

# Chemo- and regioselective reduction of nitroarenes, carbonyls and azo dyes over nickel-incorporated hexagonal mesoporous aluminophosphate molecular sieves

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**Abstract**—Nickel-incorporated hexagonal mesoporous aluminophosphate (NiHMA) molecular sieves were found to be highly efficient heterogeneous catalysts for the chemo- and regioselective reduction of nitroarenes and carbonyl compounds as well as the reductive cleavage of azo functions, including bulkier substrates, by the hydrogen transfer method.  
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The reduction of nitroarenes and carbonyl compounds to the corresponding amines and alcohols, respectively, is an important step in the industrial synthesis of dyes and of biologically active compounds.<sup>1</sup> In comparison to the commonly used reduction processes, which involve hazardous molecular hydrogen,<sup>2</sup> catalytic transfer hydrogenation (CTH) employing hydrogen donors, for example, propan-2-ol (Meerwein–Ponndorf–Verley (MVP) reduction), is safer, highly selective and eco-friendly.<sup>3</sup> 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 ions in solution.<sup>4</sup> However, these catalysts are not reusable due to various problems such as deactivation by metal precipitation or ligand degradation, separation difficulties, etc. On the other hand, the use of heterogeneous catalysts offers several advantages over homogeneous systems with respect to easy recovery and recycling of the catalysts as well as minimization of undesired toxic wastes. In this regard, Raney-Ni has been extensively used for heterogeneous CTH reactions.<sup>5,6</sup> Although, CTH reactions are very facile using this catalyst, they are not selective towards

functional groups such as  $-X$  ( $X =$  a halogen) and  $-\text{NO}_2$ , and almost all labile functional groups undergo reduction under these reaction conditions. Furthermore, the Raney-Ni catalyst is flammable and presents hazards during handling. Hence, attention has been focused on the design of nickel-based oxide and nickel oxide supported catalysts.<sup>7</sup> However, these catalyst systems also have several drawbacks such as long reaction times, competing nucleophilic attack, the formation of by-products, low yields and the lack of true heterogeneity, etc. In this communication, we report a very efficient, highly selective and rapid method for the reduction of nitroarenes and carbonyl compounds and the reductive cleavage of azo compounds using a nickel-containing hexagonal mesoporous aluminophosphate (NiHMA) molecular sieve catalyst.

Hexagonal mesoporous aluminophosphates (HMA)<sup>8</sup> are novel molecular sieves, analogous to mesoporous silicates,<sup>9</sup> having a high surface area, and large pore size and volume. Various transition metal ion incorporated HMA catalysts have been reported.<sup>10</sup> They can be used to carry out organic transformations more efficiently than the corresponding microporous analogues or supported metal oxide systems. Since the CTH process requires Lewis acidic sites, mesoporous NiHMA, which possesses such characteristics,<sup>11</sup> may be suited for this purpose. Hence, in this investigation, we used NiHMA for CTH reactions. The catalyst was prepared by a very simple and highly reproducible procedure<sup>12</sup> and

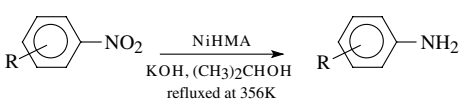
**Keywords:** Catalytic transfer hydrogenation; Nitro compounds; Carbonyl compounds; Mesoporous molecular sieves; Nickel.

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characterized using several easily available analytical and spectroscopic techniques.<sup>13</sup> The CTH reactions were carried out as per the standard procedure.<sup>14,15</sup>

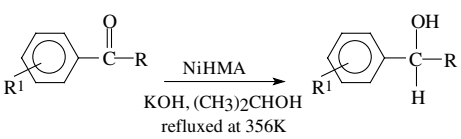
Tables 1 and 2 summarize the results of CTH of several aromatic nitro and carbonyl functions attached to an aromatic ring using the NiHMA catalyst, wherein the compounds were reduced with excellent yields to the corresponding alcohols and amines, respectively. It can be seen from Tables 1 and 2 that the activity is significantly influenced by the nature/position of the substituents on the aromatic ring. 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, did not have a significant influence on the reaction (see also Scheme 1).

**Table 1.** Reduction of nitroarenes over NiHMA

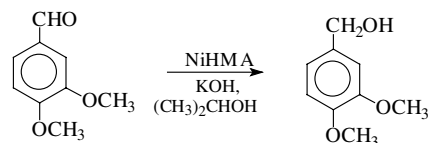


Entry	R	Time (h)	Yield (%)	
			First run	Sixth run
1	H	1.5	97	95
2	2-Cl	2.0	86	84
3	3-Cl	2.5	90	89
4	4-Cl	2.0	93	93
5	4-F	2.0	91	92
6	4-Br	2.5	93	91
7	2-CH <sub>3</sub>	1.5	82	79
8	3-CH <sub>3</sub>	2.0	90	90
9	4-CH <sub>3</sub>	1.5	89	88
10	4-OCH <sub>3</sub>	2.0	93	91
11	2-NH <sub>2</sub>	2.0	89	90
12	3-NH <sub>2</sub>	1.5	92	90

**Table 2.** Reduction of aromatic carbonyls over NiHMA



Entry	R	R <sup>1</sup>	Time (h)	Yield (%)	
				First run	Sixth run
1	H	H	2.0	90	92
2	H	2-Cl	1.5	81	79
3	H	4-Cl	1.5	89	89
4	H	4-OCH <sub>3</sub>	2.0	90	91
5	H	4-N(CH <sub>3</sub> ) <sub>2</sub>	4.0	67	65
6	H	4-CN	3.5	82	82
7	CH <sub>3</sub>	H	3.5	85	84
8	CH <sub>3</sub>	3-NH <sub>2</sub>	3.0	72	70
9	CH <sub>3</sub>	4-Cl	3.0	84	82



**Scheme 1.**

The catalyst was highly chemoselective for the reduction of nitro and carbonyl compounds, and other functional groups, viz., -F, -Cl, -Br, -OH, -CN, -NH<sub>2</sub> and -OCH<sub>3</sub>, etc. were not affected.

The catalyst also showed promise for regioselective (Table 3, entries 2 and 3) and chemoselective (Table 3; entries 5–8) reductions. Since nitro groups attached to aromatic rings can withdraw electrons more strongly in comparison to carbonyl groups, they can be adsorbed more easily onto the catalyst surface. This may explain the chemoselective reduction of a nitro group ahead of a carbonyl group. All these compounds were reduced in excellent yields affording a single product, which reduced the difficulties of separation of the products from unreacted substrates. The yields and the reaction times (1.5–4 h) for these transformations over NiHMA were encouraging from the organic synthesis point of view in terms of the practical utility of the catalyst compared to other reported catalysts (reaction time 30–50 h).<sup>16</sup> NiHMA also required less time for these conversions to achieve optimum yields, compared to mesoporous CoHMA molecular sieves. This may be due to the fact that the Lewis acid characteristics of nickel are higher than those of cobalt.

Furthermore, this reduction was also successfully carried out using heterocyclic compounds (Table 4, entries 1–3) as well as bulkier compounds (Table 4, entries 4–6) with high yields being obtained. Table 5 presents the results of the rapid (1–2 h) reductive cleavage of azo functions over the NiHMA catalyst in good yields (~90%). It is interesting to note that the cleavage of azo compounds over NiHMA is rapid (1–2 h) compared to other catalysts used for this purpose.<sup>17</sup> Unlike palladium-based catalysts, many functional groups such as -Cl, -Br and -OCH<sub>3</sub> were tolerated over NiHMA.<sup>18</sup> The Pd-based catalysts also gave poor yields due to the formation of intermediate hydrazo compounds, which were not observed when using NiHMA. Furthermore, the catalyst showed true heterogeneity for all the above substrates over six cycles. In contrast, the use of the NiO/ZrO<sub>2</sub> supported system<sup>18</sup> exhibited very good activity for the reduction of nitrobenzene, however, it showed a loss in activity upon recycling and the yield decreased drastically. Isopropanol was found to be the best hydrogen donor compared to the others.<sup>19</sup>

The reaction mechanism for the reactions under study may relate to the MPV reduction of ketones that were reported using aluminium isopropoxide.<sup>20</sup> Accordingly, adsorption of propan-2-ol onto the catalyst is followed by the formation of an alkoxide, which is also known to

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