Partial Hydrogenation of Alkynes on Highly Selective Nano-Structured Mesoporous silica MCM-41 Composite Catalyst

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Summary: In this research, we have developed a silica MCM-41/Metformin/Pd (II) nano composite catalyst for the selective hydrogenation of alkynes to the corresponding (Z)-alkenes under a mild condition of atmospheric pressure and room temperature. Firstly, functionalized Si-MCM-41 metformin catalyst with the optimum performance was prepared. Then, the synthesized catalyst was elucidated by X-ray powder diffraction, BET surface area, FT-IR spectrophotometer, Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) and applied in partial hydrogenation of different alkynes, with high selectivity and high yield. The products were characterized by ^{1}H-NMR, ^{13}C-NMR, FT-IR, and Mass Spectrometry (MS) that strongly approved the (Z)-double bond configuration of produced alkenes. This prepared catalyst is competitive with the best palladium catalysts known for the selective liquid phase hydrogenation of alkynes and can be easily recovered and regenerated with keeping high activity and selectivity over at least three cycles with a simple regeneration procedure.

Keywords: Heterogeneous, Selective partial hydrogenation, Mesoporous silica, Nano composite, Alkynes, alkenes.

Introduction

Nowadays because of the significance of heterogeneous catalysis, has been much research focused on it. Therefore, the catalysts with new feature to fulfil highly product selectivity in synthesis are extremely desirable [1, 2]. Heterogeneous catalysis is of paramount significance in catalyst separation from the product in comparable with homogeneous ones that help in the provision of continuous chemical processes. Furthermore, heterogeneous catalysts are quintessentially more adaptable to rough conditions than their homogeneous correspondent. Therefore, extending of new versions of heterogeneous catalysts with the unique feature of activity and selectivity in a certain reaction is a leading plan of modern chemistry.

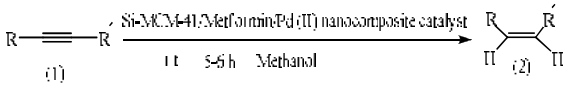
Regarding alkyne hydrogenation, the major aim is to avoid hydrogenation to single bond and in the case of non-terminal alkynes is to give superiority to the extreme conversion and selectivity to the *(Z)*-alkene [3-5]. Partially poisoned catalysts were extended for the hydrogenation of alkynes to alkenes. The well-known Lindlar catalyst, for example, is constituted of palladium on a calcium carbonate carrier which is partially poisoned with lead acetate in the presence of amines (*e.g.* quinoline). The hydrogenation with Lindlar catalyst is a stereospecific *cis* hydrogenation.

Despite the fact that there are a large number of materials with suitable selectivity to double bond formation, innovation and designing new catalysts using modern methods in catalysis is ongoing demand [6].

In recent years, synthesis and application of highly selective catalysts for partial hydrogenation of alkynes have drawn more attention as a result of its concern in the synthesis of intermediate products [7-11].

Because of the wide application of Z-alkenes in the synthesis of some industrial fine chemicals, development of new catalyst in partial hydrogenation of alkynes is essential.

To solve this problem, we investigated on a new recyclable, highly selective and obtainable catalyst for selective hydrogenation of alkynes to Z-alkenes (scheme-1).



Scheme-1: Selective hydrogenation of alkynes to Z-alkenes.

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Experimental

Preparation of metformin/functionalized Si-MCM-41 nanoparticles (Si-MCM-41/Met)

All chemicals were purchased from Merck except Pluronic123, metformin hydrochloride, and palladium acetate which were obtained from Aldrich. Transmission electron microscopy (TEM) micrographs were taken using a Philips CM300 operating at 100 kV electron beam accelerating voltage. Scanning electron microscopy (SEM) images were obtained with type KYKY-EM3200, 26 kV.

X-ray powder diffraction data of the synthesized catalysts were acquired on a Philips XPERT diffractometer using nickel filtered Cu Karadiation k= 1.5406 Å. BET surface area analysis was carried out on a Micromeritics TriStar 3000 apparatus. Infrared spectra were prepared on a TENSOR 27 FT-IR spectrophotometer, Bruker Corporation. ^{1}H and ^{13}C-NMR spectra were recorded on a Brucker Advance spectrophotometer (250 MHz) in $CDCl_3$. The mass spectra were recorded on a Finnigan-MAT-8430EI-MS spectrometer at 70 eV; in m/z (rel. %). The synthesis of mesoporous Si-MCM-41 was achieved according to a familiar procedure [12]. In 100 ml round-bottom flask was introduced consecutively 50 ml of dried toluene, 1.50 gr of Si-MCM-41 and 0.90 gr (4.49 mmol) of 3-chloropropyl trimethoxy silane. The mixture was refluxed for 24 h under an inert atmosphere of anhydrous N_2, filtered and washed later with toluene, dichloromethane, and methanol, and dried under reduced pressure at 80 ^{o}C for 12 h, and chloropropyl- functionalized Si-MCM-41 product was obtained. In the same another flask, to a solution of 1.50 g (8.79 mmol) of metformin hydrochloride in 45 ml acetonitrile, 0.38 gr (9.31 mmol) NaOH was added. The solution was stirred for 1 hour. Then 1.50 gr (9.04 mmol) KI and 1.00 gr of as-prepared 3-chloropropyl functionalized Si-MCM-41 were added to the mixture and kept under reflux for 12 h, filtered and washed with distilled water and dried at 80 ^{o}C under reduced pressure to provide 1.4 gr of metformin- functionalized mesoporous Si-MCM-41 nanoparticles.

Preparation of functionalized Si-MCM-41/ metformin/ palladium catalyst

0.9 gr functionalized Si-MCM-41 with sillylchloropropyl and metformin was poured in 100 ml flask and then 20 ml acetone added to it. The mixture was stirred and 198 mg $Pd(OAc)_2$ (0.88 mmol) added to the corresponding mixture and allowed this mixture to stir 24 h at room temperature. After that, the mixture was filtered and rinsed with acetone and dried THF twice. Then the solid was dried at 80˚C in low pressured oven for 4 h. The result brownish catalyst was obtained and its structure characterized by FT-IR.

Partial hydrogenation of alkyne to the corresponding alkene by functionalized Si-MCM-41/ metformin/ palladium catalyst

120 mg prepared catalyst mixed in 100 cc methanol was poured in a flask and 20 mmol alkyne was added to this mixture. Hydrogenation set is filled by H_2 at atmospheric pressure and hydrogenation was carried on for 5 h. Progress in the reaction was followed each 1 h by gas chromatography. After completion of reaction and disappearing of starting alkyne that took 5-6 h, the crude product was filtered. The filtrate was evaporated at low pressure by a rotary evaporator. The products were characterized by ^{1}H-NMR, ^{13}C-NMR, FT-IR, MS, that strongly approved the (Z)-double bond configuration of produced alkene.

2a) phenyl ethylene, IR (KBr): 1630 (C=C), 908, 991 (OOP =CH); ^{1}H-NMR ($CDCl_3$): 5.18 (1H, dd, J=10.2 Hz, 2.1 Hz); 5.61 (1H, dd, J= 16.8 Hz, J= 2.1 Hz); 6.65 (1H, dd, J= 16.8 Hz, J= 10.2 Hz); 7.33 (1H, t, J=7.5 Hz); 7.40 (2H, t, J= 7.5 Hz); 7.60 (2H, d, J=7.5 Hz); ^{13}C-NMR ($CDCl_3$): 137.9, 136.1, 128.6, 128.5, 127.9, 114.3. MS: 104 (100, M^{+}), 103 (41), 78 (35), 51 (17), 50 (7), 39 (6).

2b) 2-propen-1-ol, IR (KBr): 3350 (OH), 3080 (=CH), 1645 (C=C), 920 (OOP =CH); ^{1}H-NMR ($CDCl_3$): 1.95 (1H, s); 4.15 (2H, d, J= 6.2 Hz); 5.10 (1H, dd, J= 16.8 Hz, J=2.1 Hz); 5.40 (1H, dd, J= 10.2 Hz, J= 2.1 Hz); 6.10 (1H, ddt, J= 16.8 Hz, J=10.2 Hz , J=6.2 Hz); ^{13}C-NMR ($CDCl_3$): 60.2, 115.7, 138.2. MS: 58 (23, M^{+}), 57 (100), 39 (28), 31 (41), 29 (25), 27 (23).

2c) (Z)-2-buten-1-ol, IR (KBr): 3350 (OH), 3082 (=CH), 1658 (C=C), 670 (OOP =CH); ^{1}H-NMR ($CDCl_3$): 2.05 (3H, d, J= 6.4 Hz, CH_3); 3.65 (1H, s, OH); 4.18 (2H, d, J= 6.2 Hz, CH_2); 5.64 (1H, td, J=10.9 Hz, J=6.2 Hz, CH); 5.70 (1H, qd, J=10.9 Hz, J=6.4 Hz, CH); ^{13}CNMR ($CDCl_3$) 11.6, 57.9, 125.9, 130.6. MS: 72 (33, M^{+}), 57 (100), 43 (23), 41 (24), 39 (29), 31 (21), 29 (29), 27 (25).

2d) 3-buten-1-ol, IR (KBr): 3360 (OH), 3080 (=CH), 1641 (C=C), 990, 915 (OOP =CH); ^{1}HNMR ($CDCl_3$) 2.32 (2H, td, J= 7.1 Hz, J=6.2 Hz,

CH_2); 2.76 (1H, s, OH); 3.65 (2H, t, J=7.1 Hz, CH_2); 5.10 (1H, dd, J=10.0 Hz, J=2.1 Hz, CH); 5.13 (1H, dd, J=16.8 Hz, J=2.1 Hz, CH); 5.81 (1H, ddt, J=16.8 Hz, J=10 Hz, J=6.2 Hz, CH); ^{13}CNMR ($CDCl_3$) 37.1, 61.6, 117.2, 135.0. MS: 72 (7, M^+), 42 (100), 31 (67).

2e) 3-buten-2-ol, IR (KBr): 3390 (OH), 3080 (=CH), 1650 (C=C), 980, 922 (OOP =CH); ^{1}HNMR ($CDCl_3$): 1.27 (3H, d, J= 6.8 Hz, CH_3); 2.06 (1H, s, OH) 4.29 (1H, qd, J= 6.8 Hz, J= 6.2 Hz, CH); 5.07 (1H, dd, J= 10 Hz, J= 2.1 Hz, CH); 5.21 (1H, dd, J= 16.8 Hz, J= 2.1, CH); 5.90 (1H, ddd, J=16.8 Hz, J=10 Hz, J= 6.2 Hz, CH); ^{13}CNMR ($CDCl_3$) 23.0, 68.8, 113.6, 142.6. MS: 72 (3, M^+), 71 (14), 57 (100), 43 (73), 29 (24), 28 (4).

2f) (Z)-2-buten-1,4-diol, IR (KBr): 3337 (OH), 3025 (=CH), 1660 (C=C), 690 (OOP =CH); ^{1}HNMR ($CDCl_3$): 2.90 (2H, s, 2OH); 4.30 (4H, d, J= 6.2 Hz); 5.70 (2H, t, J= 6.2 Hz); ^{13}CNMR ($CDCl_3$) 44.0, 130.0. MS: 70 (38), 57 (100), 42 (95), 31 (55).

2g) propenoic acid, IR (KBr): 2400-3400 (COOH), 3070 (=CH), 1705 (C=O), 1636 (C=C), 1245, 1297 (C-O), 987 (OOP =CH); ^{1}H-NMR ($CDCl_3$): 5.75 (1H, dd, J= 16.8 Hz, J= 2.1 Hz); 6.22 (1H, dd, J= 16.8 Hz, J=10.2 Hz); 6.50 (1H, dd, J= 10.2 Hz, J= 2.1 Hz), 11.50 (1H, s, CO_2H); ^{13}C-NMR ($CDCl_3$): 127.5, 134.1, 170.4. MS: 72 (95, M^+), 55 (97), 45 (32), 27 (100).

2h) (Z)-ethylen-dicarboxylic acid, IR (KBr): 2400-3400 (COOH), 3070 (=CH), 1705 (C=O), 1635 (C=C), 1220, 1265 (C-O), 950 (OOP =CH); ^{1}H-NMR ($CDCl_3$): 6.28 (2H, s); 11.03 (2H, s, $2CO_2H$); ^{13}CNMR ($CDCl_3$) 130.0, 166.5. MS: 116 (2, M^+), 99 (30), 72 (100), 45 (67), 26 (45).

2i) (Z)-1,2-diphenylethylene, IR (KBr): 1600 (C=C), 700 (OOP =CH), ^{1}H-NMR ($CDCl_3$): 6.56 (2H, s); 7.30 (2H, t, J= 7.5 Hz); 7.45 (4H, t, J= 7.5 Hz); 7.72 (4H, d, J= 7.5 Hz); ^{13}C-NMR ($CDCl_3$): 127.4, 127.9, 128.5, 128.6, 137.5. MS: 180 (100, M^+), 179 (92), 178 (50), 165 (38), 89 (12), 77 (7).

2j) 1-pentene, IR (KBr): 3080 (=CH), 1645 (C=C), 910, 990 (OOP =CH), ^{1}H-NMR ($CDCl_3$): 0.91 (3H, t, J=8 Hz, CH_3); 1.43 (2H, qt, J=8 Hz, J=7.1 Hz, CH_2); 2.02 (2H, td, J=7.1 Hz, J=6.2 Hz, CH_2); 4.93 (1H, dd, J=10.2 Hz, J=2.1 Hz, CH); 4.97 (1H, dd, J=16.8 Hz, J=2.1 Hz, CH); 5.81 (1H, tdd, J=16.8 Hz, J=10.2 Hz, J=6.2 Hz, CH); ^{13}CNMR ($CDCl_3$) 13.7, 22.3, 36.1, 114.4, 139.0. MS: 70 (39, M^+), 55 (65), 42 (100), 29 (21), 27 (18).

2k) (Z)-2-pentene, IR (KBr): 3015 (=CH), 1667 (C=C), 700 (OOP =CH), ^{1}H-NMR ($CDCl_3$): 0.96 (3H, t, J= 8.0 Hz, CH_3); 1.60 (3H, d, J= 6.2 Hz, CH_3), 2.04 (2H, qd, J= 8.0 Hz, J= 6.2 Hz, CH_2); 5.15 (1H, td, 11.2 Hz, 6.2 Hz); 5.64 (1H, dq, J= 11.2 Hz, J= 6.2 Hz); ^{13}C-NMR ($CDCl_3$): 12.6, 14.2, 20.2, 123.1, 132.6. MS: 70 (39, M^+), 55 (100), 42 (42), 29 (20).

2l) 1-hexene, IR (KBr): 3080 (=CH), 1642 (C=C), 912 (OOP =CH), ^{1}H-NMR ($CDCl_3$): 0.90 (3H, t, J= 8.0 Hz, CH_3); 1.07 (2H, m, CH_2); 1.50 (2H, m, CH_2); 2.06 (2H, td, J= 7.1 Hz, 6.2 Hz, CH_2); 4.92 (1H, dd, J= 10.0 Hz, J= 2.1 Hz, CH); 4.96 (1H, dd, J= 16.8, J=2.1 Hz, CH); 5.80 (1H, ddt, J= 16.8 Hz, J= 10.0 Hz, J= 6.2 Hz, CH); ^{13}C-NMR ($CDCl_3$): 14.0, 22.4, 31.3, 33.7, 114.2, 139.2. MS: 84 (29, M^+), 69 (24), 56 (100), 42 (72), 41 (95), 29 (19).

2m) 1-octene, IR (KBr): 3075 (=CH), 1644 (C=C), 991 (OOP =CH), ^{1}H-NMR ($CDCl_3$): 0.87 (3H, t, J= 8.0 Hz, CH_3); 1.04-1.53 (8H, m); 2.02 (2H, dt, J= 7.2 Hz, J= 6.2 Hz, CH_2); 4.91 (1H, dd, J= 10.2 Hz, J= 2.1 Hz); 4.97 (1H, dd, J= 16.8 Hz, 2.1 Hz); 5.77 (1H, ddt, J= 16.8 Hz, J= 10.2 Hz, J= 6.2 Hz); ^{13}C-NMR ($CDCl_3$): 14.1, 22.7, 28.9, 29.1, 31.9, 33.9, 114.1, 139.2. MS: 112 (20, M^+), 83 (34), 70 (86), 54 (99), 43 (100), 29 (35).

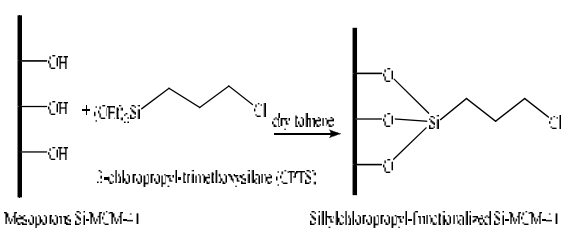
Catalyst recovering and regeneration

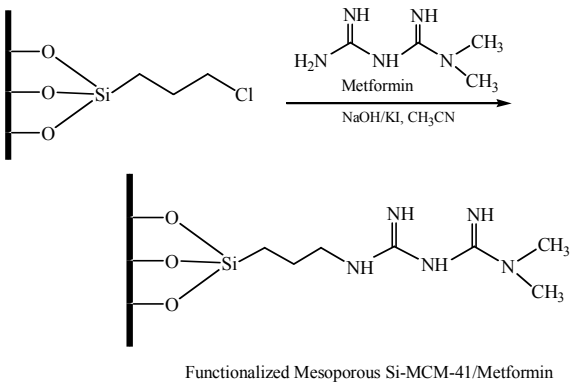
After completion of the reaction, the catalyst was filtered off and washed with sufficient methanol and the residue was dried under vacuum at room temperature. Then, the resulted powder was transferred into a flask and the system was purged with pure nitrogen for 10 min.

Results and Discussion

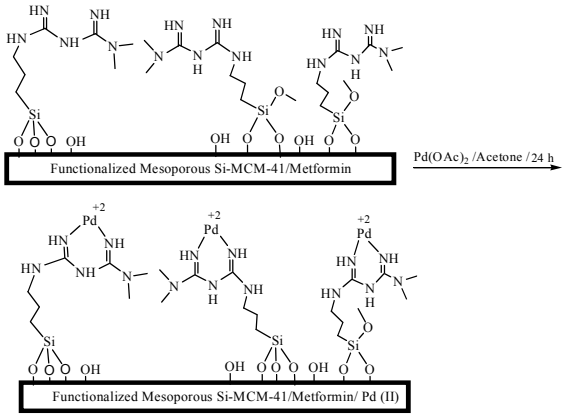
Synthesis and characterization of functionalized Si-MCM-41/Metformin/Pd(II)

The schematic pathways for the synthesis of catalyst are depicted in Scheme 2a and 2b.





Scheme-2a: The pathway for the preparation of functionalized mesoporous Si-MCM-41/Metformin.



Scheme: 2b: The pathway for the preparation of functionalized mesoporous Si-MCM-41/Metformin/Pd (II)

Si-MCM-41/Metformin was prepared on the basis of the reported method [13]. Then, palladium acetate was added to Si-MCM-41/Metformin in acetone and the mixture was stirred for 24 h at room temperature to obtain Si-MCM-41/Metformin/Pd(II). Synthesized catalyst has been characterized by FT-IR, XRD spectra and SEM and TEM images. The SEM micrograph of the catalyst is depicted in Fig. 1. This Fig. shows the formation of spherical particles agglomeration in the range of 50 to 80 nm (Fig. 1).

TEM image of catalyst obviously discloses the activated sites of trapped Pd(II) in metformin net in the size range of 5-10 nm (Fig. 2). TEM images obtained from reused functionalized Si-MCM-41/Metformin/Pd(II) catalyst after three times showed more verification of palladium species within the structure of modified Si-MCM-41 material (Fig. 3). The handful of dark spots are presumably the Pd(0) nanoparticles and their presence is mainly due to exposure of the final catalyst to H_2 hydrogenation which may cause the reduction of Pd(II) ions to Pd(0) species. The produced Pd(0) atom is bound to functionalized Si-MCM-41/Metformin via the coordination of terminal imino moieties of metformin with Pd(0). When the reaction is conducted for several times with the recovered catalyst, the produced Pd(0) atoms during the recycling process are mostly deposited around the preformed Pd(0) atoms and they can grow into bigger clusters and as a consequence there is no leaching of Pd(II) species from the catalyst surface, however the catalyst activity is expected to be slightly diminished to a degree by virtue of the agglomeration of the active sites of the catalyst. This might be because of the catalyst aggregates into big particles and becoming more difficult to be dispersed orderly. As a result, the surface area of the catalyst and active catalyst sites are believed to be reduced after several times catalyst recovering. However, stirring the reaction mixture and longer reaction time at atmospheric condition causes the atom particles of Pd(0) to be re-oxidized by O_2 back to the active Pd(II) sites [14] and as a result, there is no noticeable loss of amount of Pd(II) and the recycled catalyst after three times still retains its catalytic activity.

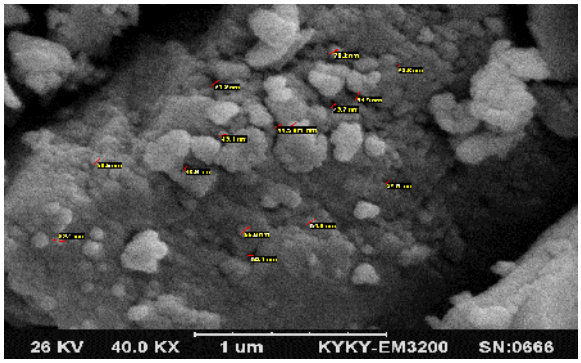


Fig. 1: SEM image of modified Si-MCM-41/metformin/palladium catalyst.

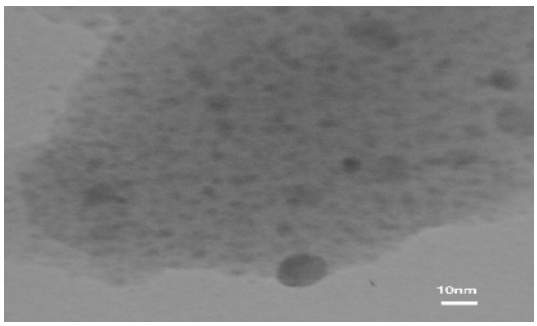


Fig. 2: TEM image of modified Si-MCM-41/metformin/palladium catalyst.

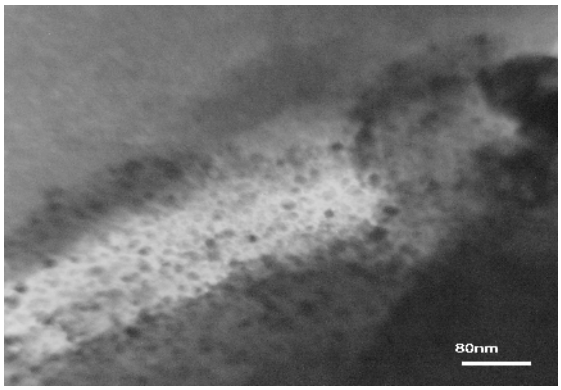
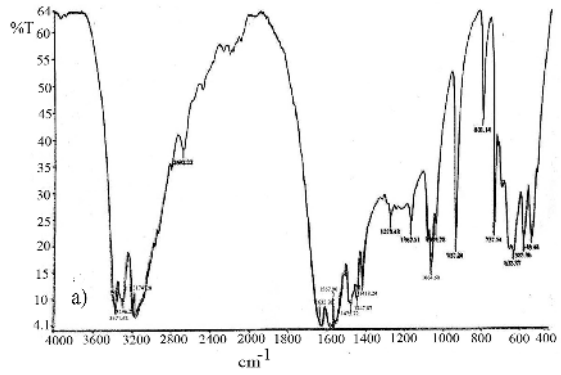


Fig. 3: TEM image of reused modified Si-MCM-41/metformin/palladium catalyst after three times.

The effect of reaction time on the yield of product was also studied and it was found that after three times, due to the aforementioned reason, the reaction time took longer to give the desired product in high (>90%) yield. Furthermore, TEM micrograph of reused catalyst after three times showed that the ordered structure of catalyst was kept and no damage in the structure of silicate framework was observed. The catalyst showed that excellent stability and efficiency after three recycles.

The successful bonding of metformin and consequent coordination of Pd(II) ions within the mesoporous Si-MCM-41 material can be characterized by using of FT-IR spectroscopy. Fig. 4 shows the FT-IR spectra resulted for (a) metformin hydrochloride (Metformin.HCl), (b) Si-MCM-41, (c) functionalized Si-MCM-41, (d) functionalized Si-MCM-41/Metformin and (e) functionalized Si-MCM-41/Metformin/Pd(II).



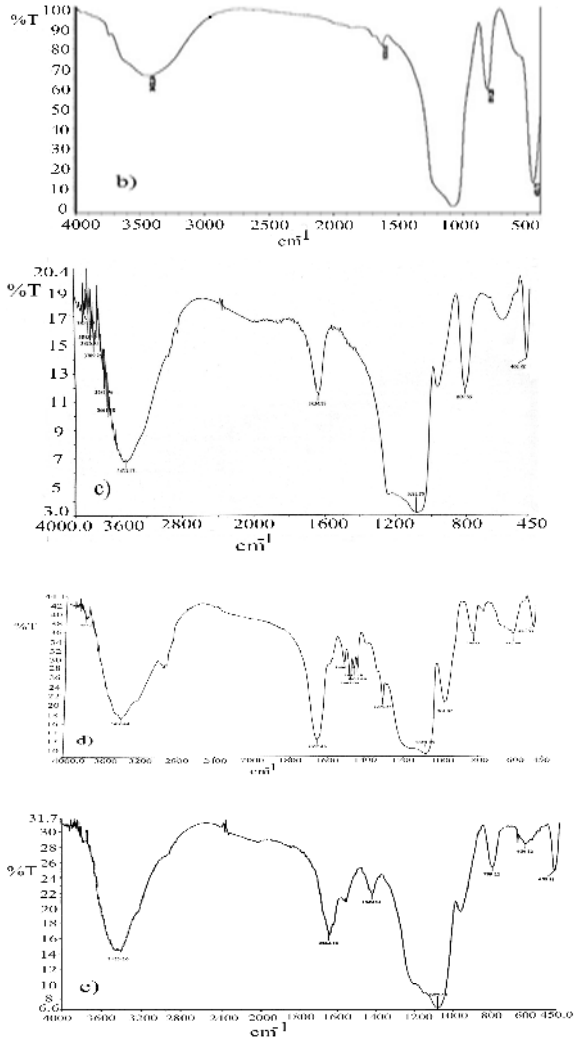


Fig. 4: FT-IR spectra for samples of (a) metformin hydrochloride, (b) Si-MCM-41, (c) Functionalized Si-MCM-41, (d) Functionalized Si-MCM-41/metformin and (e) Functionalized Si-MCM-41/metformin /Pd(II) catalyst.

Curve (a) is related to the spectrum of Metformin.HCl and the signals emerged at 1568 and 1634 cm^{-1} are ascribed to the presence of C=N stretching vibrations [15]. The signals appeared at 3150–3400 cm^{-1} regions can be attributed to the stretching vibration of N-H in C=N-H group on metformin [16]. The Si-MCM-41spectrum in curve (b) shows the broad bands in the range of 1050 and 1220 cm^{-1} which is assigned to asymmetric stretching vibration frequency of Si-O-Si, the peak at 1630 cm^{-1} is attributed to the bending vibration frequency of water molecules attached to the inorganic support and the signal becomes available at 3432 cm^{-1} can be ascribed to stretching frequency of

O-H bonds in the surface of Si-O-H groups and/or absorbed water into the porous sample. The functionalized Si-MCM-41 spectrum in curve (c) shows the similar peaks like as prepared Si-MCM-41. The Figs. 3d and 3e show the spectrum of functionalized Si-MCM-41/metformin and functionalized Si-MCM-41/metformin /Pd(II) catalysts respectively. In curves (d) and (e), the broad band in the range of 1050-1250 cm^{-1} is related to asymmetrical stretching bond of Si-O-Si bridges, which can be supportive to the being of a silica structure of Si-MCM-41 and an apparent signal in 965 cm^{-1} that is ascribed to stretching bond of Si-OH [16]. Moreover, a broad signal in the range of 3150-3410 cm^{-1} approved the existence of free surface OH and also absorbed water on the surface of the catalyst and the peaks in 1465 cm^{-1} and 1641 cm^{-1} are ascribed to C-N and C=N stretching bond respectively. The striking difference in FT-IR spectra of Metformin.HCl and Si-MCM-41 /Metformin (curves (a) and (d)) was the displacement of C=N stretching frequencies from 1568 and 1634 cm^{-1} to the broad band in 1652 cm^{-1}, relating to the elimination of HCl when metformin is bonded to the silica bed surface. In addition, the metal–ligand bond [17,18] supposedly causes a change in these two peaks again to an inferior frequency in 1642 cm^{-1}. This displacement can be observed in comparison with curves (d) and (e) in Fig. 4. Altogether, the preceding observations approved the attachment of Pd(II) ions on the surface of functionalized Si-MCM-41/Metformin.

The XRD pattern of catalyst exhibits no specific signals due to conversion of crystalline form of catalyst to amorphous morphology caused by encaging of Pd(II) ions into the surface structure by eliminating of signals which were observed in distinct diffraction peaks in low 2θ region before treating with $Pd(OAc)_2$ solution (Figs. 5a and 5b).

BET specific surface areas of calcined Si-MCM-41 and modified functionalized Si-MCM-41 by metformin were measured in 1020 and 425 m^2/g respectively. This result shows that the surface area of treated sample with metformin is considerably reduced. The surface area of palladium treated functionalized Si-MCM-41 /metformin sample slightly decreased and finally reached to 410 m^2/g. It can be concluded that palladium mostly trapped by metformin instead of the void pores of Si-MCM-41.

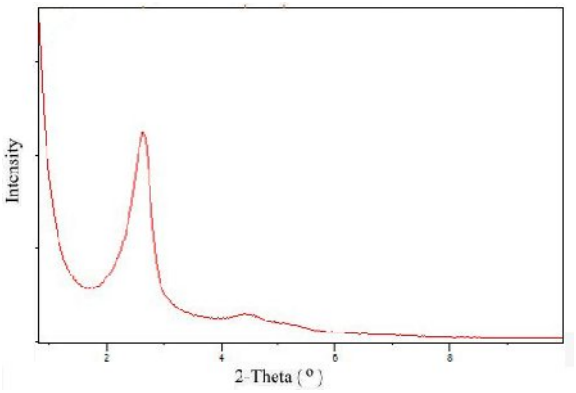


Fig. 5a: XRD spectrum of calcined Si-MCM-41.

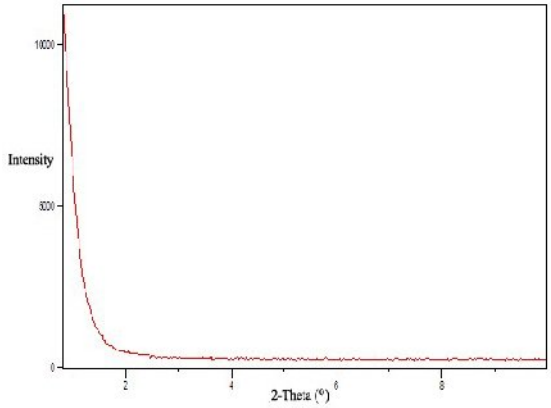


Fig. 5b: XRD spectrum of functionalized Si-MCM-41/metformin /Pd(II) catalyst.

13 different alkynes were treated by this catalyst (scheme 1) and the structure of products assigned by FT-IR, ^{1}H-NMR, ^{13}C-NMR and MS spectra that are undoubtedly in agreement with corresponding (Z)-alkenes. The results summarized in Table-1. These obtained data from partial hydrogenation of different alkynes using applied catalyst shows a high yield of produced (Z)-alkenes.

There is a strong possibility that the high yield of reaction can be related to the optimized amount of loaded metformin within the mesoporous structure of Si-MCM-41 with high surface area which provides more available sites to metformin and accordingly, high amount of covalently bonded Pd(II) ions to the surface of metformin to create higher interaction of reactant with the surface of the catalyst and better catalytic performance.

Table-1: The yields for the partial hydrogenation of alkynes using functionalized Si-MCM-41/metformin/ Pd(II) catalyst

Yield (%)	Time (h)	Product	R′	R	Entry
78±1	5.0	phenylethylene	-H	- Ph	2a

97±1	**5.0**	**2-propen-1-ol**	**-H**	**$-CH_2OH$**	**2b**
94±1	**6.0**	**(Z)-2-buten-1-ol**	**$-CH_3$**	**$-CH_2OH$**	**2c**
87±1	**5.0**	**3-buten-1-ol**	**-H**	**$-CH_2CH_2OH$**	**2d**
88±1	**5.0**	**3-buten-2-ol**	**-H**		**2e**
97±1	**5.5**	**(Z)-2-buten-1,4-diol**	**$-CH_2OH$**	**$-CH_2OH$**	**2f**
94±1	**5.5**	**propenoic acid**	**-H**	**-COOH**	**2g**
92±1	**6.0**	**(Z)-ethylen-dicarboxylic acid**	**-COOH**	**-COOH**	**2h**
73±1	**6.0**	**(Z)-1,2- diphenylethylene**	**- Ph**	**-Ph**	**2i**
96±1	**5.0**	**1-pentene**	**$-CH_2CH_2CH_3$**	**-H**	**2j**
88±1	**5.0**	**(Z)-2-pentene**	**$-CH_2CH_3$**	**$-CH_3$**	**2k**
93±1	**5.5**	**1-hexene**	**$-CH_2CH_2CH_2CH_3$**	**-H**	**2l**
86±1	**6.0**	**1-octene**	**$-CH_2(CH_2)_4CH_3$**	**-H**	**2m**

For example, the ^{1}H-NMR spectrum of 2i exhibits one singlet for the same two olefin protons in 6.5 ppm that is in agreement with (Z)-structure for stilbene. Aromatic protons appeared in the region between 7.3-7.7 ppm with expected pattern for mono substituted benzene. FT-IR spectrum of resulted product clearly approved the conversion of triple bond to Z-isomer of a double bond by strong peak appeared in 1600 cm^{-1} instead of the signal for trans isomer that usually shifted to lower frequencies because of its better conjugation system interaction.

Catalyst Regenerating and Recycling

Leaching of palladium species from the catalyst support is one of the major issues for deactivation of catalyst in liquid phase reactions [19-21]. To investigate the activity of used catalyst, the functionalized/metformin/Pd catalyst was recovered, regenerated and reused for selective hydrogenation of typical alkyne, for instance, 2-butyn-1,4-diol three times. The results of comparison with fresh and used catalysts in the liquid hydrogenation of 2-butyn-1,4-diol were summarized in Table-2. The results showed that this nanocomposite catalyst could be reused at least three times without any modification and that no palpable loss of activity or selectivity was observed.

Table-2: Yields for partial hydrogenation of 2-butyn-1,4-diol to (Z)-2-buten-1,4-diol using fresh and reused functionalized Si-MCM-41/metformin/palladium catalyst after three times.

Catalysts	Time (h)	Yield (%)
Functionalized Si-MCM-41/ metformin/palladium (fresh)	**5.5**	**97±1**
Functionalized Si-MCM-41/ metformin/palladium (used) (first time)	**5.5**	**95±1**
Functionalized Si-MCM-41/ metformin/palladium(used) (second time)	**6**	**92±1**
Functionalized Si-MCM-41/ metformin/palladium (used) (third time)	**6.5**	**91±1**

Conclusion

To sum up, we introduced a novel catalyst for selective partial hydrogenation of alkynes to (Z)-alkenes in high yields. The structural determination of produced catalyst implies that they have a stable structure with metformin ended organic moieties covalently bonded to their surfaces. The optimized final produced catalyst with more available active sites supplies more effective interaction of alkynes to the surface of Pd(II) ions which allows higher performance of the catalyst and consequently higher yield of resulted alkenes. Moreover, the synthesized catalyst was found to be efficient for partial hydrogenation of alkynes and presents some of the following advantages: (1) environmentally benign (2) highly selectivity (3) easily recycling and reusing (4) and readily to prepare.

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