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An effective medium of H₂O and low-pressure CO₂ for the selective hydrogenation of aromatic nitro compounds to anilines†

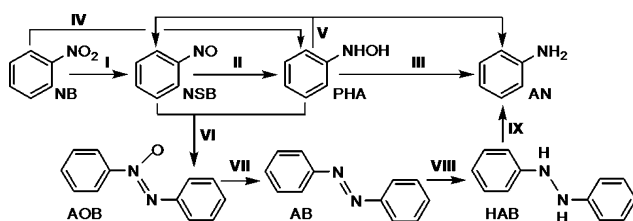
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Chemoselective hydrogenation of water-insoluble aromatic nitro compounds can be achieved over Ni catalysts in a H₂O-compressed CO₂ system at 35–50 °C without using any environmentally harmful solvent. The effective CO₂ pressure is much lower than the critical pressure of CO₂. 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 CO₂.³ The use of compressed CO₂ and supported Ni catalysts is effective for producing the aniline compounds with almost 100% selectivity in the whole range of



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.

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conversion. The rate of hydrogenation depends on CO₂ pressure and is maximized at high pressures of *ca.* 9–12 MPa.³ Here, we report that the combination of H₂O and CO₂ is more beneficial for these selective hydrogenation reactions and the effectiveness of CO₂ 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.

Fig. 1 gives the results of NB hydrogenation in different reaction media using a 41 wt% Ni/Al₂O₃ catalyst (the details of catalyst preparation and hydrogenation run are given in ESI†). The influence of CO₂ pressure on the conversion of NB depends on the medium used (Fig. 1a). In the absence of CO₂, the conversion was larger in ethanol and *n*-hexane (66% and 29%) than that in H₂O and solvent-less NB (6% and 3%). However,

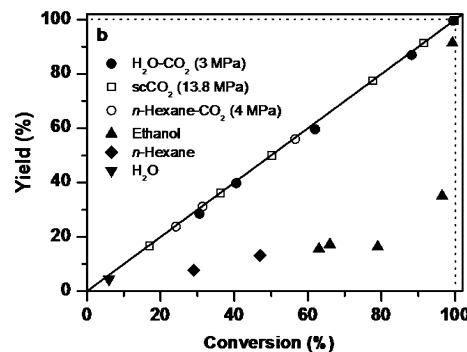
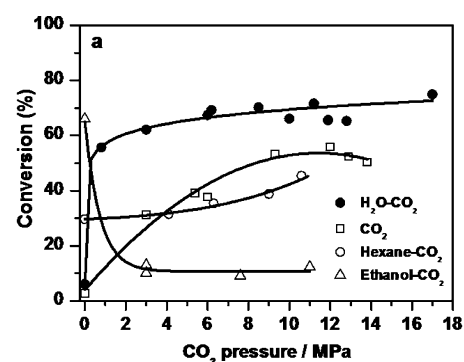


Fig. 1 (a) Influence of CO₂ pressure on the conversion of NB after 30 min reaction and (b) the yield of AN against the conversion of NB in different reaction systems. (Ni/Al₂O₃ 0.1 g, NB 19.5 mmol, H₂ 6 MPa, 50 °C).

Table 1 Hydrogenation of NB, NSB, and PHA^a

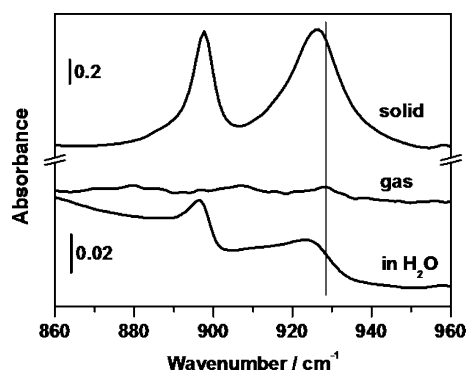
Entry	Medium	Substrate	Conv. (%)	Selectivity (%) ^b		
				AN	NSB	PHA
1	H ₂ O	NB	21	61.9	9.0	1.9
2		NSB ^c	8	20.4	— ^d	— ^d
3		PHA	100 ^e	94.6	— ^d	— ^d
4	H ₂ O–CO ₂ (3 MPa)	NB	55	95.1	2.4	2.4
5		NSB	13	36.9	— ^d	— ^d
6		PHA	100 ^e	95.3	— ^d	— ^d

^a Conditions: H₂O 10 cm³, Ni/Al₂O₃ 0.1 g, substrate 9.75 mmol, H₂ 6 MPa, 50 °C, 10 min. ^b The other byproduct was AOB. ^c 30 min. ^d Not detected. ^e 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.

the conversion was significantly enhanced when the H₂O–NB mixture was compressed by CO₂ at a low pressure such as 0.8 MPa; the conversion was comparable to that obtained in the supercritical 12 MPa CO₂–NB mixture. For the H₂O–NB, the conversion gradually increased with CO₂ pressure up to 17 MPa. The pressurization with CO₂ 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 scCO₂, CO₂–*n*-hexane, and CO₂–H₂O 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 H₂O–CO₂ medium and Ni catalyst is a better reaction system for the selective hydrogenation of NB to AN under mild conditions (low temperature and CO₂ pressure) without any organic solvent.

To examine the features of our H₂O–CO₂ reaction media, hydrogenation runs were conducted with NB, NSB, and PHA in H₂O and H₂O–CO₂ systems (Table 1). In both systems, the rate of hydrogenation followed the order PHA > NB > NSB. For NB hydrogenation in pure H₂O, the selectivity to AN was *ca.* 62% and NSB and AOB were the main byproducts (entry 1). In the H₂O–CO₂ 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 H₂O–CO₂ system the NB transforms directly to PHA and this step is the rate-determining one. The coupling of NSB and PHA should be suppressed due to their low concentrations. In pure H₂O, in contrast, the NB should also change to PHA *via* NSB in addition to the direct transformation to PHA. The coupling reaction between NSB and PHA is also possible to occur.

The molecular interactions of H₂O with a hydrophilic intermediate of PHA were examined by FTIR (experimental details are in the ESI†). Fig. 2 shows a slight red-shift of $\nu(\text{NO})$ in the H₂O compared to that in the gas phase. The N–O bond of PHA is weakened through interactions with H₂O, possibly *via* OH...O and OH...N bonding.⁴ Several authors reported the promotion effects of H₂O on the hydrogenation of aromatic nitro compounds in organic solvents, but the reasons are still unclear.⁵ Now, the results of Table 1 and Fig. 2 allow us to

**Fig. 2** FTIR spectra of PHA in the $\nu(\text{NO})$ region.

propose that H₂O can promote the reaction step III accepted as the rate-determining step in organic solvents, enhancing the reaction rate and the selectivity to aniline.

To further inspect the features of the present H₂O–CO₂ system, NB was hydrogenated in a H₂O–compressed N₂ (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 H₂ and CO₂.⁶ 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–H₂O–CO₂ (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–H₂O–CO₂ system can be explained by a few different factors. CO₂ is soluble in H₂O, its mole fraction being 0.25% and 2.0% at 0.8 and 9.4 MPa, respectively, at 50 °C.⁷ The dissolution of CO₂ enhances the solubility of a gaseous reactant H₂ in the H₂O and NB phases. The H₂O phase of H₂O–CO₂ mixture was acidic (*ca.* pH 3⁸). A reaction run was also conducted in a 0.8 mol dm⁻³ NaHCO₃ buffered H₂O solution at 3 MPa CO₂ (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. NaHCO₃ can also be hydrogenated to NaHCO₂ with Ru complex or supported Pd catalyst,⁹ but supported Ni catalysts do not give significant NaHCO₂ concentrations.^{9a} When the concentration of NaHCO₃ was changed from 0.8 to 0.2 mol dm⁻³, the hydrogenation of NB gave the same conversion, indicating that the influence of NaHCO₃ hydrogenation on the reaction of NB is marginal in our systems. Thus, the acidic nature of the H₂O phase might be one of positive factors, but its effect is small. Our previous *in situ* FTIR show that compressed CO₂ 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 H₂O–CO₂–NB reaction system. In addition, the solid catalyst granules were well dispersed in the H₂O 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 H₂O (*ca.* 82 mmol dm⁻³ in saturated salt solution at 0 °C¹⁰). Therefore, the hydrogenation of NB and PHA is likely to occur at the NB–H₂O

interfacial layer and in the H₂O phase. In the H₂O–CO₂ system, the rate of AN formation is controlled by the conversion of NB into PHA. Interfacial H₂O 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 hydrogen bonds between interfacial water molecules and reactants or transition state.¹² In addition, da Rocha *et al.* studied the molecular structure of the H₂O–compressed CO₂ 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 H₂O phase was easily separated from the organic product phase. This H₂O phase containing 0.35 mol dm⁻³ AN was further used for the second reaction, giving the same results as that using pure H₂O. Hence, the H₂O phase can be recyclable without any post-purification, which is of practical significance.

Furthermore, the potential of the H₂O–CO₂ medium was examined for the hydrogenation of CNB at 35 °C, which is less soluble in H₂O than NB. A 9 wt% or 16 wt% Ni/TiO₂ catalyst was used since the selectivity to chloroaniline (CAN) was slightly better than that obtained with the Ni/Al₂O₃ (Table S1 in ESI†). Fig. 3a shows the conversion of *o*-CNB over 9 wt% Ni/TiO₂ as a function of CO₂ pressure for the reaction mixtures in the presence and absence of H₂O. One can see again that the H₂O significantly promoted the hydrogenation of

o-CNB similar to NB but the conversion increased with CO₂ pressure through to 13 MPa. The positive effect of H₂O was also observed in the hydrogenation of *m*- and *p*-CNB over 16 wt% Ni/TiO₂. 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 H₂O and low-pressure CO₂ for the selective hydrogenation of aromatic nitro compounds to anilines.

In conclusion, the interactions of CO₂ and H₂O with the reacting species, the *in situ* formed acidity, and the better dispersion of Ni catalyst in the H₂O phase are responsible for the fast and selective hydrogenation of NB in the H₂O–CO₂ system, in which the conversion of NB into PHA may be the rate-determining step.

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Notes

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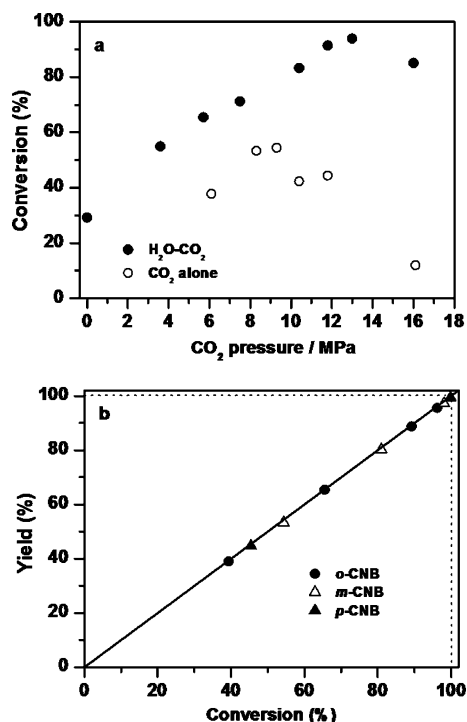


Fig. 3 (a) Influence of CO₂ pressure on the conversion of *o*-CNB over 9 wt% Ni/TiO₂ after 50 min of hydrogenation in the systems of H₂O–CO₂ and compressed CO₂ alone; (b) CAN yield against CNB conversion during the hydrogenation of CNB isomers in the H₂O–CO₂ (6 MPa) system. (CNB 9.52 mmol, Ni/TiO₂ 0.15 g, H₂ 4 MPa, 35 °C).