

Regio- and Chemoselective Catalytic Transfer Hydrogenation of Aromatic Nitro and Carbonyl as Well as Reductive Cleavage of Azo Compounds over Novel Mesoporous NiMCM-41 Molecular Sieves

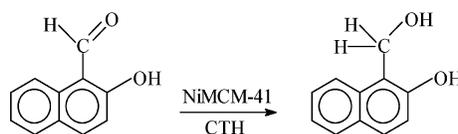
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ABSTRACT



Regio- and chemoselective reduction of nitroarenes and carbonyl compounds and reductive cleavage of azo compounds, including bulkier molecules, was achieved by the catalytic transfer hydrogenation method (CTH) using a novel nickel-containing mesoporous silicate (NiMCM-41) molecular sieve catalyst. In addition, the catalyst was also found to behave as a truly heterogeneous catalyst as the yield was practically unaffected.

The reduction of nitroarenes and carbonyl compounds to the corresponding amines and alcohols, respectively, is an important step in the industrial synthesis of dyes, biologically active compounds, pharmaceuticals, rubber chemicals, and photographic and agricultural chemicals.¹ A variety of methods have been developed for this purpose.² In comparison to the commonly used reduction processes, which involve hazardous molecular hydrogen or Fe/HCl³ or Sn/HCl,⁴ catalytic transfer hydrogenation (CTH) employing hydrogen

donors, e.g., propan-2-ol, is safer, highly selective, and eco-friendly.⁵ Furthermore, unlike conventional hydrogenation methods, CTH reactions do not require any elaborate experimental setup or high-pressure reactors. A wide variety of homogeneous metal complexes have been reported for the CTH process and most of them involve metal-catalyzed hydrogenations, complex hydrides, or metal ion in solution.⁶ However, it has been observed that controlling the reduction rates is difficult with these active catalysts.⁷ On the other hand, the use of heterogeneous catalysts offers several advantages over homogeneous systems with respect to easy recovery and recycling of catalysts as well as minimization of undesired toxic wastes. However, these processes require

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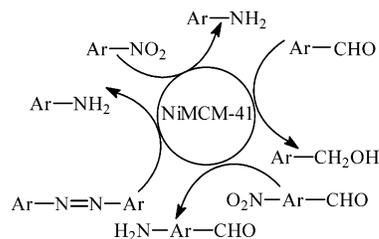
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moisture-sensitive reagents or catalysts^{3,8,9} such as using Raney Ni, Pd/C, PtO₂, etc. Among these, Raney Ni catalyst has frequently been used with hydrazine hydrate or isopropyl alcohol for CTH reactions.^{8,9} Further it has been observed that the use of Raney Ni for the reduction of ketones leads to hydrogenolysis.⁸ Although CTH reactions are very facile over these catalysts, they are, however, not selective toward functional groups such as -CO, -CX, and -NO₂, and almost all labile functional groups undergo reduction under reaction conditions. Furthermore, the Raney Ni catalyst is flammable and presents considerable hazards during handling. Hence, attention has been focused on the design of nickel-based oxide and nickel oxide supported catalysts.¹⁰ However, these catalyst systems too have several drawbacks such as typically longer reaction times, nucleophilic attack, byproducts, low yield, etc. Furthermore, the activity of most of these catalysts decreases with subsequent recycling. In this letter, we report here, for the first time, a very efficient, highly selective, and rapid method for the reduction of nitroarenes, carbonyl functions, and reductive cleavage of azo compounds using newly developed nickel-incorporated mesoporous silicate (NiMCM-41) molecular sieve catalyst (Scheme 1). To the best of our knowledge, this study also

Scheme 1. Reduction of Aromatic Compounds over NiMCM-41 by the CTH Method



forms first of its kind on the reduction of azo groups to the corresponding amines by catalytic hydrogenation using molecular sieves.

Mesoporous silicate materials are novel molecular sieves,^{11,12} having high surface area and large pore size and volume. The transition metal ion incorporated mesoporous catalysts can be used to carry out certain important organic transformations¹³ more efficiently than the corresponding microporous analogues or supported metal oxide systems. The NiMCM-41 catalyst was hydrothermally synthesized¹⁴ and characterized using several analytical and spectroscopic techniques.¹⁵ Since the CTH process requires acidic sites,

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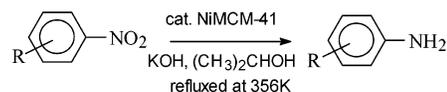
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mesoporous NiMCM-41, which possesses such characteristics,¹⁶ may be very well suited for this purpose. Hence, in this investigation, we used NiMCM-41 as the catalyst for the CTH process. The CTH reactions were carried out as per standard procedures¹⁷ using propan-2-ol as the hydrogen donor.¹⁸

Tables 1 and 2 summarize the results of CTH of several aromatic nitro and carbonyl functions attached to the aromatic

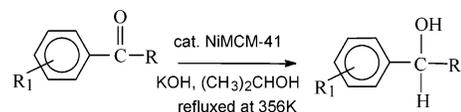
Table 1. Reduction of Nitroarenes



entry	R	time (h)	yield (%)	
			1st run	6th run
1	H	4.0	93	92
2	2-Cl	5.0	85	84
3	3-Cl	4.5	89	89
4	4-Cl	4.0	92	90
5	4-F	4.0	88	88
6	4-Br	4.5	91	90
7	2-CH ₃	4.5	80	80
8	3-CH ₃	4.0	88	87
9	4-CH ₃	4.5	80	81
10	4-OCH ₃	4.0	90	87
11	2-NH ₂	4.0	85	84
12	3-NH ₂	3.5	88	89

ring over the NiMCM-41 catalyst, wherein the compounds were reduced with excellent yields. However, the activity

Table 2. Reduction of Aromatic Carbonyls

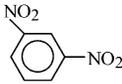
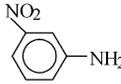
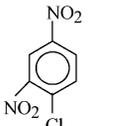
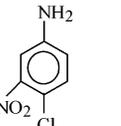
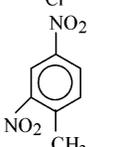
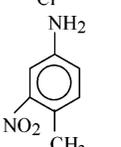
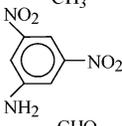
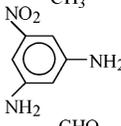
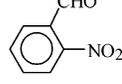
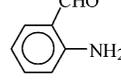
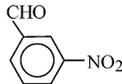
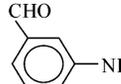
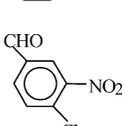
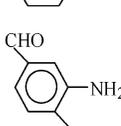
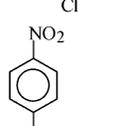
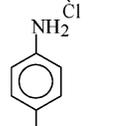
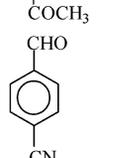
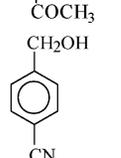


entry	R	R ₁	time (h)	yield (%)	
				1st run	6th run
1	H	H	2.5	94	94
2	H	2-Cl	3.5	77	77
3	H	4-Cl	3.5	87	87
4	H	4-OH	4.0	85	85
5	H	4-OCH ₃	4.0	86	86
6	H	4-N(CH ₃) ₂	5.5	68	65
7	CH ₃	H	3.0	92	90
8	CH ₃	3-NH ₂	3.0	68	65
9	CH ₃	4-Cl	3.5	84	84

was significantly influenced by the nature/position of the substituents on the aromatic ring. For example, in the case of nitroarenes, only amines were obtained in the product. The presence of a methyl group *ortho* to the nitro group decreased the yield to a larger extent than at the *para* position due to steric effects. On the other hand, electron withdrawing/

donating groups such as chloride, amine, and methoxy do not have a significant influence on the reaction. Furthermore, several functional groups, viz., -F, -Cl, -Br, -OH, -CN, -NH₂, -CH₃, and -OCH₃, are tolerated. The catalyst also shows promise for regioselective (Table 3; entries 1–4) and

Table 3. Regio- and Chemoselective Reduction of Aromatic Compounds over NiMCM-41

entry	substrate	time (h)	product	yield (%)	
				1 st run	6 th run
1		4.5		83	83
2		4.5		84	83
3		3.5		82	82
4		4.5		78	79
5		5.0		84	83
6		4.5		89	89
7		5.0		91	90
8		5.0		83	83
9		3.5		76	77

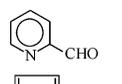
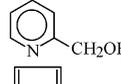
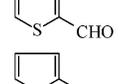
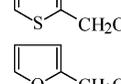
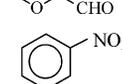
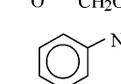
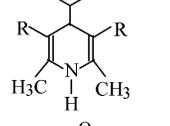
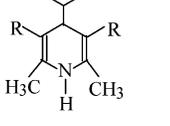
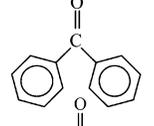
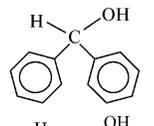
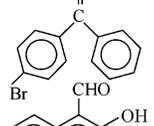
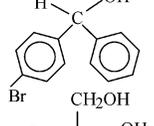
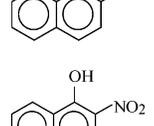
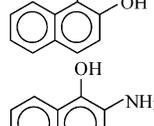
chemoselective (Table 3; entries 5–9) reductions with high yields. Since the nitro groups attached to aromatic rings can withdraw electrons more strongly from benzene compared with carbonyl groups, they can easily be adsorbed on the

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catalyst surface. This may be the reason for the chemoselective reduction of a nitro group ahead of a carbonyl group. Likewise, the catalyst also shows promise for regioselective reduction of dinitro compounds.

Furthermore, this reduction was also successfully carried out for certain heterocyclic (Table 4; entries 1–4) compounds

Table 4. Reduction of Heterocyclic and Bulky Aromatic Compounds over NiMCM-41

entry	substrate	time (h)	product	yield (%)	
				1 st run	6 th run
1		4.0		63	63
2		3.5		67	66
3		4.0		71	73
4		6.0		75	71
5		3.5		90	89
6		3.5		81	78
7		5.5		83	83
8		4.0		86	86

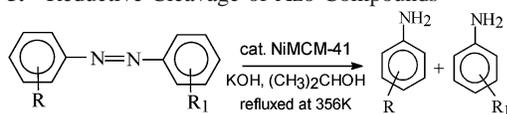
R = COOCH₃

as well as for bulkier molecules (Table 4; entries 4–8) with high yields being obtained. Table 5 presents the results of an elegant and rapid (1–2 h) reductive cleavage of azo

(14) The hydrothermal synthesis of NiMCM-41 is carried out by the final molar gel composition: 1 SiO₂:0.27 CTAB:0.26 NaOH:0.26 TMAOH:60 H₂O:0.02 NiO for 24 h. Nickel nitrate hexahydrate was used as the metal source. Removal of the template molecules was carried out by calcination of the as-synthesized sample at 823 K for 2 h in a flow of N₂, followed by 6 h in air. For further details, see: Sakthivel, A.; Badamali, S. K.; Selvam, P. *Micropor. Mesopor. Mater.* **2000**, 39, 457.

(15) The powder X-ray diffraction (XRD) patterns of both as-synthesized (*a*₀ = 44.5 Å) and calcined (*a*₀ = 40.8 Å) NiMCM-41 samples are typical of hexagonal mesoporous MCM-41 structure.^{11,12} Further, N₂ sorption measurements (BET surface area = 920 m² g⁻¹, pore volume = 0.52 cm³ g⁻¹, and pore size = 30 Å) support the mesoporous nature of the sample. Inductively coupled plasma-atomic emission (ICP-AES) analysis shows 4.3 wt % Ni loading in the catalyst.

(16) Thermogravimetric (TG) analysis of calcined NiMCM-41 shows a 20% weight loss indicating its acidic nature. This is well supported by the temperature-programmed desorption of ammonia studies. Differential thermal analysis (DTA) shows corresponding endothermic transition.

Table 5. Reductive Cleavage of Azo Compounds

entry	R	R ₁	time (h)	yield (%)	
				1st run	6th run
1	H	H	2.0	91	89
2	4-Cl	4 ¹ -Cl	2.0	88	88
3	3-Br	3 ¹ -Br	3.0	85	85
4	3-CH ₃	3 ¹ -CH ₃	2.0	90	91
5	4-CH ₃	4 ¹ -CH ₃	2.5	91	90
6	4-OCH ₃	4 ¹ -OCH ₃	3.5	90	86
7	H	4-NH ₂	3.0	41 ^a 39 ^b	38 ^a 32 ^b
8	H	3-CH ₃	4.0	52 ^a 35 ^b	50 ^a 33 ^b

^a Aniline. ^b Substituted Anilines.

functions over NiMCM-41 catalyst. All the compounds reduced were obtained in good yields. Many functional groups such as -Cl, -Br, -CH₃, and -OCH₃ are tolerated. Furthermore, the catalyst is more effective than several other catalytic systems such as hydrazine/Raney Ni,⁹ cyclohexane/Pd on asbestos,¹⁹ and nickel-based oxide catalysts.¹⁰ Furthermore, all these systems require longer reaction times, typically 22–48 h under refluxing conditions. The NiMCM-41 catalyst was also tested for reusability and it was found

(17) In a typical CTH reaction, KOH pellets (20 mmol) were dissolved in propan-2-ol (20 mL) to which substrate (20 mmol) was added along with 100 mg of catalyst. It was then refluxed at 356 K for a few hours depending upon the nature of the substrate. The products were analyzed using a gas chromatograph fitted with an OV-101 column. For recycling purposes, the catalyst was recovered, after the first reaction, by simple filtration and washed three times with acetone followed by water, then it was dried at 373 K. This catalyst was reused for the subsequent cycles.

that it can very well be reused without affecting either the activity (see Tables 1–5) or the catalyst characteristics.²⁰ On the other hand, the use of a NiO/ZrO₂ supported system²¹ exhibited very good activity for the reduction process of nitrobenzene; it, however, showed a continuous loss in activity upon recycling and the yield was decreased drastically. Although the method described here is safer, rapid, and highly selective compared to the reduction processes with molecular hydrogen, the use of KOH, however, makes the workup procedure a bit difficult.

Acknowledgment. The authors thank RSIC, IIT-Bombay for TG, DTA, and ICP-AES data.

Supporting Information Available: Powder X-ray diffraction (XRD) patterns of NiMCM-41 catalyst before and after CTH reaction. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(18) The effect of various hydrogen donors such as primary and secondary alcohols on the CTH of nitrobenzene was performed over NiMCM-41. The former gave lower yields (ethanol/15%; propan-1-ol/66%; butan-1-ol/59) while the latter (propan-2-ol/93%; butan-2-ol/81%) gave higher yields of aniline. In addition, the dehydrogenation product is ketone, which can easily be removed from the reaction system. In the case of tertiary alcohols, e.g., 2-methylpropan-1-ol, the reaction did not proceed as there is no α -hydrogen and hence they cannot act as hydrogen donors. Therefore, in this study, we used propan-2-ol as the hydrogen donor.

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(20) The powder XRD (see Supporting Information: the diffraction patterns show all the prominent reflections characteristic of hexagonal mesoporous MCM-41 structure, and it can also be deduced from the pattern that the structure remains intact even after the recycling experiments, as no significant change in the pattern is observed) as well as N₂ adsorption data of NiMCM-41 catalyst before and after recycling (6th run) experiments indicate that the structure remains intact. However, a slight broadening of the reflections can be noticed, which may possibly be due to the finer particle size of the catalyst generated upon cycling. The unit cell parameter ($a_0 = 41.1 \text{ \AA}$) of the catalyst is nearly the same even after the 6th run. Furthermore, the mesoporous nature of this catalyst is also confirmed by N₂ sorption measurements (BET surface area = 885 m² g⁻¹, pore volume = 0.47 cm³ g⁻¹, and pore size = 30 \AA).

(21) The reduction of nitrobenzene was carried out over NiO/ZrO₂ (7.85% Ni) under identical reaction conditions, which gives >95% yield in the 1st run, and 83% yield for the 6th run.