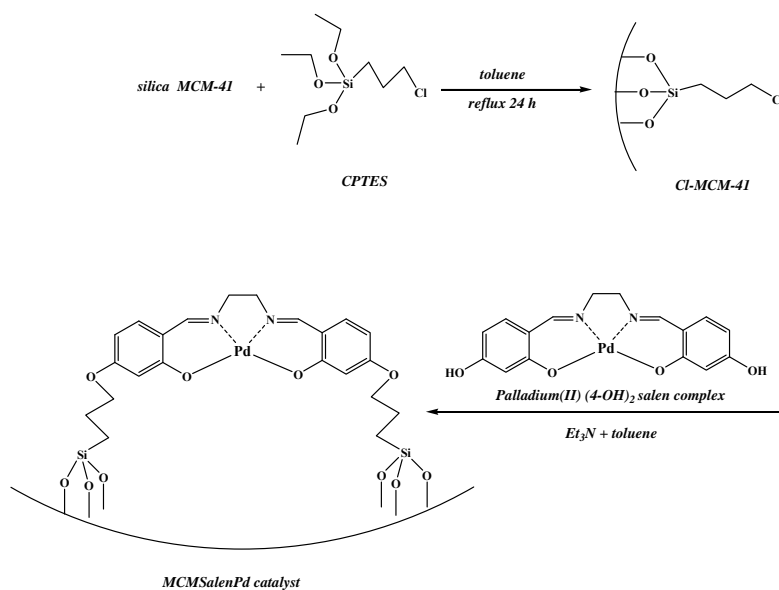
Scheme 1: Synthesis of MCMSalenPd catalyst.

2.3   Catalyst Characterisation

FTIR spectra were recorded on an FTIR (Perkin Elmer System 2000) spectrometer. ^{13}C and ^{29}Si solid state NMR spectra were recorded on an NMR spectrometer (Bruker, 400 MHz). Powder XRD (low angle) diffraction patterns were obtained from an X-ray diffractometer (Siemens Diffractometer D5000, Kristalloflex) using CuKα radiation. Nitrogen gas porosimetry measurements were performed on an ASAP 2020 surface area and porosity analyser (Micromeritics) after the samples were outgassed under vacuum at 100°C for 4 h. TEM images were obtained from a Philips CM12 Instrument. SEM images were obtained on a Leo Supra 50 VP instrument. EDX spectra were recorded on an EDAX Falcon System. AAS was measured on an AA spectrometer (PerkinElmer A Analyst 200).

2.4   Catalyst Experiments – Suzuki-Miyaura Reaction

In a typical experiment, the MCMSalenPd catalyst was tested with a Suzuki-Miyaura reaction using various halobenzene compounds (1 mmol) as substrates, phenylboronic acid (1.1 mmol), *n*-dodecane (20 μl) as an internal standard, K_2CO_3 (2 mmol) as a base, Pd as a catalyst (0.05 g, 0.184 mol%) and dimethylformamide: H_2O (8:1 ml) as a mixed reaction solvent, all in a 25 ml two-neck, round bottom flask. The reaction was performed while subjected to magnetic stirring under air at the appropriate temperatures and durations. Changes in the concentration of halobenzene and the biphenyl product in the reaction system were monitored quantitatively by a gas chromatograph (PerkinElmer Clarus 500) equipped with a capillary elite-5 column (30 m length and 0.32 mm inner diameter) and FID detector. The product was identified using a GCMS (PerkinElmer Clarus 600) equipped with a capillary elite-5 column (30 m length and 0.25 mm inner diameter) and mass detector.

The performance of the MCMSalenPd catalyst was evaluated quantitatively by the percentage conversion of halobenzene; percent conversion was calculated as $(1 - C_t/C_o) \times 100$, where C_o is the initial concentration and C_t refers to the concentration of halobenzene at time t. After completing the reaction, the reaction mixture was cooled to room temperature and extracted with diethyl ether (4 ml × 8 times). The organic layers were collected and concentrated, and the product was passed through column chromatography using silica gel as the solid phase to purify the product. The product was evaluated by melting point, FTIR, ^1H NMR and ^{13}C NMR measurements.

The leaching test was carried out by filtering out the catalyst from the reaction medium after half an hour. The reaction was allowed to carry out to completion under the same reaction conditions.

The recycling test was performed as follows: for the initial reaction, a mixture of 7 mmol of bromobenzene, phenylboronic acid (7.7 mmol), K_2CO_3 (14 mmol), and MCMSalenPd catalyst (0.35 g, 0.184 mol% Pd) was stirred at 130°C for 2 h in a solvent of DMF:H_2O (56:7 ml). After the completion of each reaction, the used catalyst was separated by filtration, washed thoroughly with water, chloroform and diethyl ether, and dried under vacuum at 70°C overnight before reuse. The reactions were repeated several times by weighing the recovered catalyst with the same mole ratio of new substrate and solvent.

3.   RESULTS AND DISCUSSION

3.1   The Preparation of MCM-41

Ordered silica MCM-41 was successfully prepared from naturally occurring silica in RHA; its characterisation is discussed compared to that of Cl-MCM-4 and the MCMSalenPd catalyst.

3.2   Catalyst Characterisation

3.2.1   Fourier transforms infrared spectra (FTIR)

The FTIR spectra of the functionalised silica Cl-MCM-41, the Pd-(4-OH)$_2$salen complex and the MCMSalenPd catalyst are shown in Figure 1. The bands at 1537 and 1609 cm^{-1} of the inorganic Pd-(4-OH)$_2$salen complex are clearly visible with small shifts after immobilisation. The bands at 1637 cm^{-1} in Cl-MCM-41 were shifted to 1625 cm^{-1}, which indicates the successful immobilisation of the Pd-(4-OH)$_2$salen complex on Cl-MCM-41, forming the MCMSalenPd catalyst.
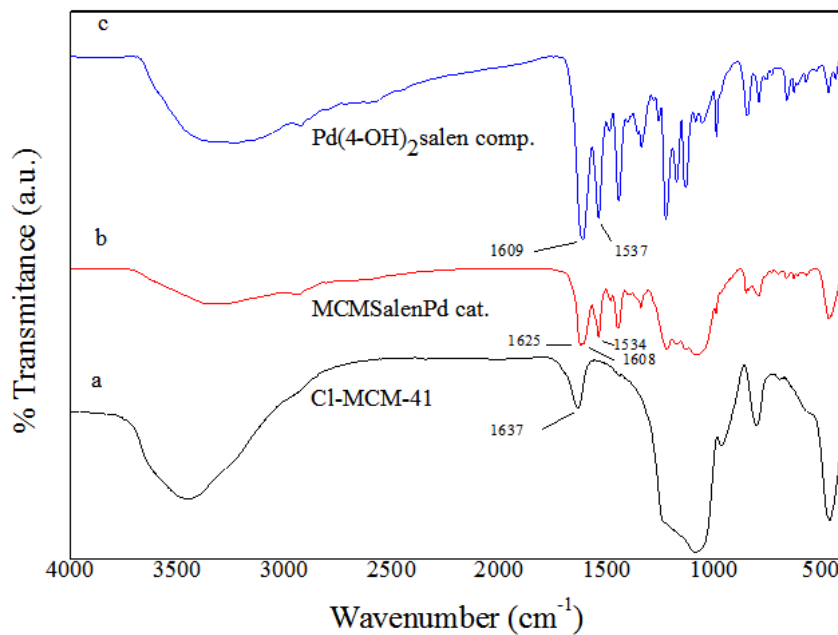
Figure 1:   FTIR spectra of Cl-MCM-41, MCMSalenPd catalyst and Pd(4-OH)$_2$salen complex.

3.2.2   The solid state ^{13}C and ^{29}Si MAS NMR study

The immobilised Pd(II)(4-OH)$_2$salen complex consists of eleven symmetric carbon atoms, which are clearly evident in the ^{13}C MAS NMR (400 MHz) spectrum. These chemical shifts are seen at δ (ppm) 7.5, 9.2, 25.8, 45.4, 56.6, 104.7, 116.3, 137.0, 161.0, 163.1, and 165.3, as shown in Figure 2. These chemical shifts have been assigned according to the suggested structure of MCMSalenPd.
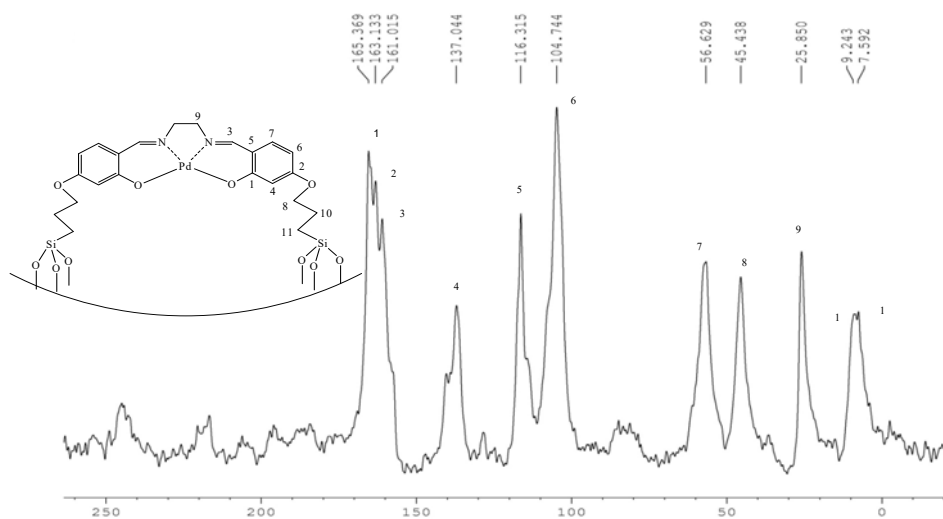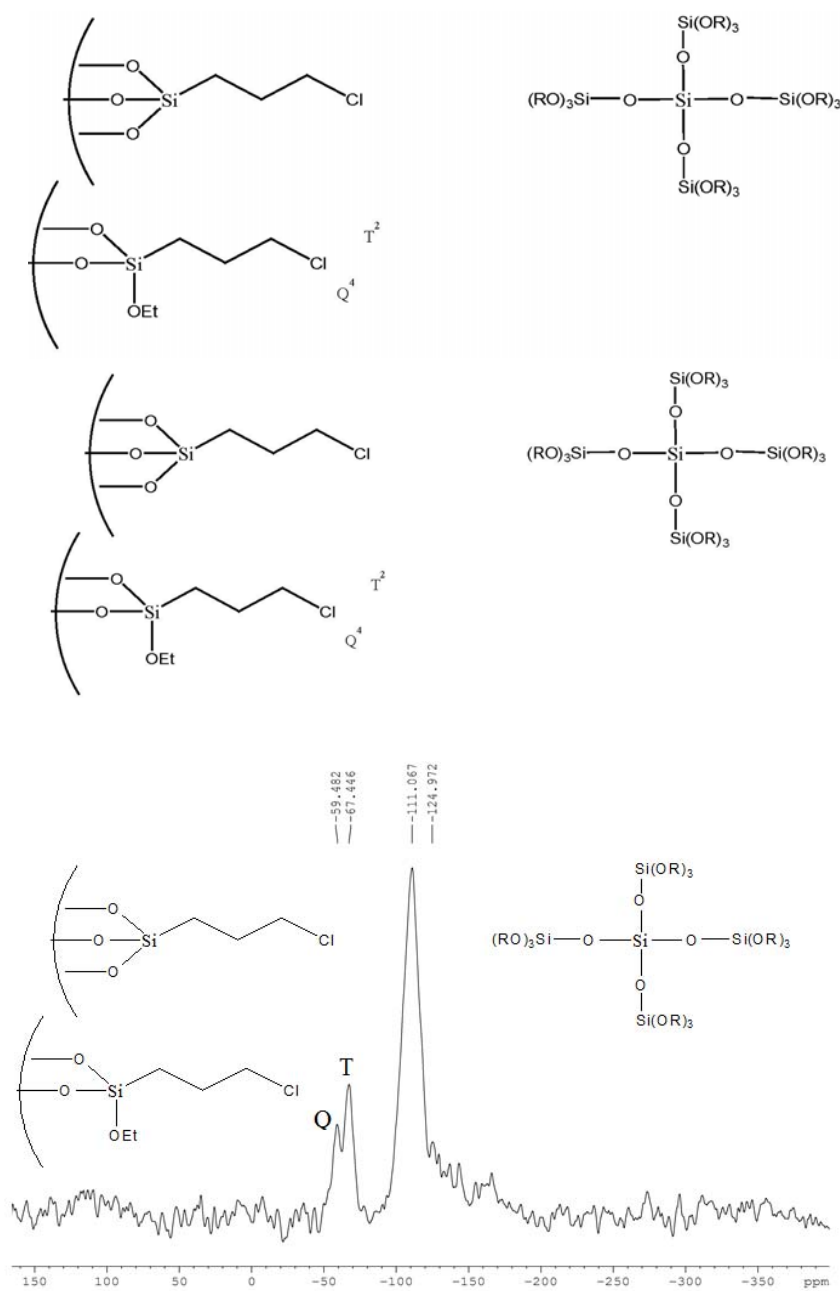
Figure 2: ^{13}C solid NMR spectrum of MCMSalenPd catalyst.

The ^{29}Si MAS NMR spectra of the MCMSalenPd catalyst confirm the presence of organic functional moieties as a part of the silica wall structure (Figure 3). Distinct resonances can be clearly observed for the silicon atoms in the siloxane $[Q^n=Si(OSi)_n(OH)_{4-n}$, n=2–4]; Q^4 at –111 ppm and the silicon atoms of the organo siloxane $[T^m=RSi(OSi)_m(OH)_{3-m}$, m=1–3]; T^3 signals are seen at –67.4 ppm, T^2 at –59.4 ppm units.

Figure 3: ^{29}Si solid NMR spectrum of MCMSalenPd catalyst.

3.2.3   XRD diffraction analysis of MCMSalenPd

The powder XRD pattern of the support material MCM-41(Figure 4) shows the hexagonal mesoporous symmetry with the typical sharp diffraction bands at $2\theta = 2.008°$ of the (100) plane.[35] The presence of three well-resolved peaks corresponding to (110), (200) and (210) planes confirms that the mesoporous MCM-41 materials possess an ordered pore system with high porosity.[36] The d value found for the (100) reflection was 4.396 nm, obtained using the Bragg's equation $[d_{100} = n\lambda/2\sin\theta]$, where n is an integer and λ is the wavelength of incident wave. The lattice parameter, a_o, of 5.076 nm was determined by the equation: $[a_o = 2d_{100}/\sqrt{3}]$. However, after the functionalisation was carried out, the diffractions were distorted, resulting in the loss of the XRD diffraction pattern, so only three of four resolved peaks were obtained. The intense peaks of the (100) plane at $2\theta = 2.166°$ and $2\theta = 2.171°$, the d values of 4.075 nm and 4.066 nm, and the lattice parameters (a_o) of 4.70 nm and 4.69 nm were found for Cl-MCM-41 and MCMSalenPd, respectively.
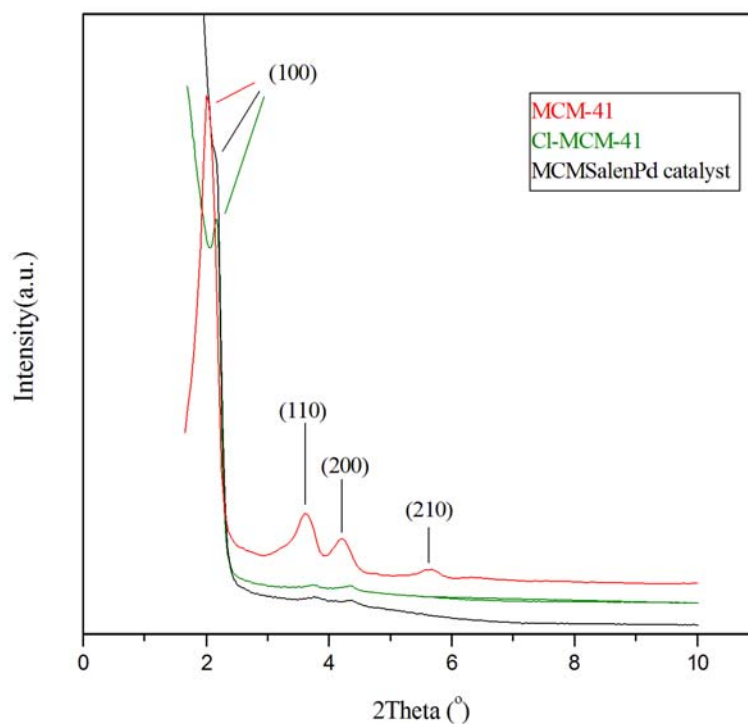

Figure 4: XRD patterns (Low angle) of MCM-41, Cl-MCM-41 and MCMSalenPd catalyst (with MCM-41 being the top among the horizontal lines, Cl-MCM-41 in the middle and MCMSalenPd catalyst bottom).

3.2.4   Nitrogen sorption studies

The surface area and pore properties were evaluated for MCM-41, Cl-MCM-41 and MCMSalenPd catalyst samples from N_2 sorption study at liquid nitrogen temperature (77 K). Figure 5 shows the N_2 adsorption-desorption isotherms of the three materials; all three are of type IV according to IUPAC classification, which is typical for mesoporous materials.[35] The physical data obtained for the surface area, pore properties and pore size distributions are summarised in Table 1.
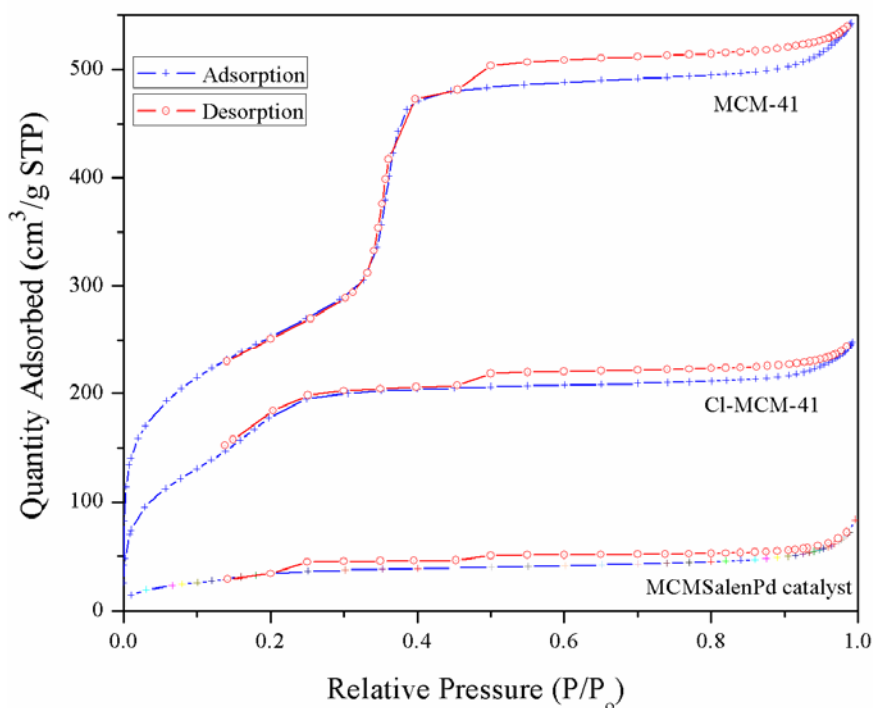

Figure 5: N_2 sorption isotherms of the MCM-41, Cl-MCM-41 and MCMsalenPd catalyst.

Table 1: Physicochemical textural parameters by the BET and TEM for MCM-41, Cl-MCM-41and MCMSalenPd catalyst.

Sample	Surface area ($m^2\,g^{-1}$)	Pore volume ($cm^3\,g^{-1}$)		Pore size (Å)		Pore diameter (nm)	Wall thickness (nm)
	BET	BET	BJH	BET	BJH	TEM	TEM
MCM-41	848	0.82	0.84	39.1	32.1	2.28	1.66
Cl-MCM-41	589	0.40	0.33	27.3	24.2	2.02	2.23
MCMSalenPd	537	0.36	0.32	25.4	22.6	1.7	2.41

Note: BET: Brunauer, Emmett, Teller; BJH: Barrett, Joyner, Halenda; TEM: Transmission electron micrograph

The pore size distributions were determined by the BJH method using the adsorption branch of the isotherms (Figure 6).
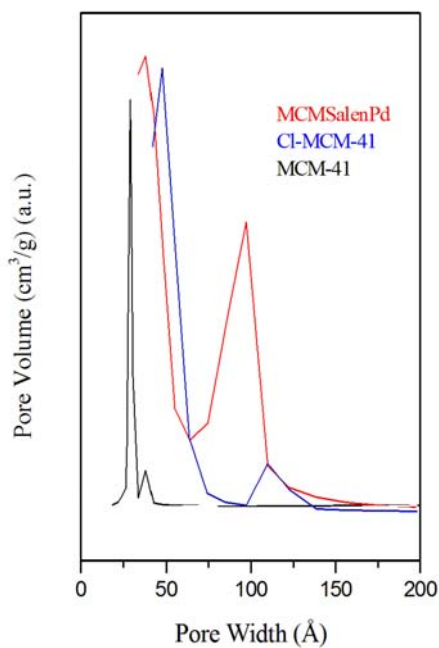

Figure 6: BJH adsorption pore size distributions for the MCM-41, Cl-MCM-41 and MCMSalenPd catalyst (with MCM-41 occupying the left part of figure, MCMSalenPd catalyst showing a significant spike, and the other being Cl-MCM-41).

3.2.5   Transmission electron micrograph

Figure 7 shows the transmission electron micrographs of the selected regions of (a) MCM-41, (b) Cl-MCM-41 and (c) MCMSalenPd materials. The hexagonal arrangement of the pores can be clearly noted in the three materials but with less regularity for Cl-MCM-41; this is due to functionalisation with CPTES. For the MCMSalenPd catalyst, there is further immobilisation with the Pd complex.[18] The TEM images were analysed using the analysis image processing software Soft Imaging Solutions (version 5.1, Olympus, 1989-2008) were used to obtain the unit cell parameters, which were similar to the parameters obtained using powder XRD for the MCM-41 material.
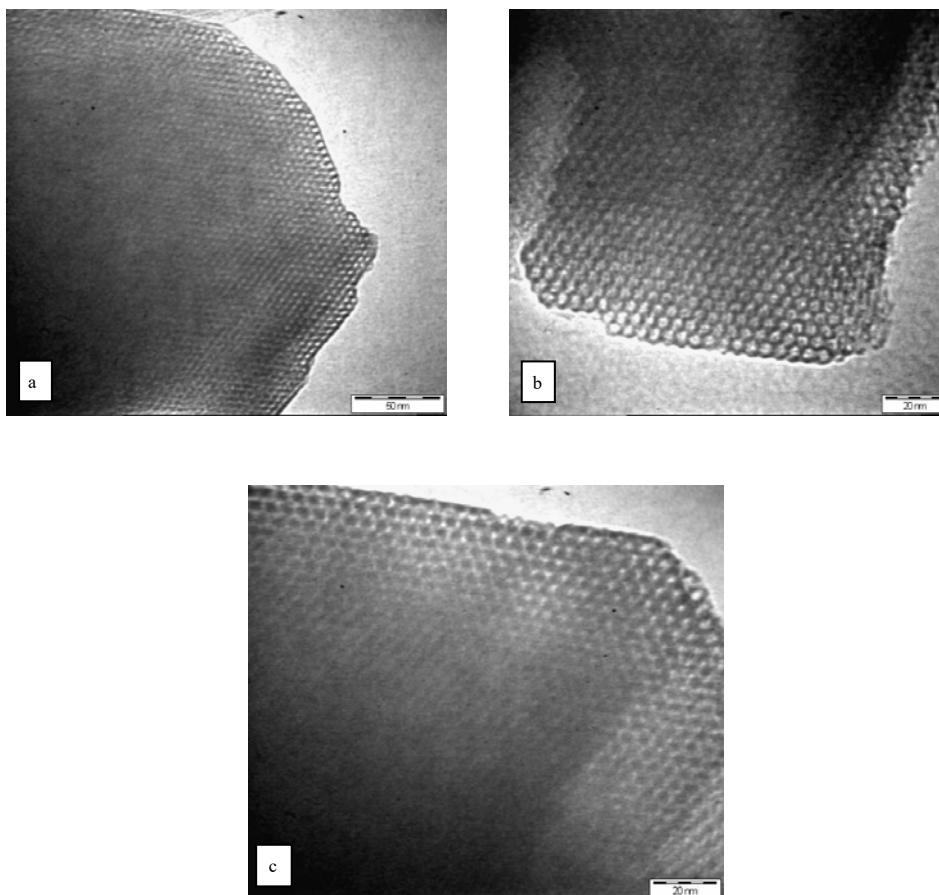

Figure 7: TEM micrographs of (a) MCM-41, (b) Cl-MCM-41 and (c) MCMSalenPd.

3.2.6 Scanning electron micrographs

The morphologies and microstructures of the MCM-41, Cl-MCM-41, and MCMSalenPd catalyst were further investigated by scanning electron microscopy. The images are shown in Figure 8. The MCM-41 (Figure8[a]) and Cl-MCM-41 (Figure8[b]) images exhibit regular, cylindrically-shaped particles with smooth surface morphology; however, the image for the MCMSalenPd (Figure8(c)) depicts some aggregates with less regularity.
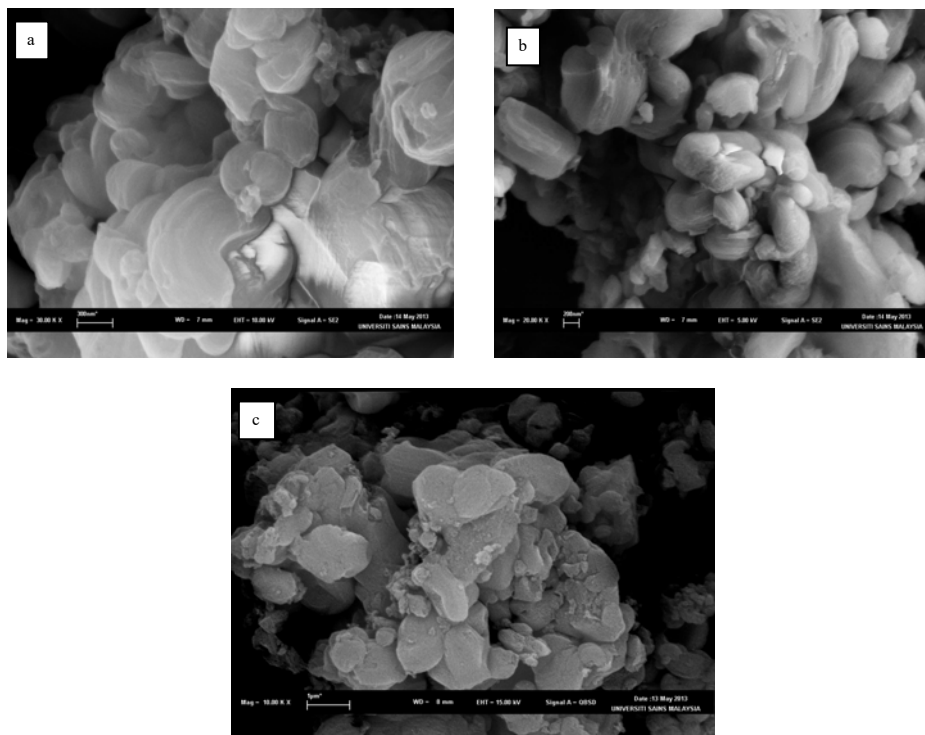
Figure 8: SEM images of (a) MCM-41, (b) Cl-MCM-41 and (c) MCMSalenPd.

3.2.7   Energy-dispersive X-ray and atomic absorption spectroscopy

The energy dispersive X-ray elemental analysis results for the MCMSalenPd catalyst (Figure 9) indicate the presence of silicon, carbon, chlorine and palladium. The palladium metal content is approximately (17.6%), agreeing somewhat with the result obtained by atomic absorption spectroscopy (19.6%). The slight discrepancy may be due to the differences in the accuracy of the different methods.
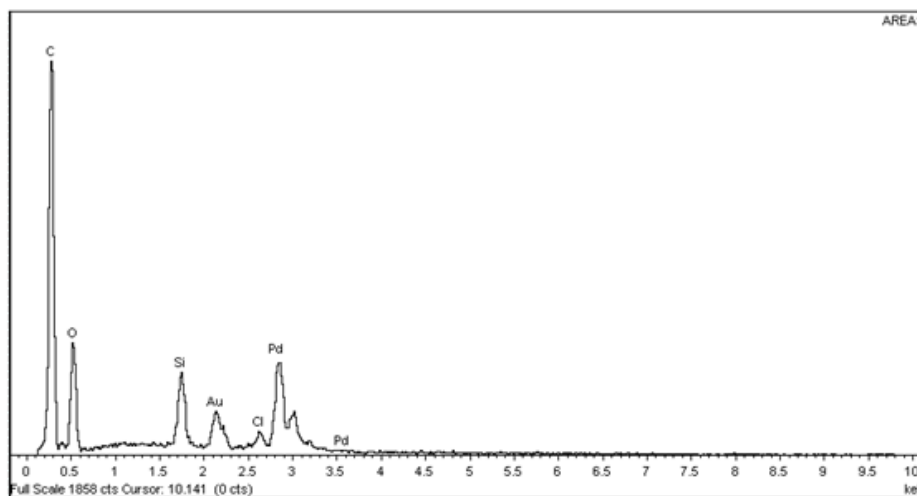
Figure 9: EDX spectrum of MCMSalenPd catalyst.

3.3 Catalytic C–C coupling reaction with MCMSalenPd

To scrutinise the catalytic competence of MCMSalenPd in the Suzuki-Miyaura reaction, a reaction between bromobenzene and phenylboronic acid was chosen as a model reaction, using DMF:H_2O (8:1 ml) as the solvent and K_2CO_3 as the base with 0.05 g catalyst (0.184 mol% pd) under atmospheric pressure at 130°C. The results of the reaction, which were altered by varying certain parameters, are tabulated in Table 2. The conversion percentage of the Suzuki-Miyaura C–C coupling when using MCMSalenPd is more than 98%, with 100% selectivity to the biphenyl product after 2 h. Notably, when the same reaction was performed at 70°C, only 40% conversion was achieved after 9 h of reaction time (Table 2, entry 1). The results of the conversion percentage with different temperatures and other parameters of the reaction conditions are summarised in Table 2.

Table 2: The effect of catalyst's mass, temperature and time for the Suzuki-Miyaura reaction[a].
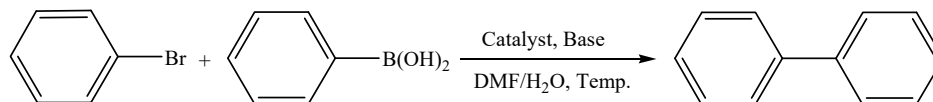
Entry	Catalyst loaded (g)	Temp. (°C)	Time (h)	Conversion (%)
1	0.05	70	9	40.3
2	0.05	80	6	54.9
3	0.05	90	6	76.9
4	0.05	100	6	88.9
5	0.05	110	6	86.1
6	0.05	120	6	98.4
7	0.05	130	2	98.7 max.
8	0.0125	130	2	96.3
9	0.025	130	2	96.8
10	0.075	130	2	95.0
11[b]	0.05	130	2	98.9 (no change)
12[c]	0.05	130	2	99.4 (no change)
13[d]	0.05	130	1	99.8
14[e]	0.05	130	3	38.4
15[f]	0.037	130	3	87.0

Notes:
[a] *Reaction condition: bromobenzene (1 mmol), phenylboronic acid (1 mmol), base (2 mmol), catalyst (0.05g, 0.184 mol% pd), DMF:H2O (8:1 ml) at various temperatures.*

[b,c] *Bromobenzene: Phenylboronic acid (1:1.5 mmol), (1:2 mmol) respectively.*

[d,e] *Iodobenzene (1 mmol), Chlorobenzene (1 mmol) respectively.*

[f] *Using same Pd mmol of Palladium(II)(4-OH)₂salen complex as a homogenous catalyst at same reaction conditions.*

3.4   Effect of Catalyst Mass

The results of the reaction with varying mass of catalyst are tabulated in Table 2 (entries 7–10). When the weight of catalyst was increased, the conversion also increased. The maximum conversion of 98% was obtained using 0.05 g of MCMSalenPd with 100% selectivity of the biphenyl product after 2 h at 130°C. However, the conversion percentage decreased to approximately 95% when 0.075 g of catalyst was used. This small decrease could be due to the agglomeration of the catalyst particles, which results in a decrease in the active surface area.

3.5   Effect of Reactant Mole Ratio

The effect of the mole ratio of bromobenzene to phenylboronic acid, either 1:1, 1:1.5 or 1:2 mmol, was studied at 130°C with 0.05 g of catalyst used, and the results are tabulated in Table 2 (entries 7, 11 and 12, respectively). There was no significant change in conversion with different mole ratios; hence, a mole ratio of 1:1 for the reactants was sufficient to obtain a conversion of more than 98%.

Moreover, diverse hallobenzene compounds (bromobenzene, iodobenzene and chlorobenzene) were studied with phenylboronic acid under the same optimised conditions, and the results are presented in Table 2 (entries 7, 13 and 14, respectively). Both bromobenzene and iodobenzene are effective substrates and give high conversion percentages of 98.7% and 99.8%, respectively. Unfortunately, the MCMSalenPd catalyst failed to give a high conversion with chlorobenzene as the substrate, giving only 38.4%, as shown in Table 2 (entry 14). In general, it should be noted that there are many instances in the literature where silica-based heterogeneous palladium complexes that showed excellent catalytic activity with bromoaryl and iodoaryl compounds failed with chloroaryl substrates.[37–39]

In addition, the homogeneous catalytic Suzuki-Miyaura C–C cross coupling reaction was carried out using the same Pd mmol of palladium(II)(4-OH)$_2$ salen complex as the catalyst at the same optimised conditions. This resulted in a conversion of 87% (Table 2, entry 15). The conversion is high but less than that of the heterogeneous catalytic reaction under the same conditions.

3.6   Effects of solvents and bases for the Suzuki-Miyaura reaction

Usually, the Suzuki-Miyaura C–C coupling reaction is performed in a polar organic solvent. The solvent effect on catalyst activity was studied using different polar solvents and different bases for further optimisation. The results are summarised in Table 3.

Initially, the reaction was performed in DMF with K$_2$CO$_3$ as base. A low conversion was obtained (ca. 19.39%, entry 2). This may be because of the low solubility of the base in organic solvents. However, no reaction was detected using H$_2$O as a solvent. When a mixed solvent was used, a maximum conversion was obtained at a solvent ratio of 8:1 $^v/_v$ of DMF:H$_2$O (entry 3). Notably, the conversion decreased when water volume increased (entries 4, 5). A high conversion percentage could still be obtained using a small volume of water with another solvent like toluene or DMSO. The conversion decreased for solvent only reactions (entries 6–8). It can be seen that using K$_2$CO$_3$ as the base resulted in the

maximum conversion (entry 3). Other bases, i.e., Na_2CO_3, Et_3N, NaOAc and $NaHCO_3$, gave significantly lower conversions (entries 10–13, respectively).

Table 3: Effects of different solvents and bases for the Suzuki-Miyaura cross-coupling reaction using MCMSalenPd as the catalyst[a].

Entry	Solvent	Base	Conversion (%)
1	H_2O	K_2CO_3	N.R
2	DMF	K_2CO_3	19.39%
3	DMF:H_2O (8:1)	K_2CO_3	98.7%
4	DMF:H_2O (8:2)	K_2CO_3	87.1%
5	DMF:H_2O (8:3)	K_2CO_3	46.85%
6	Toluene	K_2CO_3	44.7%
7	Toluene:H_2O (8:1)	K_2CO_3	82.0%
8	DMSO	K_2CO_3	51.77%
9	DMSO:H_2O (8:1)	K_2CO_3	85.53%
10	DMF:H_2O (8:1)	Na_2CO_3	93.83%
11	DMF:H_2O (8:1)	Et_3N	73.30%
12	DMF:H_2O (8:1)	NaOAc	86.49%
13	DMF:H_2O (8:1)	$NaHCO_3$	90.40%

Notes: [a] Reaction conditions: bromobenzene (1 mmol), phenylboronic acid (1 mmol), base (2 mmol), catalyst (0.05 g, 0.184 mol% pd), (9 ml) solvent, 2 h at 130 ^{o}C.

3.7 Leaching and reusability of MCMSalenPd

The catalyst showed signs of leaching once the catalyst was removed from the reaction mixture. The catalyst was removed after 30 min and the reaction was allowed to proceed. Figure 10 shows that when the catalyst was removed, the conversion was ca. 53%, and the reaction proceeds further up to ca. 75%. Hence, an increase of approximately 23% was observed without the presence of the catalyst. This could be a result of leached metal complexes acting as homogeneous catalysts. However, this increase could also be considered minimal given the high efficiency of the heterogeneous catalyst.
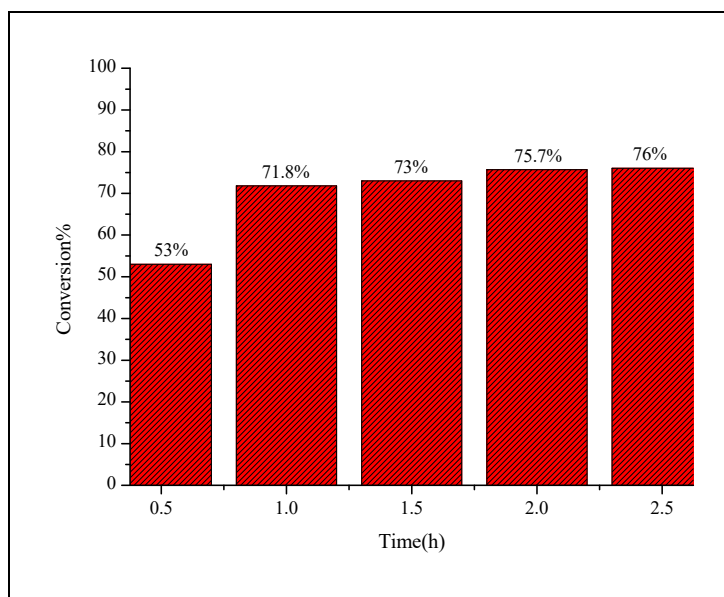
Figure 10:   Leaching test of MCMSalenPd catalyst. The catalyst was removed after 0.5 h. Subsequent bar charts show the conversion without the catalyst in the reaction.

The catalyst reusability tests showed a decrease of about 24% conversion over five consecutive runs (Figure 11). If this value is compared with the leaching test above, it can be seen that the leaching effect is significantly reduced in every subsequent reuse of the catalyst. This shows that the leached metal ion could be those that were not from the complex, but individual metal ions that were physically adsorbed on the catalyst surface.

4.   CONCLUSION

The complex, palladium(II)(4-OH)$_2$salen, was successfully immobilised onto ordered silica MCM-41 via two hydroxyl groups, creating a macro cyclic catalyst. The chlorine groups of the linking agent were substituted with two terminal hydroxyl groups in the palladium(II)(4-OH)$_2$salen complex. The catalyst has been completely characterised using normal spectroscopic techniques. The prepared catalyst gave excellent catalytic activity towards the Suzuki-Miyaura reaction of bromobenzene and phenylboronic acid. The highest conversion of more than 98% was achieved when 0.05 g of catalyst and 1:1 mole ratio of reactants in 8:1 ml of DMF:H$_2$O mixed solvent were used at 130°C for 2 h.

Although the catalyst showed some leaching during the first use, this was minimal in subsequent reuse. The catalyst was reused several times with significant high catalytic activity.
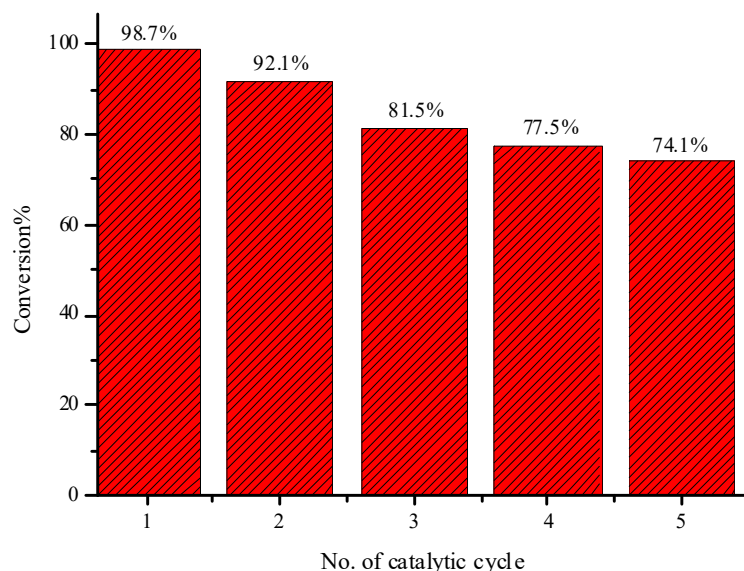

Figure 11: Reusability of MCMSalenPd catalyst.

5.   ACKNOWLEDGEMENT

6.   REFERENCES

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