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Synthesis of *Vic*-Dioxime Palladium (II) Complex: Precursor for Deposition on SBA-15 in $ScCO_2$

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***Abstract*—**Synthesizing supercritical carbon dioxide ($scCO_2$) soluble precursors would be helpful for many processes of material syntheses based on $scCO_2$. Ligand (*amphi*-(1*Z*, 2*Z*)-*N*-(2-fluoro-3-(trifluoromethyl) phenyl)-*N*'-hydroxy-2-(hydroxyimino) were synthesized from chloro glyoxime and flourus aniline and Pd(II) complex (precursor) prepared. For $scCO_2$ deposition method, organometallic precursor was dissolved in $scCO_2$ and impregnated onto the SBA-15 at 90 °C and 3000 psi. Then the organometallic precursor was reduced with H_2 in the CO_2 mixture (150 psi H_2 + 2850 psi CO_2). Pd deposited support material was characterized by ICP-OES, XRD, FE-SEM, TEM and EDX analyses. The Pd loading of the prepared catalyst, measured by ICP-OES showed a value of about 1.64% mol/g Pd of catalyst. Average particle size was found 5.3 nm. The catalytic activity of prepared catalyst was investigated over Suzuki-Miyaura C-C coupling reaction in different solvent with K_2CO_3 at 50 °C. The conversion ratio was determined by gas chromatography.

***Keywords*—**Nanoparticle, nanotube, oximes, precursor, supercritical CO_2

I. INTRODUCTION

SUPERCRITICAL fluid deposition (SCFD) is an attractive technique to prepare metallic nanoparticle on solid support such as graphene, nanotube, alumina, silica. This process involves the dissolution of a metallic precursor (MP) in a supercritical fluid and the exposure of the carbon support to the solution. After adsorption of the precursor onto the support, the MP is converted to its metal form by chemical or thermal reduction. Currently, there are only a few known precursors for SCFD [1]-[3].

The most commonly used supercritical fluid (SCF) is carbon dioxide (CO_2) because it is non-toxic, non-reactive, nonflammable and inexpensive like most SCFs; $scCO_2$ combines both the good solvent properties of a gas and a liquid. The gas-like diffusivity and viscosity of $scCO_2$ are favorable for rapid diffusion and permeation into porous substrates whereas the liquid-like density allows for the dissolution of a wide range of organometallic precursors. The low surface tension of $scCO_2$ not only permits better penetration and wetting of pores than is usually possible with liquid solvents, but also avoids the pore collapse which can occur on certain structures such as organic and silica aerogels with organic liquid solvents. Furthermore, residual CO_2 is negligible in the processed product because of the gaseous character of CO_2 near ambient conditions [1], [2].

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The use of SCFs in the deposition of metal nanoparticles on porous substrates is being increasingly researched. SCF's low viscosity and high mass transfer characteristics allow for them to transport the metal nanoparticles in a highly dispersive manner [2]. It has been shown in recent research that the solubility of the metal precursor is extremely important in the success of the deposition of the metal nanoparticles. The actual deposition of the metal takes place through a three-step mechanism (Fig. 1): First, the precursor (for example oxime complex) is dissolved in the supercritical medium and then, the precursor is adsorbed onto the substrate (the precise mechanism of how this takes place is still widely unknown), and lastly, the metal precursor is reduced to its metallic form [4].

There are various ways to reduce the metal. One of which is the use of chemicals, usually hydrogen and alcohols. SCF are advantageous due to their unique properties [1], Changing the pressure and temperature easily alters the density and viscosity. SCFs have high diffusivities and low viscosities, which result in enhanced mass-transfer characteristics. The low surface tension permits better penetration of a substrate. The use of SCF to deposit metal nanoparticle on the surface of porous solid supports has shown to be promising [5], [10].

Since the precursor plays a main role in this, there is a need for research on novel precursors aimed at creating a simple method of depositing various metal nanoparticles to carbon nanotubes. There are currently two commonly used precursors (acetyl acetone and cyclooctadiene) in the deposition of metal nanoparticles to substrates.

In this work, we synthesized new precursors for SCFD, namely precursors with *vic*-dioxime ligands. Deposition results in $scCO_2$ shows that new precursors better alternatives for known precursors and that allow for an adequately small size and uniform distribution of metal nanoparticles of Pd.

II. EXPERIMENTAL PROCEDURE

A. General Methods

Solvents were purified by standard methods which were dried with molecular sieves (4 Å), $CaCl_2$, etc. and were distilled under nitrogen or argon. All chemicals were of reagent grade quality and were used without further purification. The ^1H NMR spectra were obtained on a Bruker-Advance DPX 400 spectrometer in $CDCL_3$. ^1H NMR spectra were referenced internally or externally to tetramethylsilane. IR spectra were recorded on a PerkinElmer Mattson 1000 FT-IR spectrometer by using KBr pellets in the range of 4000–400 cm^{-1}. Elemental analysis was recorded on a LECO CHNS-932 analyzer. Melting point was determined on a

Gallenkamp apparatus in a sealed capillary and was uncorrected. CO_2 and H_2, 99.9%, were supplied by LINDE Company (Adana, Turkey). The solubility and catalytic studies were performed with stainless steel batch reactors (PARR, 50 mL, windowed, TEM: Jeol JEM 1400 Plus 120kV, FE-SEM with EDX: ZEISS Supra 55 VP.

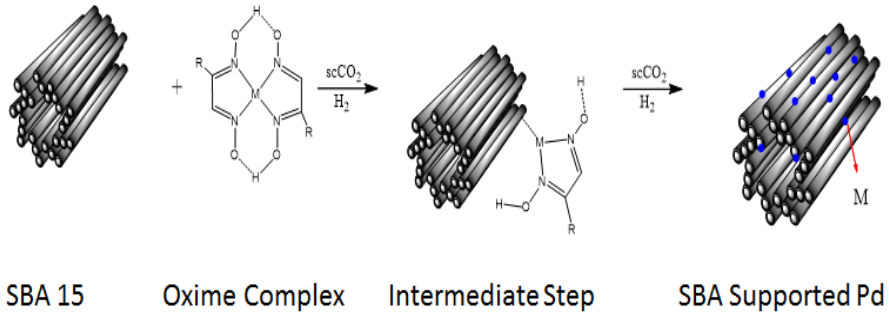


Fig. 1 Schematic notation deposition process in $scCO_2$ [4]

B. The Synthesis of bis-[(2-Fluoro-3-(Trifluoroaniline-anti-vic-Dioxim)

To a solution of *anti*-monochloroglyoxime (1.00 mmol) in 15 ml of absolute ethanol was added to a solution of 2-fluoro-3-(trifluoromethyl) aniline (1.00 mmol) in 15 ml absolute ethanol. Then the mixture was stirred 4 hours at -10 ºC. It was arranged pH=6 with 0.1 M NaOH. Ethanol was removed from the mixture and then the product dried in vacuum desiccator to furnish the pure *vic* dioxime ligand. Product recrystallized from CH_2Cl_2 and yellow product filtered (Fig. 2). Yield: 46.90%. Melting point: 189.00 ºC. Elemental analysis for $C_9H_7F_4N_3O_2$, calc.: C, 40.77; H, 2.66; N, 15.85. Found: C, 37.69; H, 2.94; N, 11.45%. FT-IR (KBr, cm^{-1}): ν(N-H) 3426.2 cm^{-1}; ν(O-H) 3339.7 cm^{-1}; ν(C-$H_{aliphatic}$) 2850.22 cm^{-1}, ν(C=N) 1644.74 cm^{-1}; ν(C=C) 1589.31 cm^{-1}; ν(C-F) 1228.27-1198.89 cm^{-1}.

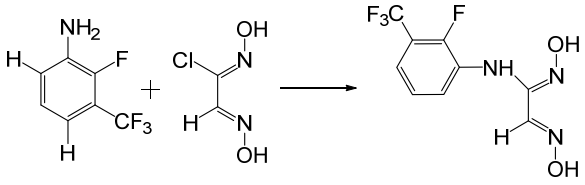


Fig. 2 Synthesis of ligand

C. The Synthesis of bis-[(2-Fluoro-3-(Trifluoroaniline-anti-vic-dioximato)]Palladium(II)

A solution of 0.5 mmol (0.1 g) $Pd(CH_3COO)_2$ in ethanol was added dropwise to a solution of 1 mmol (0.6 gr) synthesized *vic* dioxime ligand in 15 mL dissolved in ethanol and reflux 4 hours with continuous stirring. After that, the reaction mixture was cooled to the room temperature and filtered off to obtain yellow complex (Fig. 3). Yield: 89%, m.p.= 277.5 ºC, Elemental Analysis for ($C_{18}H_{12}F_8N_6O_4Pd$); calc.: C, 34.06; H, 1.91; N, 13.24. Found: C, 35.36; H, 2.50; N, 10.38%. FT-IR (KBr, cm^{-1}): ν(C=N) 1631.72 cm^{-1}; ν(N-H) 3428.85 cm^{-1}; ν(C=C, aromatic) 1574.23 cm^{-1}, ν (O-H) 3237.93 cm^{-1}; ν(C-F) 1209.86 cm^{-1} and 1171.01 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d6): δ= 5.60 (s, 2H, NH), 6.19-7.38 (m, 8H, Ar-H), 8.20 (s, 2H, HC=N), 12-13 (s, 2H, OH) ppm. ^{13}CNMR (400 MHz, DMSO-d6): 114-129.62 (C=C), 136 (C-F), 151-155 (C=N).

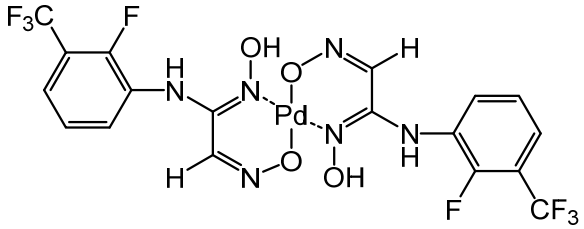


Fig. 3 Palladium (II) complexes of synthesized ligand

D. Preparation of Catalyst

For preparation of solid supported catalyst, we used $scCO_2$ as a reaction media and SBA-15 as a support material. In terms of supercritical deposition mechanism, precursor was adsorbed on SBA-15 and then reduced to its elemental form by using H_2 (g). and SBA-15 were placed in a reactor with including 10% palladium as precursor/SBA-15 ratio (W/W). Then the cell was sealed and heated up to 353 K and pressurized with CO_2 by using a syringe pump (ISCO, 260D) until reached 15.0 MPa. Following this step, H_2 (1.0 MPa) and CO_2 (20.7 MPa) which were mixed in mixing apparatus were sent to the cell and the cell was stirred four hours at desired pressure and temperature (Fig. 4). At the end of four hours, reactor stopped and was cooled to the room temperature. Then, the system was depressurized slowly by using vent valve. ICP, XRD, FE-SEM and EDX analyses were used to confirm the presence of metal nanoparticles, size of metal nanoparticles and their distribution on SBA-15.

E. Catalytic Efficiency of SBA-15 Supported Palladium Nanoparticles on Suzuki-Miyaura Reaction

Catalytic activity of catalyst was tested on Suzuki-Miyaura cross coupling reaction. For typical experiments, an oven-dried, sealed tube equipped with magnetic stir bar was charged 1 mmol bromobenzen, 1.2 mmol phenylboronic acid, 1.2 mmol base. Then the catalyst solution (0.005 mmol in 3.0 ml solvent) and 3 ml H_2O were added to the mixture. The sealed tube was placed in silicon oil bath at 50 ºC. The reaction

mixture was stirred and then allowed to cool to the room temperature [10]. After that, the reaction mixture was extracted with CH_2Cl_2. The extract was washed with water and dried over anhydrous Na_2SO_4. After the purification, the qualitative and quantitative analysis of the reactants and products were performed by Gas Chromatography. Results given in Table I and yields were based on corresponding aryl bromide.

III. Results and Discussion

XRD analysis: XRD analysis was carried out by Rigaku Miniflex CuKα, λ=0.154 nm. XRD measurements have been performed with 2θ angle and scanning with a range of 10-80. XRD patterns were interpreted by using JCPDS (Joint Committee on Powder Diffraction Standards) database (Pd card no: 01-089-4897) and given in Fig. 5. SBA-15 supported palladium nanoparticle peaks observed at 40.08^0, 46.36^0 and 68.12^0 corresponded to the Pd(111), Pd(200) and Pd (220) respectively. These values are in agreement with literature and JCPDS database [7]-[9]. The average palladium nanoparticle size was determined as 5.3 nm.

FE-SEM analysis: FE-SEM images were obtained by ZEISS SUPRA 55VP and EDX analysis of SBA-15 supported palladium nanoparticles shows that palladium was distributed homogeneously onto the SBA-15. EDX-mapping images for palladium nanoparticles are given in Fig. 6.

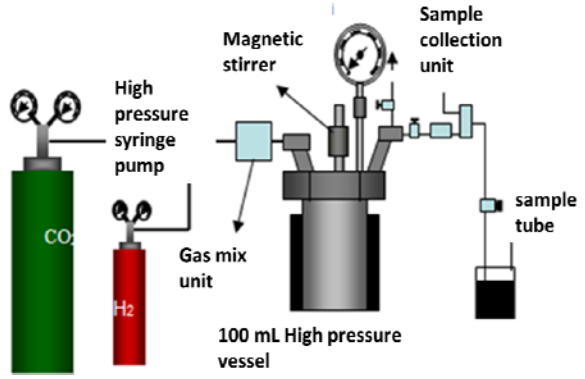


Fig. 4 SCF deposition apparatus

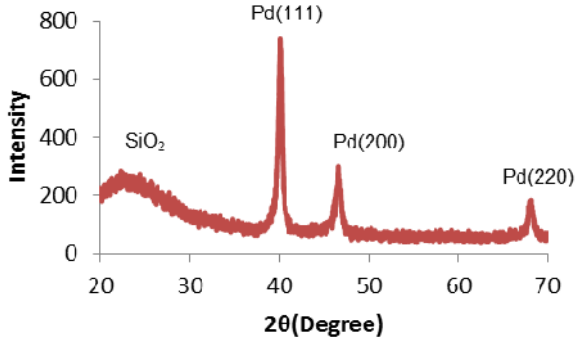


Fig. 5 XRD pattern of catalyst

Mapping application of the palladium catalyst showed the elemental distribution of presence of palladium nanoparticles and silica (Fig. 7 (a)). In mapping spectrum, Pd, Si and O were observed (Fig. 7 (b)). Pd% amount on SBA 15 has been determined via EDX point application and percentage of palladium was calculated as 3.25%. The percentage of palladium nanoparticles calculated via ICP-OES may differ from EDX result because of EDX-point data show local measurements and give metal content of volume-based area whereas ICP-OES showed all sample average Pd on to the silica [1], [10].

TEM micrographs of the Pd/SBA-15 are shown in Fig. 8. TEM images show the distribution of nanoparticles on SBA-15: (i) As spherical spots on the outer surface of SBA-15, (ii) As dark lines following the porous structure. The palladium particle size obtained ranged from 5-15 nm. Different average particle sizes obtained from TEM and XRD micrographs can be explained as XRD measurements give number-weighted value whereas TEM micrographs give a volume-weighted value.

Catalytic Activity: Pd/SiO_2 composite materials were used as catalyst on Suzuki-Miyaura C-C cross coupling reactions under mild conditions. The yield of obtained biaryl compounds was analyzed by GC. The effect of base and solvent on the yield of coupling product has been also investigated. K_2CO_3 and ethanol was found as most effective solvent/base system for this reaction (Table I) [11]. Due to the promising results, wide range aryl bromides will be examined as substrate.

TABLE I
CATALYTIC EFFICIENCY OF CATALYST ON SUZUKI-MIYAURA REACTION

Entry	Base	Solvent	Yield (%)
1	K_2CO_3	DMF	56
2	K_2CO_3	1,4 DIOXANE	63
3	**K_2CO_3**	**ETHANOL**	**90**
4	K_2CO_3	NMP	45
5	K_2CO_3	TOLUENE	20
6	K_2CO_3	THF	38

IV. Conclusion

In this study, *vic*-dioxime derivative ligand and its palladium complexes were synthesized and their structures were enlightened by FT-IR, elemental analyses and NMR spectroscopy. Usability of palladium-*vic*-dioxime complex as precursor in $scCO_2$ deposition method was investigated. The prepared palladium nanoparticles were characterized by XRD, ICP-OES and FE-SEM. The % palladium loading on SBA-15 was determined by ICP-OES (1.64%). According to XRD data, average particle size was found as 5.3 nm. These results show that the *vic*-dioxime palladium complex is effective precursor for $scCO_2$ deposition method. The catalytic performance of prepared nanoparticles was tested over Suzuki couplig reactions. % conversions were determined by GC and conversion close up to 90% has been observed in 5 hours with ethanol and K_2CO_3.

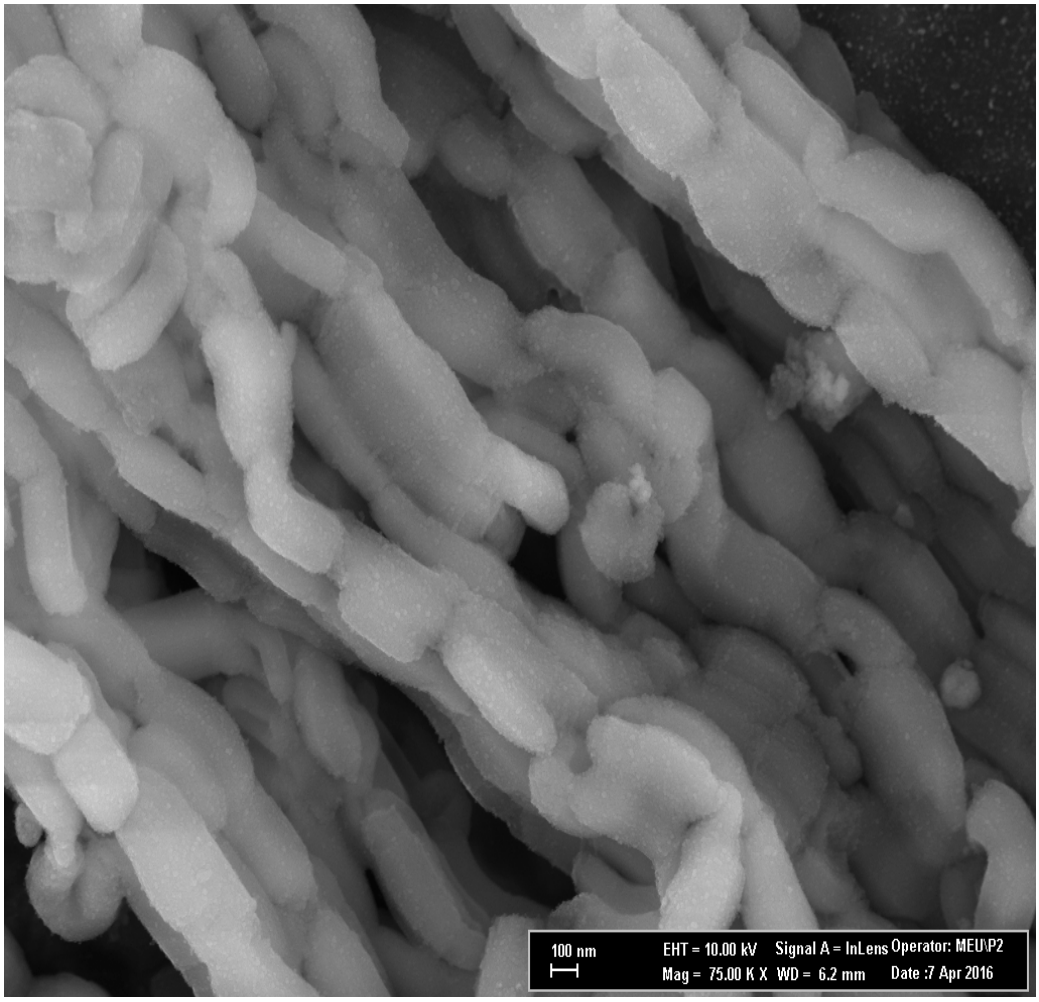
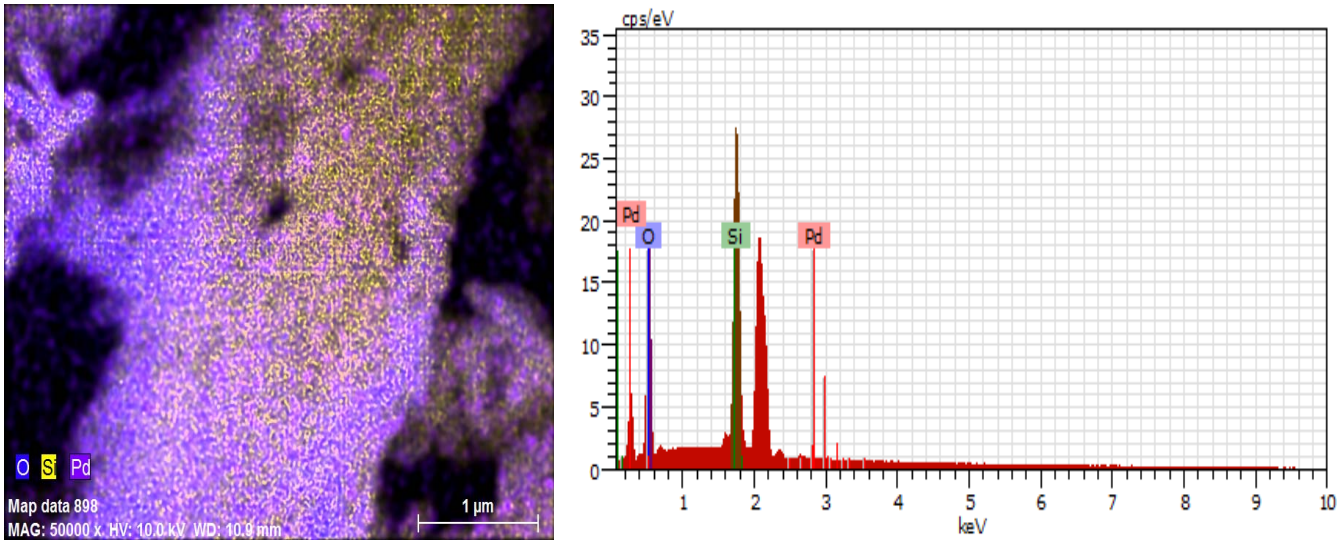


Fig. 6 FE-SEM image of catalyst: SBA-15



(a) (b)

Fig. 7 FE-SEM-EDX images of catalyst: Palladium

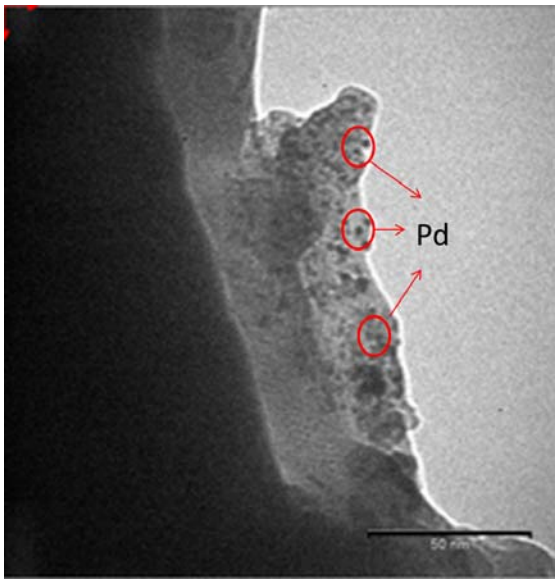


Fig. 8 TEM micrographs catalyst

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REFERENCES

[1] Y. Zhang, C. Erkey, "Preparation of supported metallic nanoparticles using supercritical fluids: a review," *J. Supercrit. Fluids*, vol. 38, pp. 252, 2006.
[2] C. Erkey, "Preparation of metallic supported nanoparticles and films using supercritical fluid deposition," *J. Supercrit. Fluids*, vol. 47, pp. 517, 2009.
[3] X.R. Ye, Y. Lin, C.M. Wai, "Decorating catalytic palladium nanoparticles on carbon nanotubes in supercritical cabon dioxide," *Chem. Commun.,* vol. 5, pp. 642, 2003.
[4] S.E. Bozbag, C. Erkey, "Supercritical deposition: Current status and perspectives for the preparation of supported metal nanostructures" *J. Supercrit. Fluids,* vol. 96, pp. 298, 2015.
[5] Lin, Chi-Kai, "Novel synthesis and characterization of precious-metal nanocatalysts for clean energy applications," *N. IL. Uni.*, pp. 128, 2011.
[6] S.K. Morley, P.C. Marr, P.B. Webb, A.R. Berry, F.J. Allison, G. Moldovan, P.D. Brown, S.M. Howdle, "Clean preparation of nanoparticulate metals in porous supports: a supercritical route," *J. Mater. Chem.,* vol. 12, pp. 1898, 2002.
[7] A. Bayrakceken, U. Kitkamthorn, M. Aindow and C. Erkey, "Decoration of multi-wall carbon nanotubes with platinum nanoparticles using supercritical deposition with thermodynamic control of metal loading" *Scripta Materialia,* 56, 101–103, 2007
[8] J. Baoa, H. Tianb, R. Tang, "Synthesis and characterization a novel europium(III)-β-diketonate complex with carbazole and triphenylamine moieties" *Inorganica Chimica Acta*, vol.401, pp.19–23, 2013.
[9] A.L. Dantas, P.D. Alves, D. Arando, M. Schmal, "Characterization of carbon supported Pd catalysts: Influence of electronic and particle size effects using reaction probes" *Appl. Catal.*, vol 277, pp. 71-81, 2004.
[10] Hunt A. J., Budarin V. L., Comerford J. W., Parker H. L., Lazarov V. K., Breeden S.W., Macquarrie D. J., Clark J. H.. "Deposition of Palladium Nanoparticles in SBA-15 Templated Silica Using Supercritical Carbon Dioxide" Materials Letters vol.116, pp. 408–411, 2014.
[11] Cotugno, P., M. Casiello, A. Nacci, P. Mastrorilli, M. M. Dell'Anna and A.Monopoli. "Suzuki coupling of iodo and bromoarenes catalyzed by chitosan-supported Pd-nanoparticles in ionic liquids" *Journal of Organometallic Chemistry* vol. 752: pp.1-5, 2014.

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He currently works Art and Science Faculty at Çukurova University. The primary interests in Professor Guzel's laboratory are in synthesis and application homogeneus and heterogenius catalyst from phosphine, oximes and Schiff base type ligands. Most effort is directed toward the development of new supercritical CO_2 soluble complexes for solvent free catalytic applications. Much effort has addressed the deposition of metals on multiwalled carbon nanotube for using homogeneus like heterogeneus catalyst.