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Citation	Green Chemistry, 13(3), 570-572 https://doi.org/10.1039/c0gc00246a
Issue Date	2011-03
Doc URL	https://hdl.handle.net/2115/47798
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Type	journal article
File Information	GC13-3_570-572.pdf

An Effective Medium of H_2O and Low-presure CO_2 for the Selective Hydrogenation of Aromatic Nitro Compounds to Anilines

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Chemoselective hydrogenation of water-insoluble aromatic nitro compounds can be achieved over Ni catalysts in a H_2O–compressed CO_2 system at 35–50°C without using any environmentally harmful solvent. The effective CO_2 pressure is much lower than the critical pressure of CO_2. The hydrogenation of nitro group should be the rate-determining step.

The selective hydrogenation of aromatic nitro compounds to the corresponding anilines is an industrially important reaction.[1] The proposed reaction pathways (Scheme 1) include direct (I–II–III and IV–III) and indirect (VI–VII–VIII–IX) routes.[2] The reduction of PHA to AN is the common rate-determining step in the direct route.[2] The authors studied the hydrogenation of nitrobenzene (NB) and chloronitrobenzene (CNB) over supported Ni catalysts in compressed CO_2.[3] The use of compressed CO_2 and supported Ni catalysts is effective for producing the aniline compounds with almost 100% selectivity in the whole range of conversion. The rate of hydrogenation depends on CO_2 pressure and is maximized at high pressures of ca. 9–12 MPa.[3] Here, we report that the combination of H_2O and CO_2 is more beneficial for these selective hydrogenation reactions and the effectiveness of CO_2 pressurization can appear at a lower pressure of 0.8 MPa. The rate-determining step is the transformation of NB in the present reaction instead of the hydrogenation of PHA.
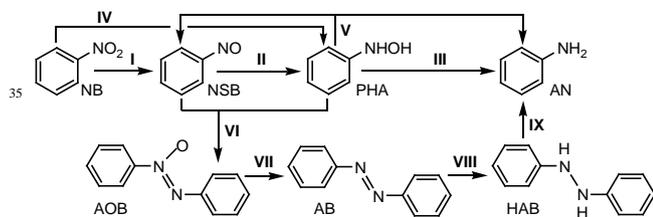

Scheme 1 Possible reaction pathways for the reduction of nitrobenzene.
NB: nitrobenzene, NSB: nitrosobenzene, PHA: *N*-phenylhydroxylamine, AN: aniline, AOB: azoxybenzene, AB:azobenzene, HAB: hydrazobenzene.

Fig. 1 gives the results of NB hydrogenation in different reaction media using a 41 wt-% Ni/Al_2O_3 catalyst (the details of catalyst preparation and hydrogenation run are given in ESI). The influence of CO_2 pressure on the conversion of NB depends on the medium used (Fig. 1a). In the absence of CO_2, the conversion was larger in ethanol and *n*-hexane (66% and

29%) than that in H_2O and solvent-less NB (6% and 3%). However, the conversion was significantly enhanced when the H_2O–NB mixture was compressed by CO_2 at a low pressure such as 0.8 MPa; the conversion was comparable to that obtained in the supercritical 12 MPa CO_2–NB mixture. For the H_2O–NB, the conversion gradually increased with CO_2 pressure up to 17 MPa. The pressurization with CO_2 had a drastically negative impact and a slightly positive effect on the conversion of NB in ethanol and in *n*-hexane, respectively. Note that the selectivity to AN was almost 100% in the whole range of conversion for the reactions in $scCO_2$, CO_2–*n*-hexane, and CO_2–H_2O systems. In ethanol and *n*-hexane, undesired PHA and AOB were formed in large quantities, resulting in small yields of the desired product of AN (Fig. 1b and Fig. S1 in ESI). Hence, the combination of H_2O–CO_2 medium and Ni catalyst is a better reaction system for the selective hydrogenation of NB to AN under mild conditions (low temperature and CO_2 pressure) without any organic solvent.
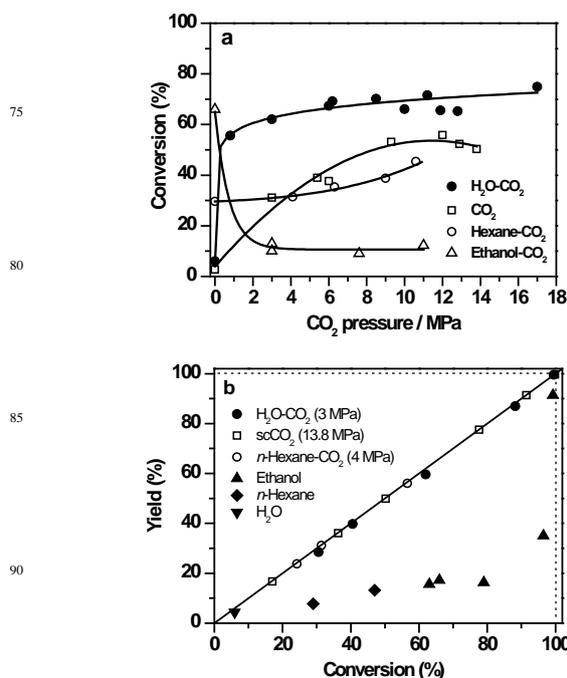
Fig. 1 (a) Influence of CO_2 pressure on the conversion of NB after 30 min reaction and (b) the yield of AN against the conversion of NB in different reaction systems. (Ni/Al_2O_3 0.1 g, NB 19.5 mmol, H_2 6 MPa, 50°C)

To examine the features of our H_2O–CO_2 reaction media, hydrogenation runs were conducted with NB, NSB, and PHA in H_2O and H_2O–CO_2 systems (Table 1). In both systems, the rate of hydrogenation followed the order PHA > NB > NSB. For NB hydrogenation in pure H_2O, the selectivity to AN was ca. 62% and NSB and AOB were the main byproducts (entry 1). In the H_2O–CO_2 system, however, the selectivity to AN was 95%; NSB and AOB were little formed in the hydrogenation of NB (entry 4) although the conversion of NSB was very slow (entry 5). It is likely, therefore, that in this H_2O–CO_2 system the NB transforms directly to PHA and this step is the rate-determining one. The couping of NSB and PHA should be suppressed due to their low concentrations. In pure H_2O, in contrast, the NB should also change to PHA via NSB in addition to the direct transformation to PHA. The coupling reaction bewteen NSB and PHA is also possible to occur.

Table 1 Hydrogenation of NB, NSB, and PHA[a]

Entry	Medium	Substrate	Conv. (%)	Selectivity (%)[b]		
				AN	NSB	PHA
1	H_2O	NB	21	61.9	9.0	1.9
2		NSB[c]	8	20.4		-[d]
3		PHA	100‡	94.6	-[d]	
4	H_2O–CO_2 (3 MPa)	NB	55	95.1	2.4	2.4
5		NSB	13	36.9		-[d]
6		PHA	100‡	95.3	-[d]	

[a] Conditions: H_2O 10 cm^3, Ni/Al_2O_3 0.1 g, substrate 9.75 mmol, H_2 6 MPa, 50°C, 10 min. [b] The other byproduct was AOB. [c] 30 min. [d] Not detected.

The molecular interactions of H_2O with a hydrophilic intermediate of PHA were examined by FTIR (experimental details are in ESI). Fig. 2 shows a slight red-shift of $v(NO)$ in the H_2O compared to that in the gas phase. The N–O bond of PHA is weakened through interactions with H_2O, possibly via OH···O and OH···N bonding.[4] Several authors reported the promotion effects of H_2O on the hydrogenation of aromatic nitro compounds in organic solvents, but the reasons are still unclear.[5] Now, the results of Table 1 and Figurte 2 allow us to propose that H_2O can promote the reaction step III accepted as the rate-determining step in organic solvents, enhancing the reaction rate and the selectivity to aniline.
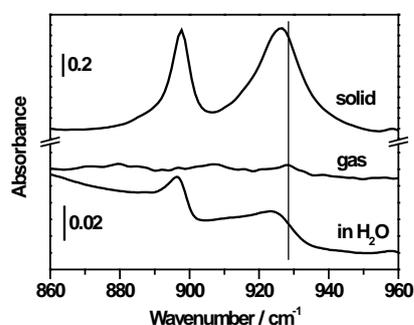
Fig. 2 FTIR spectra of PHA in the $v(NO)$ region.

To further inspect the features of the present H_2O–CO_2

system, NB was hydrogenated in a H_2O–compressed N_2 (7 MPa) medium, but no positive effects on the conversion and the selectivity to AN were observed. It is known that CO may be formed via the reverse water gas shift reaction during hydrogenation reactions in the presence of H_2 and CO_2.[6] Although no CO was detected for the gas phase by GC analysis in our reaction, an attempt was made to add 0.2 MPa 9.9%CO/He into the reaction mixture of NB–H_2O–CO_2 (3 MPa). This was found to cause a significant decrease in the conversion from 62% to 15%. Thus, in the present hydrogenation reactions, the formation of CO was unlikely.

The enhancement of NB conversion in NB–H_2O–CO_2 system can be explained by a few different factors. CO_2 is soluble in H_2O, its mole fraction being 0.25% and 2.0% at 0.8 and 9.4 MPa, respectively, at 50°C.[7] The dissolution of CO_2 enhances the solubility of a gaseous reactant H_2 in the H_2O and NB phases. The H_2O phase of H_2O–CO_2 mixture was acidic (ca. pH 3[8]). A reaction run was also conducted in a 0.8 mol dm^{-3} $NaHCO_3$ buffered H_2O solution at 3 MPa CO_2 (pH > 6[8b]); the conversion (48%) was slightly lower than that in the unbuffered system (62%), while the high selectivity to AN did not change. $NaHCO_3$ can also be hydrogenated to $NaHCO_2$ with Ru complex or supported Pd catalyst;[9] but supported Ni catalysts do not give significant $NaHCO_2$ concentrations.[9a] When the concentration of $NaHCO_3$ was changed from 0.8 to 0.2 mol dm^{-3}, the hydrogenation of NB gave the same conversion, indicating that the influence of $NaHCO_3$ hydrogenation on the reaction of NB is marginal in our systems. Thus, the acidic nature of the H_2O phase might be one of positive factors, but its effect is small. Our previous *in situ* FTIR show that compressed CO_2 interacts with the reacting species, NB, NSB, and PHA, decreasing the reactivity of NB but increasing the reactivity of NSB and PHA.[3] These molecular interactions should also be important in the H_2O–CO_2–NB reaction system. In addition, the solid catalyst granules were well dispersed in the H_2O phase but not in the NB phase, due to hydrophilic nature of the oxide support materials (Fig. S2 in ESI). NB is sparingly soluble (ca. 17 mmol dm^{-3} at 25°C) and PHA is soluble in H_2O (ca. 82 mmol dm^{-3} in saturated salt solution at 0°C[10]). Therefore, the hydrogenation of NB and PHA is likely to occur at the NB–H_2O interfacial layer and in the H_2O phase. In the H_2O-CO_2 system, the rate of AN formation is controlled by the conversion of NB into PHA. Interfacial H_2O and NB molecules form hydrogen bonding, OH···ONO,[11] which may weaken the N–O bond of NB. Previously, a striking rate increase was observed in some reactions on water and this was ascribed to the H bonds between interfacial water molecules and reactants or transition state.[12] In addition, da Rocha et al. studied the molecular structure of the H_2O–compressed CO_2 interface and observed excess accumulation of the fluids on both sides of the interface.[13] The local density enhancements can have a large impact on the chemical reactions.[14]

After the reaction, the H_2O phase was easily separated from the organic product phase. This H_2O phase containing 0.35 mol dm^{-3} AN was further used for the second reaction, giving the same results as that using pure H_2O. Hence, the H_2O phase can be recyclable without any post-purification, which is of

practical significance.

Furthermore, the potential of the H_2O–CO_2 medium was examined for the hydrogenation of chloronitrobenzne (CNB) at 35°C, which is less soluble in H_2O than NB. A 9 wt-% or 16 wt-% Ni/TiO$_2$ catalyst was used since the selectivity to chloroaniline (CAN) was slightly better than that obtained with the Ni/Al$_2$O$_3$ (Table S1 in ESI). Fig. 3a shows the conversion of o-CNB over 9 wt-% Ni/TiO$_2$ as a function of CO_2 pressure for the reaction mixtures in the presence and absence of H_2O. One can see again that the H_2O significantly promoted the hydrogenation of o-CNB similar to NB but the conversion increased with CO_2 pressure through to 13 MPa. The positive effect of H_2O was also observed in the hydrogenation of m- and p-CNB over 16 wt-% Ni/TiO$_2$. In Fig. 3b the yield of CAN is plotted against the total conversion of o-, m-, and p-CNB substrates (the change of conversion and selectivity with reaction time is shown in ESI Fig. S3). For all the isomers, no dehalogenation and coupling occurred and so the selectivity to CAN was almost 100% at any conversion, confirming the effectiveness of the present reaction system including H_2O and low-pressure CO_2 for the selective hydrogenation of aromatic nitro compounds to anilines.
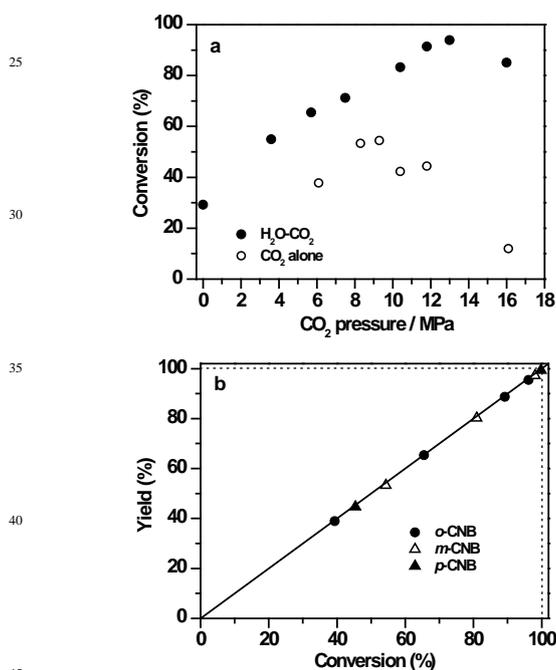
Fig. 3 (a) Influence of CO_2 pressure on the conversion of o-CNB over 9 wt-% Ni/TiO$_2$ after 50 min of hydrogenation in the systems of H_2O–CO_2 and compressed CO_2 alone; (b) CAN yield against CNB conversion during the hydrogenation of CNB isomers in the H_2O–CO_2 (6 MPa) system. (CNB 9.52 mmol, Ni/TiO$_2$ 0.15 g, H$_2$ 4 MPa, 35°C)

In conclusion, the interactions of CO_2 and H_2O with the reacting species, the *in situ* formed acidity, and the better dispersion of Ni catalyst in the H_2O phase are responsible for the fast and selective hydrogenation of NB in the H_2O–CO_2 system, in which the conversion of NB into PHA may be the rate-determining step.

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental procedures, phase behavior observations, and hydrogenation data. See DOI: 10.1039/b000000x/

‡ PHA decomposed partly into NSB, AN, and AOB during GC analysis (Fig. S4 in ESI). Both PHA and NSB were not detected during GC analysis of the product, indicating PHA is consumed completely after 10 min of reaction. The total pressure in the reactor dropped to a constant value in 6-8 min, further confirming the complete conversion of PHA.

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