DOI: 10.1002/adsc.201000514

An Efficient Hydrogenation of Dinitrile to Aminonitrile in Supercritical Carbon Dioxide

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Received: June 30, 2010; Published online: September 30, 2010

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201000514.

Abstract: The highly selective hydrogenation of adiponitrile proceeds effectively in supercritical carbon dioxide ($scCO_2$) to produce 6-aminocapronitrile with excellent selectivity of 100% over rhodium/alumina (Rh/Al_2O_3) and without any additive, which is impossible in classical organic solvents. The presence of CO_2 can be beneficial or mandatory for the exclusive formation of the aminonitrile as it can act as a solvent to enhance the activity and also as temporary protecting agent to increase the selectivity. These results successfully show the general concept of using $scCO_2$ as a protective medium for the selectivity control of dinitrile to aminonitrile reactions. Recycling of the catalyst and further extension of this method to other dinitriles were also investigated.

Keywords: adiponitrile; 6-aminocapronitrile; heterogeneous catalysis; hydrogenation; supercritical carbon dioxide

Nylon-6 and Nylon-6,6 are two commercial polyamides and account for more than 95% of the total amount of nylon used in the world.[1] Between them, Nylon-6 covers 60% of this amount and is industrially prepared from a monomer called caprolactam, which is obtained *via* a traditional cyclohexanone process. The cyclohexanone process is costly and environmentally hazardous due to the generation of large amounts of ammonium sulfate.[2] Therefore, a greener method has been established for the formation of caprolactam from 6-aminocapronitrile (ACN); a partial hydrogenation product of adiponitrile (ADN). Recently, BASF AG (Germany) patented a novel synthesis method to convert ACN to caprolactam.[3]

The hydrogenation of ADN is important as reflected from the large number of literature reports.[4] However, most of the studies are related to the formation of hexamethylenediamine (HMD) and are performed in conventional organic solvent using high hydrogen pressures, large amounts of NH_3 and various metal catalyst.[5–8] The main problem associated with the formation of an aminonitrile through dinitrile hydrogenation is the formation of secondary and tertiary amines as by-products. Generally, the nylon industry requires a high level of purity for the ACN product because the presence of a by-product in the ppm level could cause a defect to the nylon thread. Thus, several attempts have been made to achieve only ACN *via* ADN hydrogenation. For instance, Rh embedded in PVP was described as a highly selective catalyst to the formation of ACN (85%), but conversion was low (33%).[9] Again, Mares et al.[10] found that in the neat NH_3 medium, Rh/MgO was selective for ACN (selectivity 94.1%; conversion 70%) production. Instead of NH_3, Alini et al.[8] used NaOH and claimed 99% selectivity of ACN with 60% conversion over Rh/Al_2O_3 prepared by an ion exchange technique. However, to the best of our knowledge, no attempt has been made to perform the selective hydrogenation of ADN in supercritical carbon dioxide, to exploit its potential as a temporary protecting agent for the amino group.

Supercritical carbon dioxide ($scCO_2$) is an alternative "green" reaction medium and is receiving continuous attention from academic and also industrial researchers. The unique properties of CO_2 such as nontoxicity, high diffusivity, variable solvency, mass transport capability and complete miscibility with other gases (attractive when one of the reactants is a gas) are highly suitable for environmentally benign chemical synthesis. It is considered a most promising reaction medium for the rapid and selective hydrogenation promoted by homogeneous and heterogeneous

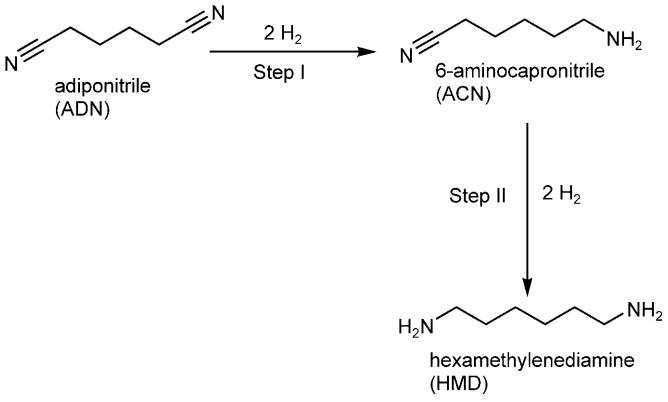
catalysts.[11] In addition, it can play an important role in the stabilization of the reaction intermediate and often has a decisive influence on the selectivity of a particular reaction.[12]

The hydrogenation of nitrile to amine in $scCO_2$ is advantageous because amines can react with CO_2 to form carbamic acid or carbamates and some of them can be isolated in solid form. As a result of the interaction between a sufficiently basic amine group and CO_2, the nucleophilicity of the nitrogen atom is decreased and this makes it less reactive in CO_2.[13] This criterion of CO_2 can be used as a temporary protecting agent to "mask" an amino group for further reaction and, consequently, control the product distribution.[15]

The aim of this work was to study the selective formation of ACN by the hydrogenation of ADN in CO_2 to avoid the cost of purification from HMD; a deep hydrogenated product. The described method is free from using NH_3 or NaOH-like additives or any organic solvent.

Scheme 1 depicts the reaction path of the hydrogenation of ADN. At first one of the −CN groups of ADN is hydrogenated to ACN followed by the formation of HMD through the hydrogenation of both of the −CN groups. However, under the present reaction conditions in $scCO_2$ only ACN was formed. No other products were detected as confirmed by GC-MS and NMR techniques (please see Supporting Information for details).

The hydrogenation of ADN was performed using different supported noble metal catalysts that are generally used in the hydrogenation of nitriles. Our results are summarized in Table 1. It has to be mentioned that, independent of the catalyst used, ACN was the only product detected. However, the conversion of ADN is strongly based on the nature of the metal ion. For example, with Pd/C (entry 1), Pt/C (entry 3) and Rh/C (entry 5), although they possess almost the same dispersion of 12–16%, the activity



Scheme 1. Reaction scheme for adiponitrile (ADN) hydrogenation.

Table 1. Various supported metal catalysts used for the hydrogenation of ADN in $scCO_2$.[a]

Entry	Catalyst	Conversion [%]	Dispersion[b] [%]
1	5% Pd/C	3.9	12.1
2	5% Pd/Al_2O_3	5.7	17.0
3	5% Pt/C	1.9	16.2
4	5% Pt/Al_2O_3	10.2	15.4
5	5% Rh/C	69.8	16.0
6	5% Rh/Al_2O_3	96.6	27.0
7	5% Rh/Al_2O_3	96.8	–
8	5% Rh/Al_2O_3	96.2	–
9	5% Rh/Al_2O_3	95.0	–
10	5% Rh/Al_2O_3	89.2	–
11[c]	5% Rh/Al_2O_3	70.1	–

[a] Reaction conditions: catalyst = 0.1 g, substrate = 1.2 g, P_{CO_2} = 8 MPa, P_{H_2} = 4 MPa, temperature = 80 °C, time = 6 h; entries 7–10 showing 1st, 2nd, 3rd and 4th recycles; catalysts from entries 1–5 are from Aldrich, entry 6 is from Wako.

[b] Approximate expression of metal dispersion = 0.9/diameter (in nm); [see: M. Boudart, G. Djega-Mariadassou, *Kinetics of Heterogeneous Catalytic Reaction*, Princeton University Press: Princeton, NJ, **1984**].

[c] In ethanol, the products were ACN (75.6%) and HMD (24.4%).

varied widely; Pd and Pt catalysts exhibit very poor conversion within the range of 1–10% (Table 1; entries 1–4), whereas Rh-containing catalysts (Table 1 entries 5 and 6) exhibit high efficiency towards ADN hydrogenation. It is evident that 5% Rh/Al_2O_3 (Table 1; entry 6, conversion = 96.6%) shows the best activity in comparison with 5% Rh/C (entry 5; conversion = 89.8%). Therefore, Rh/Al_2O_3 has been employed to study the different optimization parameters like CO_2 and H_2 pressure, reaction time and temperature to reach the targeting parameter of maximum conversion as ACN was the only product formed.

Figure 1 depicts the effect of CO_2 pressure on the conversion of ADN. Independent of the CO_2 pressure, ACN was the only product formed. When the pressure was increased from 6–8 MPa the conversion changes from *ca.* 46% to 96.6%, and then started to decrease as the pressure reached more than 12 MPa. The conversion of ADN dropped to 20% at the higher pressure of 20 MPa. This interesting effect of increased conversion at low CO_2 pressure is most likely attributed to the shifts of partition coefficient of the substrate in favour of the liquid phase and thus an increasing availability of substrate in the vicinity of the catalyst. This explanation is supported by the observation that, at higher pressure, when the amount of the substrate in CO_2 phase is higher than in the liquid phase, conversion was decreased. Notably, the hydrogenation of ADN under the same conditions, but without CO_2 gave $<20\%$ conversion (Figure 1) with

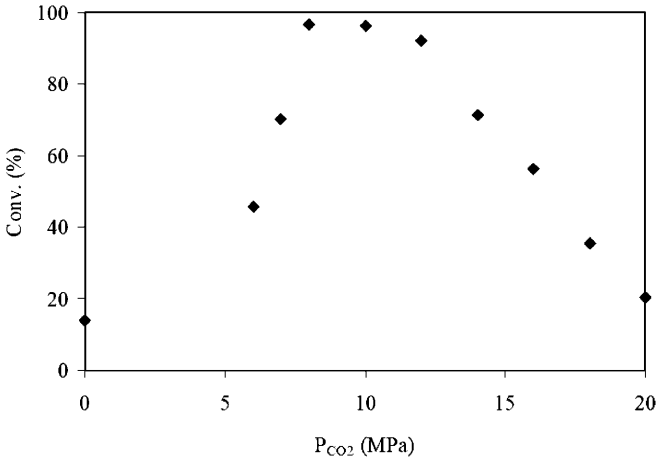


Figure 1. Effect of CO_2 pressure on ADN conversion; in each case the selectivity of ACN was 100%. *Reaction conditions:* catalyst = 0.1 g, substrate = 1.2 g, P_{H_2} 4 MPa, temperature = 80 °C, time = 6 h.

the formation of the mixture of ACN (44.7%) and HMD (55.3%). Again, in ethanol also ACN (75.6%) and HMD (24.4%) were produced with the ADN conversion of 70% being comparatively lower than that in CO_2. These observations suggested that CO_2 is playing an important role to dictate the product distribution. To explain the formation of only ACN in CO_2, the phase behaviour of ACN (Figure 2) in the presence of CO_2 was studied at 80 °C using a view cell. A clear change was detected through the visual observation before (Figure 2, a) and after (Figure 2, b) the introduction of 8 MPa of CO_2, which reveals the possible formation of carbamic acid due to the interaction of the amine group with CO_2. Once one nitrile group has been reduced to an amine, it rapidly reacts with CO_2 to produce carbamic acid and effectively removes the second nitrile group from the reaction and stops further reaction, which explains the high selectivity of ACN. Figure 2c also confirms the regeneration of ACN after depressurization of CO_2. However, in the liquid phase hydrogenation of a dinitrile compound, Hoffer et al. observed that co-adsorption of two nitrile groups of the substrate is unlikely. So, one of the nitrile groups is first selectively hydrogenated to amine, and there would be an enhanced competition between dinitrile and aminonitrile for same active site because of the presence of similar groups and a mixture of the products might be expected.[15]

Experimental runs were carried out for ADN hydrogenation by varying the reaction time at a constant temperature of 80 °C and fixed pressures of CO_2 and H_2 (Figure 3).

According to the results, the conversion of ADN was poor in the beginning (*ca.* 10–20%) and then started to increase with time. The maximum conversion of 96.6% was reached within 6 h. An attempt was made to achieve complete conversion with an extension of the reaction time to 24 h, but no further enhancement of ADN conversion was observed. These results might be related to the (i) deactivation of the catalyst or (ii) reactant and the product are strongly competitive to each other for thesame active sites. In a primary observation on the kinetics of adiponitrile hydrogenation under studied conditions, the data in Figure 3 are consistent with the Langmuir–Hinshelwood kinetic law, derived on the basis of the reaction (1) (please see Supporting Information for details).

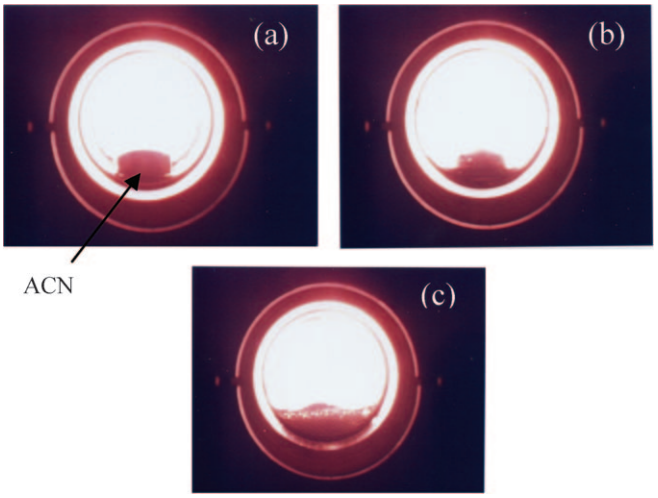


Figure 2. View cell observation of ACN in CO_2; (**a**) before introduction, (**b**) after the incorporation of 8 MPa of CO_2 and (**c**) during depressurization.

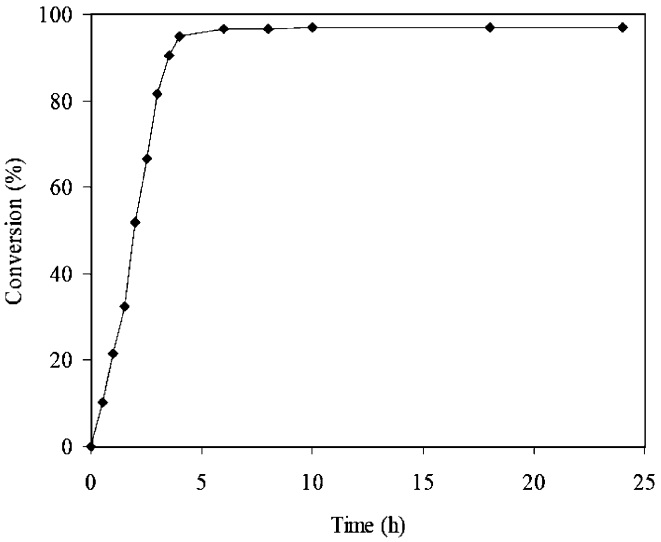


Figure 3. Effect of reaction time on ADN conversion; in each case the selectivity of ACN was 100%. *Reaction conditions:* catalyst = 0.1 g, substrate = 1.2 g, P_{CO_2} = 8 MPa, P_{H_2} = 4 MPa, temperature = 80 °C

A plot of experimental against calculated conversion showing very good agreement (Supporting Information, Figure S2) and the obtained ratio of adsorption constant of the substrate and product ($K_{ADN}/K_{ACN}=3.12$) indicated the preferential adsorption of ADN on the catalytic site rather than ACN as both of them are competing for the same active site, which explains the constant conversion after a certain period of reaction time. In the liquid phase hydrogenation of ADN over similar a Rh/Al_2O_3 catalyst, further hydrogenation of ACN to HMD was reported.[7] However, no significant effect on the selectivity of ACN was found, after the prolonged reaction time of 24 h, which again suggested the amine protection by CO_2.

The conversion profile of the ADN hydrogenation also shows a strong dependence on the hydrogen pressure at fixed temperature and CO_2 pressure. An increase in hydrogen pressure from 1 to 4 MPa, increases the surface concentration of H_2 according to the Langmuir isothermal equation. Consequently, the conversion was enhanced from 28.4% to 96.6% and remained constant above 4 MPa, which could account for the promoting effect of H_2 on the reaction rate. However, the selectivity of the reaction was unaffected. Thus, an optimized H_2 pressure of 4 MPa was used in the current condition. Moreover, in a dense CO_2 atmosphere, at a fixed total pressure (CO_2+H_2) of 12 MPa ($CO_2/H_2=11/1$, 10/2, 9/3 and 8/4) a variation in the conversion from 11.2 to 96.6% of ADN was observed attributed to the positive effect of hydrogen pressure on the ADN conversion.

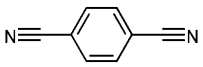
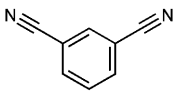
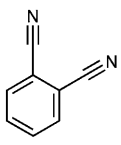
The effect of temperature is an integral part of the hydrogenation in $scCO_2$ because it is related to the density of the medium and the solvent properties. The positive influence of the temperature was also clearly observed on ADN hydrogenation. The reaction was conducted at 35, 50, 60, and 80 °C at the fixed pressure of CO_2 (8 MPa) and H_2 (4 MPa). At low temperature (35 °C), the conversion was very low (5.2%). An increase in the system temperature from 50 to 80 °C favours the conversion of ADN from 52.5% to 96.6% and remains constant until 90 °C. However, the selectivity of the product remains unaltered. To explain the influence of temperature on the hydrogenation of ADN is not very easy because it may affect the reaction in different ways. An increase in temperature would have a positive effect on the kinetic constant as defined by the transition state theory. On the other hand, temperature would have changed the density of the medium and thus the solubility of the reactant. Hence, the effect of temperature has been checked at fixed fluid density rather than at a specified constant pressure. Therefore, the phase behaviour of ADN at 35 °C (8.5 MPa, $d=0.61\ g\,mL^{-1}$) and 80 °C (20 MPa, $d=0.59\ g\,mL^{-1}$)[16] was studied (please see Supporting Information for details, Figure S3), which revealed a single phase for the ADN-CO_2-H_2 system. Under similar conditions, the ADN conversion was changed from *ca.* 5% to 20% (Figure 1) as the temperature changed from 35 °C to 80 °C. So, in this case it is better to suggest that the temperature has a straightforward effect on the conversion, and it is very difficult to predict the actual reason behind the increased conversion with temperature in CO_2 medium.

Recycling is the most important advantage for heterogeneous catalysts. After the reaction, the catalyst can be separated easily by filtration for reuse. The results of recycling are shown in Table 1 (entries 7–10), suggesting the possible reuse of the catalyst. Therefore, the catalyst deactivation that is generally caused by the blocking of the metal sites in nitrile hydrogenation could be prevented in CO_2.

This method was also applied to the hydrogenation of terephthalonitrile, isophthalonitrile and phthalonitrile containing two −CN groups with *para*-, *meta*- and *ortho*-positions with respect to each other, respectively, under similar reaction conditions and the results are presented in Table 2. All the compounds selectively produced their corresponding aminonitriles. The lowest activity was observed for the *ortho*-compound which has been attributed to a steric effect.[17] The presented result is again supported by the adsorption of only one nitrile group to the catalyst and the selective formation of aminonitrile.

In conclusion, the present study has demonstrated that it is possible to achieve complete selectivity for the aminonitrile in $scCO_2$. The system is free from any additive and the use of any organic solvent. The product can be isolated easily. Recycling of the studied catalyst was opposed by the deactivation. This method is also shows its successful application to other isomeric dinitrile compounds. The described

Table 2. Hydrogenation of different dinitrile substrates

Entry	Substrate	Conversion [%]	Yield[a] [%]	TOF[b]
1		95.9	94.2	1069.6
2		60.1	53.1	679.2
3		51.1	32.6	570.0

[a] Yield of the corresponding aminonitrile. *Reaction conditions:* substrate = 1.0 g, catalyst = 0.1 g, $P_{CO_2}=8$ MPa, $P_{H_2}=4$ MPa, temperature = 80 °C, time = 6 h.

[b] Turnover frequency (TOF) = no. of moles reacted/moles of metal × time.

process could be highly relevant to develop clean and green methodology for aminonitrile formation leading to the synthesis of caprolactam, which is a future target.

Experimental Section

Materials

Adiponitrile, terephthalonitrile, isophthalonitrile and phthalonitrile (Aldrich) were used as received. Carbon dioxide (>99.99%) was supplied by Nippon Sanso Co. Ltd. All catalysts were reduced in H_2 at 300 °C for 2 h prior to the reaction.

Catalytic Activity

The hydrogenation of adiponitrile was studied at 80 °C over 5% Rh/Al_2O_3 catalyst. All reactions were carried out in a 50-mL stainless steel batch reactor placed in a hot-air circulating oven and the details are given elsewhere.[12] Briefly, 0.1 g of catalyst and 1.2 g of the reactant were introduced in the reactor. After the required temperature had been attained, H_2, followed by CO_2, were charged into the reactor using a high-pressure liquid pump and then compressed to the desired pressure. The crude liquid product was separated from the catalyst simply by filtration using Minisart RC 15 single-use syringe filters. After that the product was subjected to structural characterization using NMR and FT-IR (Please see Supporting Information for details). Finally, the selectivity of the product was analyzed by GC/MS and GC. It has to be mentioned that for NMR analysis, after the reaction $CDCl_3$ was added to the product catalyst mixture and separated from the solid catalyst as described above.

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