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Selective reduction of alkenes, α,β-unsaturated carbonyl compounds, nitroarenes, nitroso compounds, N,N-hydrogenolysis of azo and hydrazo functions as well as simultaneous hydrodehalogenation and reduction of substituted aryl halides over PdMCM-41 catalyst under transfer hydrogen conditions

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Abstract—Chemoselective reductions of alkenes, α,β-unsaturated carbonyl compounds, nitro and nitroso compounds, N,N-hydrogenolysis of azo and hydrazo functions as well as simultaneous reduction and hydrodehalogenation of substituted aryl halides, including bulkier substrates, were achieved by catalytic transfer hydrogenation (CTH) using mesoporous PdMCM-41 catalyst. The yields were practically unaffected upon recycling of the catalyst. Further, the CTH process is accomplished without affecting the reduction of any other reducible functional group.

The selective reduction of alkenes, α,β-unsaturated carbonyl compounds, nitro and nitroso compounds as well as simultaneous reduction and hydrodehalogenation of substituted aryl halides is an important step in the industrial synthesis of dyes and biologically active compounds.[1] Hence, attempts have been devoted to developing suitable synthetic methods for such transformations.[2] Among the various available processes, catalytic transfer hydrogenation (CTH)[3] is emerging as a viable alternative to the commonly used reduction processes, which involve hazardous molecular hydrogen or a metal hydride donor. Such reactions have also been performed over homogeneous catalysts.[4] However, in view of the drawbacks of the homogeneous catalyzed processes as well as environmental concerns associated with these methods, in recent years the scientific community has switched over to heterogeneous catalysts for such transformations,[5] which offer several advantages over homogeneous counterparts with respect to handling, easy recovery and recycling of catalysts as well as minimization of undesired toxic wastes. Furthermore, the process is simple, reaction conditions are mild, and reduction of bulky molecules can be carried out without the use of expensive reagents. In this regard, palladium supported[6] or functionalized[7] catalysts are, in general, considered good catalysts.

We recently reported several transition metal-based mesoporous silicate and aluminophosphate molecular sieves, which show promise for a variety of industrially important organic reactions and the use of which may represent a possible alternative to standard syntheses of a wide variety of precursors and intermediates.[8] Furthermore, they were also found to be very efficient, highly selective, and rapidly synthesized. More importantly, these materials catalyzed some of the following reactions, for example, oxidation of alkyl aromatics,[8a] phenols,[8b] cyclohexane,[8c–e] and cyclohexene,[8f] reduction of aromatic nitro and carbonyl functions,[8g–i] more efficiently than the corresponding microporous analogues or supported metal oxide systems. In continuation of

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Keywords: Alkenes; α,β-Unsaturated carbonyl compounds; Nitroarenes; Nitroso compounds; Azo and hydrazo functions; Aryl halides; PdMCM-41 catalyst; Hydrogen transfer.

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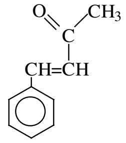
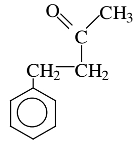
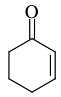
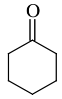
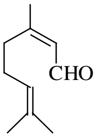
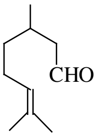
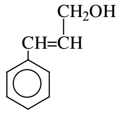
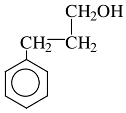
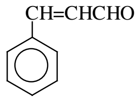
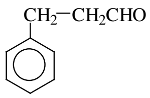
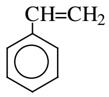
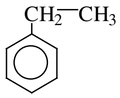
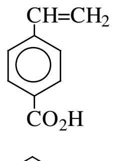
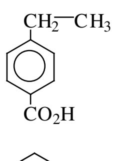
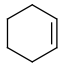
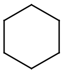
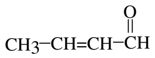
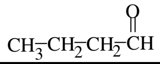
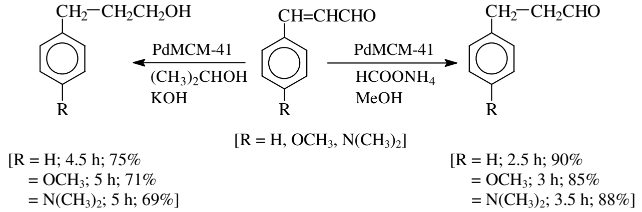
our work on the development of novel eco-friendly molecular sieves-based heterogeneous catalysts and catalytic processes, as well as realizing the importance of the development of novel synthetic methods for certain important transformations, including bulkier molecules, we report herein the first of a series of studies that explore a CTH approach for the reduction of aromatic α,β-unsaturated ketones, nitroso compounds, and hydrodehalogenation of substituted aryl halides using a newly developed palladium-based mesoporous silicate molecular sieve catalyst, designated as PdMCM-41.[9] Mesoporous materials are novel molecular sieves, having a high surface area, and large pore size and volume.[10] The PdMCM-41 catalyst was hydrothermally synthesized[11] and characterized using various analytical and spectroscopic techniques. Since, the CTH process requires acidic sites, this catalyst is very well suited for this purpose, as it possesses such characteristics,[12] and therefore, in this investigation mesoporous PdMCM-41 catalyst was employed for the titled reactions.[13] Furthermore, the mesoporous matrix gives a better dispersion of the active palladium ions as compared to other supported systems in addition to the benefits from having a low palladium content.

Table 1 summarizes the results of CTH of several alkenes and α,β-unsaturated carbonyl compounds over PdMCM-41 catalyst, wherein the substrates were reduced in excellent yields. The catalyst reduces only the olefinic bonds, the carbonyl groups remaining unaffected. The selective reduction can be explained on the basis of the actual active species involved in the reduction process, which strongly depends on the reaction conditions. Thus, when PdMCM-41 is used in combination with ammonium formate and methanol, selective reduction of the olefinic bonds produces saturated carbonyl compounds. Interestingly, when PdMCM-41 was used in combination with potassium hydroxide and isopropanol, the unsaturated carbonyl compounds were transformed into saturated alcohols (Scheme 1) since the catalyst in combination with potassium hydroxide and isopropanol produces metal alkoxide,[8i] which has an

Table 1. CTH of unsaturated carbonyl compounds over PdMCM-41

Entry	Substrate	Time (h)	Product	Yield (%)	
				First run	Third run
1		3.5		87	88
2		2.0		92[a]	89
3		4.0		91	88
4		2.0		89	88
5		2.5		90	89
6		3.0		93[a]	91
7		5.0		80	80
8		1.5		62	60
9	 $CH_3-CH=CH-\overset{\overset{O}{\|}}{C}H$	1.5	 $CH_3-CH_2-CH_2-\overset{\overset{O}{\|}}{C}H$	88	84

[a] Isolated yield based on single experiment.

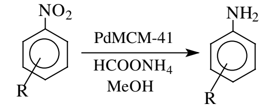


Scheme 1.

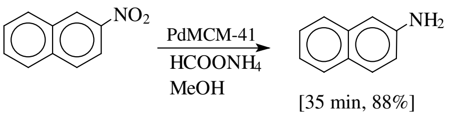
affinity for carbonyl groups and therefore produces saturated alcohols.

Table 2 lists the results of transfer hydrogenation of some aromatic and heterocyclic nitroso compounds over the PdMCM-41 catalyst. It can be seen from the table that the catalyst successfully reduces aromatic nitroso compounds to aromatic amines with good yields (entries 1 and 2), while denitrosofication takes place due to –N–N– bond cleavage, in the case of aliphatic and aromatic nitrosoamines (entries 3–5). The catalyst was also used for the chemoselective reduction of nitroarenes and it was found to be more efficient (Table 3) than other mesoporous-based catalysts.[7,12] It is also noteworthy here that the PdMCM-41 catalyst can successfully reduce a relatively hindered aromatic nitro compound, 2-nitronaphthalene (Scheme 2), with good yields in a much shorter time than that reported in literature.[7,14] However, one of the most important characteristics of the PdMCM-41 catalyst is the simultaneous cleavage of both –N=N– and –C–X (X = a halogen) bonds. Thus, the reduction of nitroso, nitro, azo, and hydrazo compounds yields aniline (Scheme 3).

Table 3. CTH of nitroarenes over PdMCM-41



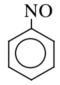
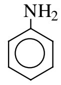
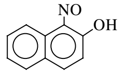
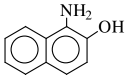
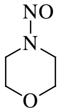
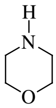
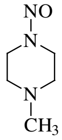
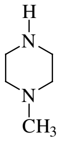
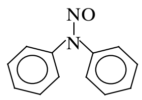
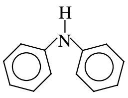
Entry	R	Time (min)	Yield (%)
1	H	30	99
2	2-CH_3	40	92
3	3-CH_3	45	90
4	4-CH_3	40	93
5	3-CO_2H	30	85
6	4-CO_2H	40	88
7	4-$COCH_3$	40	80
8	3-CHO	30	82
9	4-OCH_3	45	88
10	2-OH	60	86
11	4-OH	50	85
12	3-CH_3CHOH	45	85
13	2-NH_2	35	87
14	3-NH_2	45	85
15	4-NH_2	40	89
16	4-CH_2CN	60	83

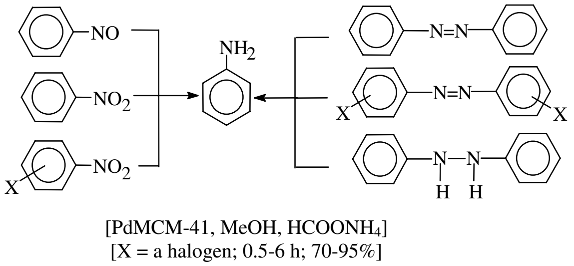


Scheme 2.

Table 4 summarizes the results of hydrodehalogenation of aryl halides over PdMCM-41. The hydrodehalogenations of –Cl and –Br functions were achieved in good yields. Functional groups such as –CHO were tolerated. However, it is important to note that both reduction (of carbonyl groups) and hydrodehalogenations (of halides) takes place concurrently when isopropanol and KOH were used for the reaction (Scheme 4). Indeed, with time,

Table 2. CTH of nitroso compounds over PdMCM-41

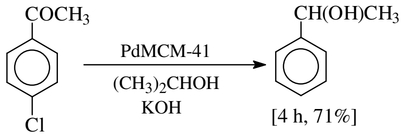
Entry	Substrate	Time (min)	Product	Yield (%)	
				First run	Third run
1		30		91	89
2		50		86	81
3		120		80	77
4		150		71	74
5		180		62	63



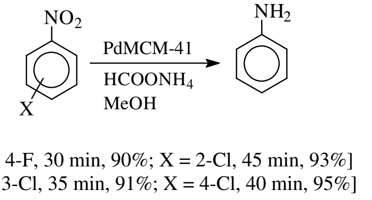
Scheme 3.

both the reduction and hydrodehalogenation can easily be followed throughout the reaction with nitro aryl halides (Scheme 5). Furthermore, the PdMCM-41 catalyst is more effective than several other catalytic systems, which require much longer reaction times, typically 1–2 days, to achieve similar yields.[5d,e]

In summary, PdMCM-41 was found to be a promising heterogeneous catalyst under mild transfer hydrogenation conditions[15] for the selective reduction of alkenes, α,β-unsaturated carbonyl compounds, aromatic nitro and nitroso compounds, N,N-hydrogenolysis of azo and hydrazo functions as well as simultaneous reduction and hydrodehalogenation of substituted aryl halides, including hindered substrates. The conversion was much faster and cleaner than conventional methods and moreover, in the present case, the reaction occurs under mild reaction conditions. Thus, the CTH method employing PdMCM-41 catalyst is a highly selective route for environmentally benign organic reductions.



Scheme 4.



Scheme 5.

Acknowledgements

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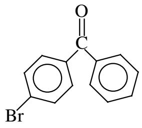
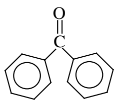
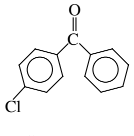
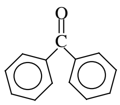
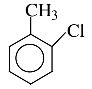
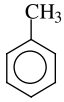
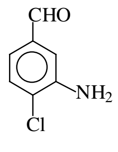
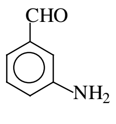
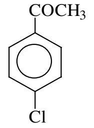
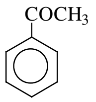
References and notes

1. (a) Imamoto, T. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 8, pp 793–809; (b) Kabalka, G. W.; Verma, R. S. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 8, pp 363–379; (c) Huang, Z.; Tang, Y. *J. Org. Chem.* **2002**, *67*, 5320–5326.

Table 4. Hydrodehalogenations over PdMCM-41

Entry	Substrate	Time (h)	Product	Yield (%)	
				First run	Third run
1		4.0		91	88
2		5.0		86	86
3		3.0		83	85
4		4.0		85	81
5		3.5		71	70

2. (a) Keinan, E.; Greenspoon, N.; Rappoport, P. *The Chemistry of Enones, Part 2*; Wiley: New York, 1989; (b) Baik, W.; Rhee, J. U.; Lee, N. H.; Kim, B. H.; Kim, K. S. *Tetrahedron Lett.* **1995**, *36*, 2793–2794; (c) Corey, E. J.; Helal, C. J. *Angew. Chem., Int. Ed.* **1998**, *37*, 1986–2012; (d) Larock, R. C. *Comprehensive Organic Transformations: A Guide to Functional Group Preparation*, 2nd ed.; Wiley-VCH: New York, 1999; pp 821–828; (e) Ohkuma, T.; Takeno, H.; Honda, Y.; Nayori, R. *Adv. Synth. Catal.* **2001**, *343*, 369–375; (f) Alonso, F.; Beletskaya, I. P.; Yus, M. *Chem. Rev.* **2002**, *102*, 4009–4092; (g) Moisan, L.; Hardouin, C.; Rousseau, B.; Doris, E.. *Tetrahedron Lett.* **2002**, *43*, 2013–2015; (h) Jurkauskas, V.; Sadighi, J. P.; Buchwald, S. L. *Org. Lett.* **2003**, *5*, 2417–2420.
3. (a) de Graauw, C. F.; Peters, J. A.; van Bekkum, H.; Huskens, J. *Synthesis* **1994**, 1007–1017; (b) Node, M.; Nishide, K.; Shigeta, Y.; Shiraki, H.; Obata, K. *J. Am. Chem. Soc.* **2000**, *122*, 1927–1936; (c) Ukisu, Y.; Miyadera, T. *J. Mol. Catal. A* **1997**, *125*, 135–142; (d) Ukisu, Y.; Miyadera, T. *Appl. Catal. B* **2003**, *40*, 141–149; (e) Aramendía, M. A.; Borau, V.; Jiménez, C.; Marinas, J. M.; Ruiz, J. R.; Urbano, F. *Appl. Catal. A* **2003**, *249*, 1–9.
4. (a) Beaupere, D.; Bauer, P.; Nadjo, L.; Uzan, R. *J. Organomet. Chem.* **1982**, *238*, C12–C14; (b) Visintin, M.; Spogliarich, R.; Kaspar, J.; Graziani, M. *J. Mol. Catal.* **1984**, *24*, 277–280; (c) Khai, B. T.; Arcelli, A. *Tetrahedron Lett.* **1996**, *37*, 6599–6602; (d) Grushin, V. V.; Alper, H. *Chem. Rev.* **1994**, *94*, 1047–1062.
5. (a) Gallezot, P. In *Handbook of Heterogeneous Catalysis*; Wiley: New York, 1997; Vol. 5, pp 2209–2221; (b) Ryndin, Y. A.; Santini, C. C.; Prat, D.; Basset, J. M. *J. Catal.* **2000**, *190*, 364–373; (c) De Bruyn, M.; De Vos, D. E.; Jacobs, P. A. *Adv. Synth. Catal.* **2002**, *344*, 1120–1125; (d) Adimurthy, S.; Ramachandraiah, G.; Bedekar, A. V. *Tetrahedron Lett.* **2003**, *44*, 6391–6392; (e) Cellier, P. A.; Spindler, J.-F.; Taillefer, M.; Cristau, H.-J. *Tetrahedron Lett.* **2003**, *44*, 7191–7195.
6. (a) Sommovigo, M.; Alper, H. *Tetrahedron Lett.* **1993**, *34*, 59–62; (b) von Holleben, M. L. A.; Zucolotto, M.; Zini, C. A.; Oliveira, E. R. *Tetrahedron* **1994**, *50*, 973–978; (c) Urbano, F. J.; Marinas, J. M. *J. Mol. Catal. A* **2001**, *173*, 329–345.
7. Kantam, M. L.; Bandyopadhyay, T.; Rahman, A.; Reddy, N. M.; Choudary, B. M. *J. Mol. Catal. A* **1998**, *133*, 293–295.
8. (a) Sakthivel, A.; Badamali, S. K.; Selvam, P. *Catal. Lett.* **2002**, *80*, 73–76; (b) Mohapatra, S. K.; Hussain, F.; Selvam, P. *Catal. Commun.* **2003**, *4*, 57–62; (c) Sakthivel, A.; Selvam, P. *J. Catal.* **2002**, *211*, 134–143; (d) Mohapatra, S. K.; Sahoo, B.; Keune, W.; Selvam, P. *Chem. Commun.* **2002**, 1466–1467; (e) Sakthivel, A.; Dapurkar, S. E.; Selvam, P. *New J. Chem.* **2003**, *27*, 1184–1190; (f) Sakthivel, A.; Dapurkar, S. E.; Selvam, P. *Appl. Catal. A* **2003**, *246*, 283–293; (g) Mohapatra, S. K.; Sonavane, S. U.; Jayaram, R. V.; Selvam, P. *Tetrahedron Lett.* **2002**, *43*, 8527–8529; (h) Mohapatra, S. K.; Sonavane, S. U.; Jayaram, R. V.; Selvam, P. *Appl. Catal. B* **2003**, *46*, 155–163; (i) Selvam, P.; Mohapatra, S. K.; Sonavane, S. U.; Jayaram, R. V. *Tetrahedron Lett.* **2004**, *45*, 2003–2007.
9. X-ray diffractograms (Rigaku-miniflex, Cu-Kα) of both synthesized and calcined PdMCM-41 showed patterns typical of hexagonal mesoporous systems.[7] Further, N_2 adsorption measurements (BET surface area; $970\,m^2\,g^{-1}$, pore volume; $0.78\,cm^3\,g^{-1}$, and pore size; 31 Å) support the mesoporous nature of the sample. ICP-AES analysis shows 2.8 wt% Pd loading in the catalyst.
10. (a) Kresge, C. T.; Leonowicz, M. E.; Roth, W. T.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710–712; (b) Selvam, P.; Bhatia, S. K.; Sonwane, C. G. *Ind. Eng. Chem. Res.* **2001**, *40*, 3237–3261.
11. The preparation of PdMCM-41 was carried out as follows: Initially, 6.8 mL of tetramethylammonium hydroxide (TMAOH; 25% in water; Aldrich) was taken in 10 mL of water and stirred for 15 min. To this, one-third (1.5 g) of the total fumed silica (SiO_2; Aldrich; an exceptionally pure form (98.8%) of nano-sized (11 nm) silica with high surface area ($255\,m^2\,g^{-1}$)) was added slowly and the resulting mixture was designated as 'Solution-A'. In the next step, 'Solution-B' was prepared by stirring 7.02 g cetyltrimethylammonim bromide (CTAB; Aldrich) and sodium hydroxide (NaOH; 0.742 g in 5 mL water; Loba) in 18 mL distilled water, and stirred for 30 min. Subsequently, 'Solution-A' was added dropwise to 'Solution-B' followed by the addition of the remaining fumed silica (3.0 g), which resulted in the formation of a gel. The resulting gel was then stirred for another 30 min. In addition, the gel was further stirred for another 30 min after adding 10 mL of water. Finally, palladium acetate solution (0.127 g in 5 mL water; Loba) was added dropwise to the gel and stirred for 15 min. A final volume of water (29 mL) was then added to the gel, which was then stirred for a further 1 h so that a homogeneous gel resulted. The pH was maintained at 11.4. The final gel had the following (molar) composition: $1SiO_2{:}0.27CTAB{:}0.26NaOH{:}0.26TMAOH{:}60H_2O{:}0.01PdO$ (Si/Pd = 100). The gel was then transferred into a Teflon-lined stainless steel autoclave and kept in an air oven for crystallization at 423 K for 72 h. The solid product, that is, synthesized PdMCM-41, obtained was washed, filtered, and dried in air oven at 353 K for 12 h. The synthesized sample was calcined under a N_2 flow at 823 K for 2 h followed by 8 h in air. The yield of PdMCM-41 obtained was about 85% with respect to the starting amount of fumed silica.
12. The presence of strong Lewis acid sites was confirmed by NH_3–TPD measurements (peak in the range 833–913 K).
13. In a typical reaction, the substrate (10 mmol) was dissolved in methanol (10 mL) to which ammonium formate (30 mmol) was added as a hydrogen donor along with the catalyst (PdMCM-41; 50 mg). The reaction mixture was then refluxed at 343 K for several minutes to a few hours depending on the nature of the substrates. The progress of the reaction was monitored by TLC, and the products were analyzed using GC (Eshika) fitted with an OV-17 column. After completion of the reaction, the catalyst was recovered for the recycling studies by simple filtration, washed several times with acetone followed by distilled water, then activated at 373 K for 6 h.
14. Han, B. H.; Jang, D. G. *Tetrahedron Lett.* **1990**, *31*, 1181–1182.
15. The PdMCM-41 catalyst was also tested for its reusability, and interestingly, the yield was practically unaffected for up to three cycles for these substrates. The catalyst was also used for the reduction of cinnamaldehyde (up to six cycles) without significant change in the yield of cinnamyl alcohol (first run = 90%; sixth run = 88%). The XRD pattern of the recycled PdMCM-41 catalyst (after the sixth run) and BET surface area measurement showed that the structural integrity remained unaltered after reuse. The mesoporous nature of the reused catalyst was confirmed by N_2 adsorption measurements (BET surface area = $985\,m^2\,g^{-1}$, pore volume = $0.85\,cm^3\,g^{-1}$, and pore size 31 Å). Overall there was no major detrimental effect observed from the reaction conditions over the structural properties of PdMCM-41.