

Supplementary Information

An Effective Medium of H₂O and Low-pressure CO₂ for the Selective Hydrogenation of Aromatic Nitro Compounds to Anilines

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EXPERIMENTAL

1. Catalyst preparation

The following supported Ni catalysts were prepared: 41 wt-% Ni/Al₂O₃, 9 wt-% Ni/TiO₂, and 16 wt-% Ni/TiO₂. The former catalyst was prepared by co-precipitation using Ni(NO₃)₂·6H₂O and Al(NO₃)₃ with a Ni/Al atomic ratio of 1/1 [1]. The latter two ones were prepared by incipient wetness impregnation using TiO₂ (anatase) and Ni(NH₃)₆(NO₃)₂ (for 9 wt-% Ni/TiO₂) or Ni(NO₃)₂·6H₂O (for 16 wt-% Ni/TiO₂). The samples were dried at 120°C for 12 h and sieved out and the samples in size of <180 mesh were collected. Then the samples were heated at a rate of 5°C/min up to 450°C and calcined at this temperature for 5 h. Before hydrogenation runs, the Ni/Al₂O₃ sample was reduced under H₂ flow at 610°C and the Ni/TiO₂ samples at 450°C. The size of Ni crystallites ranges from 2 to 15 nm with an average diameter of 8.5 nm for the reduced Ni/Al₂O₃ sample, from 7 to 35 nm for the 9 wt-% Ni/TiO₂ sample, and from 5 to 28 nm for the 16 wt-% Ni/TiO₂ catalyst. The two Ni/TiO₂ catalysts, which were prepared from the different Ni precursors, were found to be the same with respect to the product selectivity but different in the total conversion because the Ni loadings were different.

The catalyst was reduced in a vertical quartz tube at that temperature for 2 h and cooled down to room temperature. The upper end of the quartz tube was externally ground and could be connected to an internally ground glass cap. A H₂ stream (70 ml/min) was introduced into the quartz tube from the upper end. After cooling, the H₂ flow was decreased to 5 ml/min; another plastic tube that was purged with high purity N₂ (5 ml/min) was connected to the

lower end of the quartz tube. The plastic tube on the upper end was removed as quickly as possible. The N₂ stream was increased to 50 ml/min and then the glass cap was replaced with a bent tube. The quartz tube and the bent glass tube were purged with N₂ for another 10 min, to remove the air in the bent tube. A certain amount of liquid (H₂O, ethanol, *n*-hexane, or NB) was added into the reactor. The N₂ flow was decreased to 5 ml/min. The open end of the bent tube was first inserted into the liquid in the reactor and then the catalyst was removed into the autoclave reactor under the protection of N₂ flow. The catalyst sample was on the bottom of the liquid and the reactor was sealed at room temperature. By careful operation, we could avoid the contact of the reduced catalyst with air.

2. Hydrogenation runs

The hydrogenation of nitrobenzene (NB) was conducted over Ni/Al₂O₃ at 50°C in a 50 cm³ autoclave reactor. The reactor was charged with NB, a catalyst sample, and, if necessary, a liquid (H₂O, anhydrous ethanol, or *n*-hexane), flushed with N₂ for 3 min, and placed into a water bath preset to the reaction temperature for 20 min. Then, H₂ was first introduced into the reactor up to 6 MPa and CO₂ (or N₂ in a few cases for comparison) to the desired total pressure with a high-pressure liquid pump. The reaction was conducted while the reaction mixture was being stirred with a magnetic stirrer. After the reaction, the reactor was cooled with an ice-water bath for 20 min and depressurized carefully. The reaction mixture in the medium of H₂O or H₂O–CO₂ was extracted with diethyl ether; in other cases, it was diluted with ethanol. The reaction products were analyzed with a gas chromatograph (GC-4000, GL Sciences, ZB-5 capillary column) using a flame ionization detector (FID) and GC-MS (Agilent 6890N). The hydrogenation of nitrosobenzene (NSB) and *N*-phenylhydroxylamine (PHA) was performed in the same reactor with similar procedures. For these reactions, anhydrous ethanol and *n*-hexane were purchased from Wako Pure Chemical Industries. NB and NSB (Sigma–Aldrich) were used as received; commercially unavailable PHA was synthesized according to the literature [2]. The formation of this compound was confirmed by FTIR and NMR (JEOL A200II) [3].

The hydrogenation of chloronitrobenzene (CNB) isomers was conducted at 35°C with the same reactor at 4 MPa H₂. The hydrogenation of *o*-CNB was performed over 9 wt-% Ni/TiO₂, and the hydrogenation of *m*- and *p*-CNB isomers over 16 wt-% Ni/TiO₂. If necessary, the reaction mixture was extracted from water by diethyl ether for GC (Shimadzu GC-2010, Rtx-5 capillary column) analysis.

3. Phase behavior and FTIR measurements

The phase behavior of the reactant mixture in the presence of compressed CO₂ was examined by the naked eye through the transparent sapphire windows attached to an 85 (or 10) cm³ high-pressure reactor.

The gas phase FTIR spectrum of PHA was collected with a FTIR spectrometer of JASCO FTIR-620 equipped with a 1.5 cm³ high-pressure cell. The measurement was made at 50°C and at 4 MPa H₂ and 0 MPa CO₂. PHA (5 mg) and H₂O (5 μL) were added into the cell at room temperature. The cell was purged with H₂ three times and heated up to 50°C. Then, H₂ was introduced to 4 MPa. The stirring was continued for 3 min and stopped, and the FTIR spectrum was collected. The gas phase spectrum of PHA was obtained by using the PHA-absent system as background. The solid phase FTIR spectrum of PHA was measured at ambient conditions for a mixed powder of PHA and KBr using the same spectrometer. The FTIR spectrum of PHA in liquid H₂O was measured for a thin liquid film jammed by KBr crystal plates under ambient conditions.

References

- [1] X. Meng, H. Cheng, Y. Akiyama, Y. Hao, W. Qiao, Y. Yu, F. Zhao, S. Fujita and M. Arai, *J. Catal.*, 2009, **264**, 1-10.
- [2] O. Kamm and C. S. Marvel, *Org. Synth.*, 1925, **4**, 57-59.
- [3] O. Corminboeuf, P. Renaud, *Org. Lett.*, 2002, **4**, 1731-1733.

RESULTS

1. Hydrogenation of NB

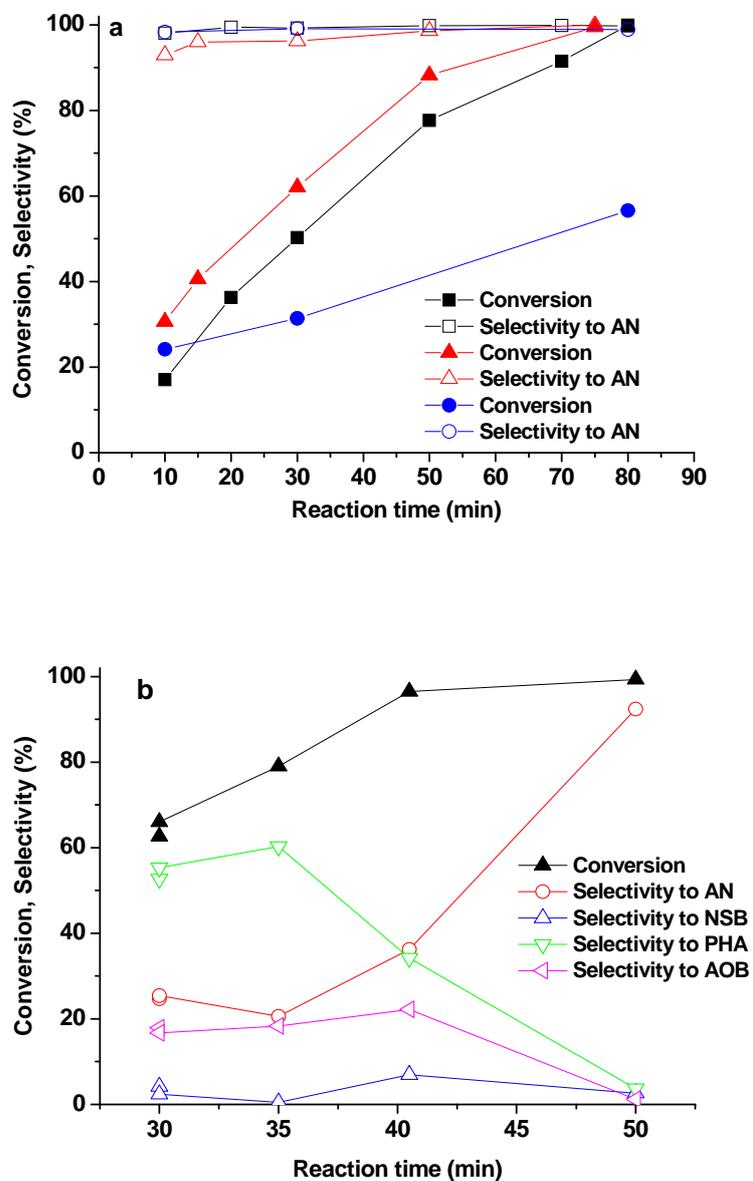


Fig. S1 Evolution of species with time during the hydrogenation of NB over Ni/Al₂O₃ in different reaction systems.

(a) (■, □) scCO₂ (13.8 MPa); (▲, △) H₂O-CO₂ (3 MPa); (●, ○) *n*-Hexane-CO₂ (4 MPa).

(b) Ethanol.

2. Phase behavior of the multiphase reaction mixture

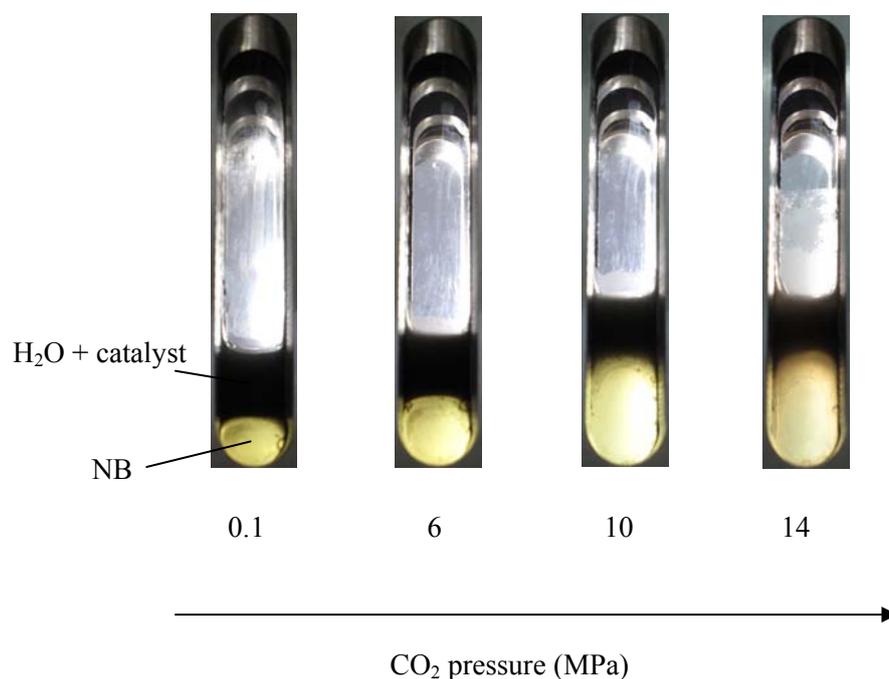


Fig. S2 Distribution of Ni/Al₂O₃ in the mixture of NB and H₂O after the stirring was stopped. (NB 10 cm³, H₂O 10 cm³, Ni/Al₂O₃ 20 mg, H₂ 4 MPa.)

3. Comparison in the performance between Ni/Al₂O₃ and Ni/TiO₂ catalysts

Table S1 Results of *o*-CNB hydrogenation in the H₂O–CO₂ system over 41 wt-% Ni/Al₂O₃ and 9 wt-% Ni/TiO₂

Entry	Catalyst	Medium	Time /min	Conv. (%)	Selectivity (%)		
					CAN ^a	AN ^b	Others
1	Ni/Al ₂ O ₃	H ₂ O (10 cm ³) + CO ₂ (6.8 MPa)	31	51	89.4	9.6	1.0
2	Ni/TiO ₂	H ₂ O (10 cm ³) + CO ₂ (3.6 MPa)	50	55	99.8	0.1	0.1

Reaction conditions: 41 wt-%Ni/Al₂O₃ 0.1 g or 9 wt-% Ni/TiO₂ 0.15 g, 35°C, H₂ 4 MPa, *o*-CNB 1.5 g (9.52 mmol).

^a CAN: chloroaniline. ^b AN: aniline.

4. Hydrogenation of CNB isomers

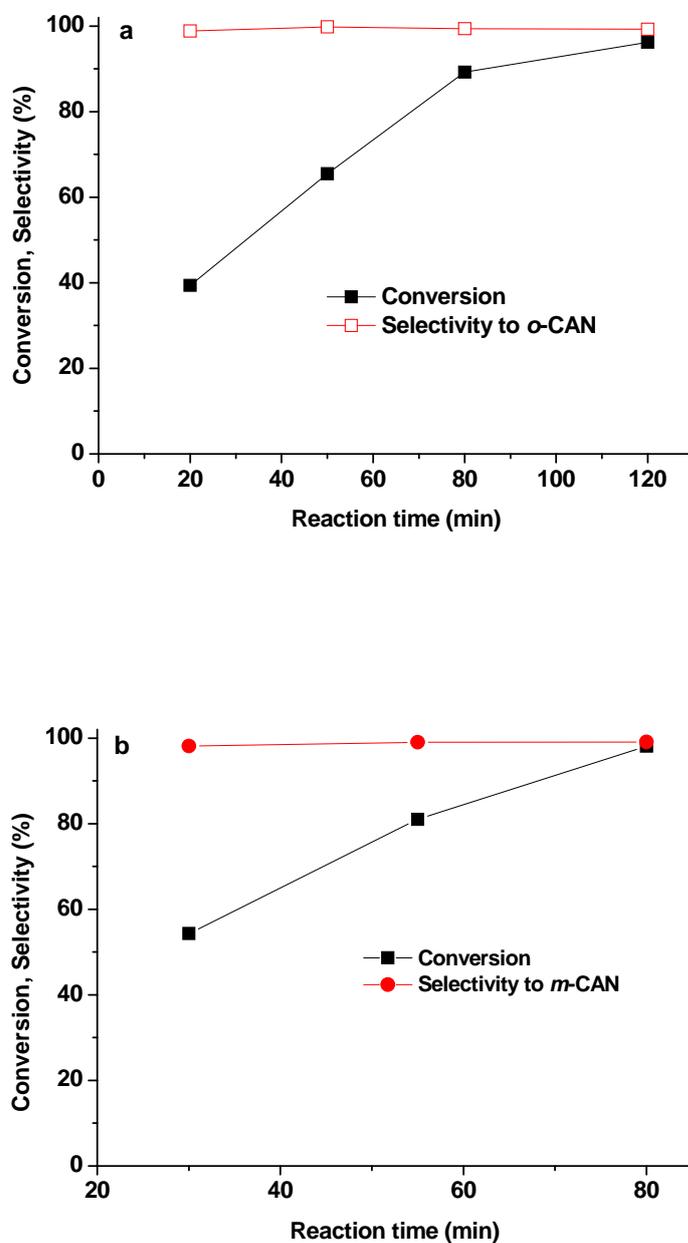


Fig. S3 Change of conversion and selectivity to CAN with reaction time during the hydrogenation of CNB isomers over Ni/TiO₂ catalysts in the H₂O-CO₂ (6 MPa) system. (a) Hydrogenation of *o*-CNB over 9 wt-% Ni/TiO₂; (b) hydrogenation of *m*-CNB over 16 wt-% Ni/TiO₂. (CNB 9.52 mmol, Ni/TiO₂ 0.15 g, H₂ 4 MPa, 35°C)

5. GC analysis for PHA

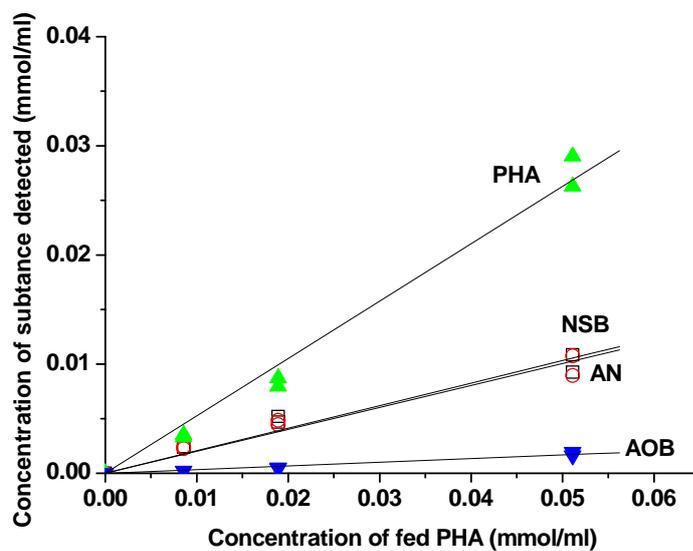


Fig. S4 PHA decomposes partly into NSB, AN, and AOB during GC analysis. Analysis conditions: INJ temperature: 250°C; FID temperature: 250°C; oven temperature: from 80 to 288°C at 8°C/min. (▲) PHA; (□) NSB; (○) AN; (▼) AOB.