Chinese Chemical Letters Vol. 16, No. 4, pp 531-533, 2005
http://www.imm.ac.cn/journal/ccl.html

A Novel Catalyst for Liquid Phase Hydrogenation of *m*-Dinitrobenzene to *m*-Phenylenediamine

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Abstract: A novel lanthana-promoted nickel catalyst supported on silica for the liquid phase hydrogenation of *m*-dinitrobenzene to *m*-phenylenediamine was prepared by an incipient wetness sequential impregnation method. It was found that Ni-La/SiO_2 catalyst exhibited high activity and stability for *m*-dinitrobenzene hydrogenation. Over this catalyst, the conversion of *m*-dinitrobenzene and the yield of *m*-phenylenediamine were up to 97.1% and 93.5%, respectively, at 373 K and 2.6 MPa hydrogen pressure after reaction for 1 h.

Keywords: Nickel catalyst, lanthana, hydrogenation, *m*-phenylenediamine, *m*-dinitrobenzene.

m-Phenylenediamine is an important raw material for chemicals and intermediates. Traditionally, *m*-phenylenediamine is manufactured by iron powder reduction. However, this method has shortcomings of higher cost, lower yield and seriously environmental pollution from residue, so that is strictly limited in many countries. Recently, much attention has been paid to the catalytic hydrogenation technique of *m*-dinitrobenzene in the liquid phase owe to its high product yield, mild reaction conditions and much less pollution to environment[1]. The hydrogenation is usually carried out over Raney Ni or the supported noble metal catalysts[2-5]. In our earlier studies[6], Ni/SiO_2 catalyst prepared by impregnation method showed high performance for *m*-dinitrobenzene hydrogenation. On the basis of these results, the liquid phase hydrogenation of *m*-dinitrobenzene to *m*-phenylenediamine over lanthana-promoted nickel catalyst was investigated in order to find a catalyst with much better catalytic activity for *m*-dinitrobenzene hydrogenation.

Ni-La/SiO_2 catalyst was prepared by an incipient wetness sequential impregnation method in which La_2O_3 was impregnated on SiO_2 (surface area=432 m^2/g) before nickel. The nitrate salt was used as the metal precursor. After being dried at 383 K overnight, the catalyst was then calcined at 773 K for 4 h in air. The reference catalyst Ni/SiO_2

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was prepared by the impregnation method, dried at 383 K and calcined at 773 K. The amounts of Ni and La were 20 wt% and 3 wt%, respectively. *Prior to* the hydrogenation of *m*-dinitrobenzene, the catalyst samples were reduced at 723 K for 2 h under hydrogen stream, and then cooled to room temperature under nitrogen atmosphere.

The liquid phase hydrogenation of *m*-dinitrobenzene was carried out in a 250 mL stainless steel autoclave at 373 K and 2.6 MPa hydrogen pressure using 2.72 g *m*-dinitrobenzene, 100 mL ethanol and 0.272 g catalyst. Samples were withdrawn at appropriate intervals and analyzed using gas chromatograph, which was equipped with flame ionization detector (FID) and a 2 m × 3 mm stainless steel column packed with 10% OV-1 on Chromosob W-HP (80-100 mesh). The temperature of chromatograph chamber was controlled at 493 K.

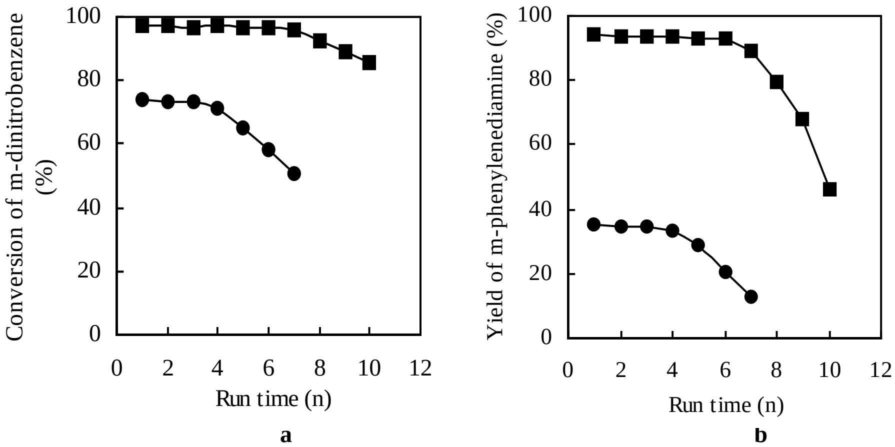
Table 1 shows the catalytic properties of Ni/SiO_2 and $Ni\text{-}La/SiO_2$ catalysts for the hydrogenation of *m*-dinitrobenzene. It can be seen that $Ni\text{-}La/SiO_2$ catalyst exhibited higher activity than Ni/SiO_2 catalyst. Under the reaction conditions used, after reaction for 1 h the conversion of *m*-dinitrobenzene and the yield of *m*-phenylenediamine were up to 97.1% and 93.5%, respectively. In contrast, in the case of Ni/SiO_2 catalyst, only 73.6% of *m*-dinitrobenzene conversion and 35.0% of *m*-phenylenediamine yield were obtained after reaction for 1 h at the same reaction conditions.

Table1 The results of *m*-dinitrobenzene hydrogenation over Ni/SiO_2 and $Ni\text{-}La/SiO_2$ catalysts after reaction for 1 h

Catalyst	*m*-Dinitrobenzene conversion (%)	*m*-Phenylenediamine yield (%)
Ni/SiO_2	73.6	35.0
$Ni\text{-}La/SiO_2$	97.1	93.5

Reaction conditions: p (H_2) = 2.6 MPa, T = 373 K, catalyst 0.272 g, *m*-dinitrobenzene 2.72 g, EtOH 100 mL.

Figure 1 Conversion of *m*-dinitrobenzene **(a)** and yield of *m*-phenylenediamine **(b)** *versus* run time of the catalysts.



a **b**

■ $La\text{-}Ni/SiO_2$, ● Ni/SiO_2. Reaction conditions: p (H_2) =2.6 MPa, T=373 K, *m*-dinitrobenzene 2.72g, EtOH 100 mL, catalyst 0.272 g, reaction time 1 h.

The stability is another important factor for practical use of the catalyst. The variations of *m*-dinitrobenzene conversion and *m*-phenylenediamine yield *versus* run time over Ni-La/SiO_2 and Ni/SiO_2 catalysts are presented in **Figure 1(a)** and **(b)**, respectively. It can be seen that Ni-La/SiO_2 catalyst did not show any significant deactivation after run six times. When consecutively run seven times, slight deactivation was observed over Ni-La/SiO_2 catalyst, while the catalyst still showed high catalytic performance with the yield of *m*-phenylenediamine 89%. For the reference catalyst Ni/SiO_2, after seven times recycle, the *m*-dinitrobenzene conversion and *m*-phenylenediamine yield decreased to 50.6% and 12.7%, respectively. This result suggested that the addition of rare-earth La_2O_3 could increase the stability of the nickel-based catalyst remarkably.

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Received 9 March, 2004