

## Electronic Supplementary Information

### EXPERIMENTAL DETAILS

#### Preparation of supports and catalysts

**Magnesium fluoride** was obtained by adding small portions of  $\text{MgCO}_3 \cdot 2\text{H}_2\text{O}$  to an aqueous solution of hydrofluoric acid until neutralisation followed by acidification with a few additional drops of the acid. The precipitate was then aged at room temperature for a few days under stirring, dried at  $80^\circ\text{C}$  and calcined at  $400^\circ\text{C}$  for 4h. After the calcination,  $\text{MgF}_2$  was ground to obtain particles of 0.2–0.5mm in size.

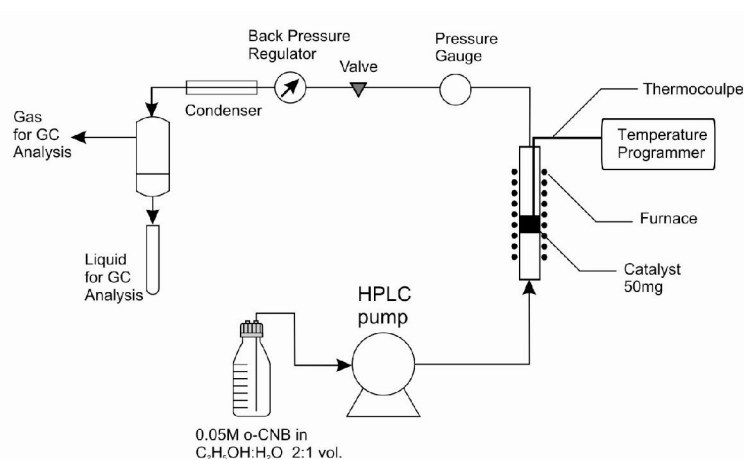
**Aluminium oxide** was prepared by hydrolysis of aluminium isopropoxide. The obtained aluminium hydroxide was washed out of isopropyl alcohol, dried at  $110^\circ\text{C}$  for 24h, then calcined at  $550^\circ\text{C}$  for 4h.

Ruthenium, platinum and iridium were deposited on  $\text{MgF}_2$  by conventional impregnation using aqueous solutions of  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ ,  $\text{H}_2\text{PtCl}_6$  and  $\text{H}_2\text{IrCl}_6$ , respectively. The required amount of metal compound was dissolved in water, then contacted with the support at room temperature for several minutes, followed by evaporation of water. The solid was dried at  $80^\circ\text{C}$ , then reduced at  $400^\circ\text{C}$  under hydrogen flow for 4h. Metal content was 1 wt.% for each catalyst.

#### Catalytic reaction

##### Aqueous-Phase Reforming coupled with o-CNB Hydrogenation (APR/HYD) in a fixed-bed flow reactor

The liquid phase *in situ* hydrogenation of o-CNB to o-CAN was carried out in a fixed-bed reactor (a stainless-steel tube of 5 mm in inner diameter) in the presence of 50mg of a catalyst under 5.0 MPa to maintain the reaction in the liquid phase. The 0.05M o-CNB (Aldrich) solution in ethanol:water mixture (2:1 by vol.) was forced in the reactor at feeding rate of  $0.13 \text{ cm}^3 \text{ min}^{-1}$  with the use of a HPLC pump (Beckman 114M Solvent Delivery Module). The liquid effluent was collected and analyzed by a gas chromatograph equipped with RESTEK MXT-5 capillary column and with thermal conductivity detector. The gas phase was analyzed for CO content using a gas chromatograph equipped with Porapak Q and 13X molecular sieves columns.



**Figure S1.** Scheme of the Aqueous-Phase Reforming/Hydrogenation (APR/HYD) system.

#### Hydrogenation in a batch reactor

Hydrogenation in a batch reactor was performed for 2h under hydrogen or carbon monoxide pressure of 2.0 MPa in a  $200 \text{ cm}^3$  stainless steel autoclave with a glass tube inside equipped with a magnetic stirrer. The autoclave was loaded with 50 mg of catalyst,  $50 \text{ cm}^3$  of 0.1M ethanolic solution of o-CNB, and  $25 \text{ cm}^3$  of distilled water. Then the autoclave was flushed

several times with helium followed by flushing with hydrogen (or CO) in order to remove air. In each case the reaction time was 2 h and stirring rate was 1000 rpm. Results of the experiments have shown that the reaction was conducted in the absence of mass transfer limitations (the stirring rates from 800-1000 rpm did not affect the reaction rate). The reaction products were analyzed on a gas chromatograph equipped with a capillary column RESTEK MXT-5. Catalytic measurements carried out with MgF<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> supports free of the platinum group metals proved inactivity of the supports for the reduction of nitric group of o-CNB.

## Surface area

The Brunauer-Emmet-Teller surface areas were determined by N<sub>2</sub> adsorption at 77 K using a Micromeritics ASAP2010 sorptometer.

## The determination of metal dispersion by hydrogen chemisorption

Prior to hydrogen chemisorption, samples were pretreated *in situ* to remove adsorbed molecules from the surface of metal. Samples were evacuated for 15min at room temperature and then at 400°C for 60min, followed by reduction in hydrogen flow (40 cm<sup>3</sup>/min) at 400°C and evacuated again for 120min at 400°C. All chemisorption experiments were performed on an ASAP 2010C sorptometer. Chemisorption of hydrogen was carried out at 100°C for ruthenium, and at 30°C for iridium and platinum catalysts. After the measurement carried out at the first set of pressures was completed, the catalyst was evacuated for 30min to remove reversibly adsorbed hydrogen and the same procedure was repeated. The difference between adsorbed hydrogen extrapolated to zero pressure value for two isotherms equals to the amount of hydrogen irreversibly bound.

By assuming that the stoichiometry of hydrogen adsorption on surface metal atoms (M<sub>s</sub>) is 1:1, the dispersion of metal is given by  $D = M_s/M_t = H/M_t$  (M<sub>t</sub> - total number of metal atoms). Metal dispersion was calculated from the amount of irreversibly chemisorbed hydrogen.

## RESULTS

**Table S1.** Supports and Catalysts characterization.

Catalyst	BET surface area / m <sup>2</sup> g <sup>-1</sup>	Metal dispersion (%)
MgF <sub>2</sub>	50	-
Al <sub>2</sub> O <sub>3</sub>	217	-
Ru/MgF <sub>2</sub>	39	19.6
Ir/MgF <sub>2</sub>	35	27.3
Pt/MgF <sub>2</sub>	35	22.6
Ru/Al <sub>2</sub> O <sub>3</sub>	255	22.5
Ir/Al <sub>2</sub> O <sub>3</sub>	246	124.0*
Pt/Al <sub>2</sub> O <sub>3</sub>	216	20.0

\* Dispersion higher than 100% can be a result of hydrogen spillover or hydrogen chemisorption stoichiometry was different from the assumed ratio of one hydrogen atom per one surface metal atom.