

Supplementary Information

Metal fluorides promoted catalytic hydrogenation of aromatic nitro compounds over Raney Ni

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Experimental procedures

Chemicals

Raney Ni (RTH-311) catalyst used in this study was purchased from Dalian Tongyong Chemical Co., Ltd., Liaoning, China. The weight percentage of nickel and aluminum in the Raney Ni catalyst was more than 90% and less than 7%, respectively. The catalyst was not pre-treated before all experiments and only kept in water-sealing storage.

All aromatic nitro compounds (*p*-chloronitrobenzene, nitrobenzene, *p*-nitrobenzotrile, and *m*-dinitrobenzene) used in experiments were purchased from Aladdin Reagent Co. Ltd. with a minimum purity of 98%. The metal fluorides (NaF, KF, MgF₂ and CaF₂) were analytical reagents and were supplied by Sinapharm Chemical Reagent Co., Ltd., Shanghai, China. The solvent methanol was HPLC grade and was obtained from Xingke High Purity Solvents (Shanghai) Co., Ltd. Deionized water was used in the reaction. The purities of hydrogen and nitrogen used in the experiments were more than 99.99%.

Catalytic procedure

All the liquid-phase hydrogenation reactions were carried out in a three-neck flask, which was attached with a thermometer, a condenser and a hydrotreater (including a hydrogen cylinder, hydrogen flowmeter, three-way valve and a nitrogen cylinder), with a magnetic stirrer. The reaction vessel (100 mL) was placed in a temperature-controlled heating water bath with a precision of ± 0.5 K. At the beginning of each experiment, 80 mL methanol, 0.51 mmol aromatic nitro compound and a certain amount of metal fluoride (added in certain percent **by weight of the catalyst**) was added into the flask. After the air in the flask was completely replaced by nitrogen, 0.20 ± 0.02 g Raney Ni was added. And then the reaction was started with a $10 \text{ mL} \cdot \text{min}^{-1}$ H₂ flow rate, 313 K reaction temperature and 1500 rpm stirring speed. During the reaction, some aliquots of the reaction mixture were taken out to analyse at set intervals.

Analytical Methods

The taken reaction mixture in the hydrogenation of aromatic nitro compounds were determined by LC/MS (Thermo Fisher Scientific LCQ Fleet) instrument equipped with a quaternary pump, an auto sampler with thermostat, a mass detector, the column and sample thermostat systems and Thermo Scientific Xcalibur LC-MS/MS software, using an Eclipse XDB-C18 column (4.6 mm \times 150 mm \times 5 μm). The mobile phase consisted of water:methanol (35:65, v/v). Prior to analysis, the basic solution samples were diluted with methanol. The mobile phase was degassed for 5 min in an ultrasonic bath before use. The samples were injected at a flow rate of $1 \text{ mL} \cdot \text{min}^{-1}$. The injection volume was 5 μL for all the samples. The column temperature was kept constant at 25 K during the runs.

The composition of the reaction mixture was analyzed by HPLC (Agilent 1200) equipped with a quaternary pump, an auto-sampler with thermostat, a variable wavelength detector, a column and a sample thermostat and a Chem Station software. Chromatographic separations were performed using a column of XDB-C18 (4.6 mm \times

150 mm × 5 μm), employing a diode array detector (DAD). The mobile phase consisted of water: methanol (35:65, v/v). The mobile phase was degassed for 10 min in an ultrasonic bath before use. The wavelength selected for the determination of compositions of the reaction was 245 nm. UV detection was carried out at this wavelength simultaneously at a flow rate of 1 mL min⁻¹. The injection volume was 5 μL for all the samples. The column temperature was kept constant at 25 K during the runs.

The F⁻ measurement was performed on a Dionex ICS-3000 ion chromatography system. Before measurement, the samples were prepared as follows. Firstly, the mixture after hydrogenation added NaF was centrifuged to separate the catalyst from the methanol solution. Then, the methanol solution was concentrated by rotary evaporation to remove the methanol, and the residual was redissolved with 2.5 volumes of water. And then 10 mL was taken out for IC measurement, labelled as sample 1. The catalyst added NaF after hydrogenation was washed with 50 mL water, filtered through a 0.45 μm membrane. And then 10 mL was taken out for IC measurement, labelled as sample 2. The results are as follows.

Sample	Ret. Time min	Peak Name	Height μS	Area μS min	Rel. Area %	Amount mg L ⁻¹
1	4.35	F	44.702	12.254	7.50	11.976
2	4.35	F	140.485	41.433	50.44	40.493

Characterizations

The used catalyst samples were separated from the solution, washed with 95% ethanol to remove the absorbed organic compounds, and dried in a N₂ flow at 473 K prior to characterization analysis. The surface morphology of the fresh and used catalysts was characterized using a Hitachi S-4800 field emission scanning electron microscope (FE-SEM) coupled with an energy dispersive X-ray spectrometer (EDXS, HORIBA EMAX Energy EX-350) for chemical elemental analysis. X-ray diffraction (XRD) patterns of the catalysts were recorded with XRD-6100 of Shimadzu with a Cu Kα radiation at 40 kV and 30 mA. The samples were scanned at a rate of 0.1 °/s over the 5° ≤ 2α ≤ 80° range with a scan rate of 5 s·step⁻¹. Specific BET surface area was performed using the commercial Micrometrics ST2000B unit. N₂ at 77 K served as sorbate. Before measurement, the samples were outgassed at 573K for 16 h.