

Supplementary Material: CO₂ Methanation on Supported Rh Nanoparticles: The combined Effect of Support Oxygen Storage Capacity and Rh Particle Size

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1. Materials characterization methods: detailed information

1.1. Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES) measurements

Rhodium metal content was determined by ICP-OES utilizing a Thermo Scientific iCAP 7400 duo instrument. Samples were digested in 5 mL HNO₃ (Fisher, 70%) and 100 mg NH₄F (Sigma Aldrich, ≥98.0%) at 190 °C via microwave irradiation (CEM-MARS microwave reactor). This was followed by addition of HCl (1 mL, Fisher, 37%) and HF neutralisation by addition of a boric acid solution (1 mL, Fisher, 3%). Subsequent analysis was carried out after sample dilution in 10% aqueous HNO₃.

1.2. BET measurements

Textural characteristics of the materials, i.e. total surface areas (S_{BET}), average pore volume and mean pore size diameters were determined according to the Brunauer–Emmett–Teller (BET) and Barret–Joyner–Halenda (BJH) methods from N₂ adsorption–desorption isotherms at relative pressures in the range of 0.05–0.30 conducted in a Quantachrome Nova 2200e instrument at -196 °C. The total pore volume calculation was based on the nitrogen volume obtained at the highest relative pressure. Prior to measurements the samples were degassed at 350 °C for 12 h under vacuum.

1.3. Powder X-ray diffraction measurements

PXRD characterization of the samples was performed with a Bruker D8 Advance Diffractometer with a LynxEye high-speed strip detector using monochromated Cu K α 1 ($\lambda=0.1542$ nm) radiation.

1.4. Hydrogen Temperature Programmed Reduction (H₂-TPR) measurements

H₂-TPR measurements were carried out in the temperature interval 30–850 °C on a Quantachrome ChemBet Pulsar TPR/TPD chemisorption analyzer equipped with an Omnistar/Pfeiffer Vacuum mass spectrometer. About 150 mg of the material (catalyst or support) was loaded into a quartz U-tube connected to the TPR apparatus and pre-oxidized *in situ* at 700 °C for 1 h under a flow of 20% v/v O₂ in He. Then the sample was cooled to room temperature under the same flux and purged under He flow for 0.5 h. After this pre-conditioning, the TPR measurement started with a continuous flow of 15 NmL/min of 1% v/v H₂ in He passing through the sample, while at the same time a linear increase (10 °C/min) in the sample temperature, from ~30 °C up to 850 °C, was imposed and the H₂ content of the effluent gas was measured by the mass spectrometer. The integrated peak areas of the as-obtained H₂-TPR spectra were used to calculate the total amount of H₂ consumed (in $\mu\text{mol H}_2 \text{ g}^{-1}$) by labile lattice oxygen; half of this quantity represents the *total* Oxygen Storage Capacity (OSC) of the sample in $\mu\text{mol O}_2/\text{g}$.

1.5. Hydrogen Chemisorption (H₂-Chem.) measurements

Isothermal (at 0 °C) hydrogen chemisorption measurements for determination of the number of Rh surface sites and the associated crystallite sizes, were carried out using the same instrumentation as employed for H₂-TPR experiments (above) as follows. About 150 mg of catalyst was loaded into a quartz U-tube connected to the analyser and pre-treated in accord to the following steps before H₂-uptake (chemisorbed H₂) data acquisition: reduction at 550 °C for 1 h with a flux of 5% H₂ in He (15 NmL/min); gas phase purging at the same temperature for 0.5 h by N₂ flux (15 Nm/min); and finally cooling at 0 °C, using an ice/water bath, under N₂ flow. Pulses of pure hydrogen (280 µL volume) were then injected until saturation, thus providing the total uptake of chemisorbed hydrogen. The low temperature used for these measurements minimizes hydrogen spillover in the case of CeO₂-containing supports.

1.6. High-resolution transmission electron microscopy (HRTEM) measurements

TEM images, typical and representative of the samples under observation, were obtained with an aberration corrected JEOL 2100-F microscope operated at 200 kV. Samples were gently ground in high-purity methanol using an agate pestle and mortar prior to TEM observations. The resulting samples were deposited on 300-mesh carbon supported copper grids and dried under ambient conditions. ImageJ 1.41 software was used for Image analysis. In order to enable comparison between Rh particle sizes obtained by H₂-chemisorption and by TEM, the latter were performed with samples that were preconditioned under the same reducing conditions as those used for the H₂-chemisorption experiments.

As shown below the results of mean Rh particle size obtained by the two independent methods (H₂-TPR and HRTEM) were found to be in a close agreement; the arithmetic mean value (\bar{d}_{Rh}) for each sample was therefore adopted for further discussion in the paper.

Table S1. Mean Rh particle sizes of Rh/ γ -Al₂O₃, Rh/ACZ and Rh/CZ catalysts [6].

Catalyst	Rh/ γ -Al ₂ O ₃ fresh	Rh/ γ -Al ₂ O ₃ treated@750	Rh/ γ -Al ₂ O ₃ treated@850	Rh/A CZ fresh	Rh/ACZ treated@750	Rh/ACZ treated@850	Rh/C Z fresh	Rh/CZ treated@750	Rh/CZ treated@850
Mean Rh particle size (H ₂ -Chem), nm	1.2	1.6	2.6	1.8	1.4	1.7	5.0	2.1	2.2
Mean Rh particle size (HRTEM), nm	1.3	1.6	1.6	1.5	2.0	1.5	5.1	2.5	2.0
Arithmetic mean value (\bar{d}_{Rh}), nm	1.2	1.6	2.1	1.7	1.7	1.6	5.0	2.3	2.1

2. Chemisorption character of CO on metal surfaces

Donation-backdonation issues of electron charge between adsorbates and metal surfaces during the formation of a chemisorptive bond and their impact on the bond strength have been thoroughly analysed by Vayenas and Brosda [1]. In accord to the authors, Electron backdonation to bonding singly occupied orbitals of an electron acceptor reactant lying below the metal Fermi level (E_F) results in strengthening of the metal-adsorbate bond, while electron backdonation to antibonding orbitals, leads to weakening of the chemisorptive bond and destabilization of the adsorbate. Also electron donation to a metal from a singly occupied orbital on an electron donor adsorbate lying above Fermi level of the metal leads in general to strengthening of the chemisorptive bond. There are cases, such as the CO chemisorption on transition metals, where both donation of electrons (from the adsorbate

to the metal) and backdonation of electronic charge (from the metal to the adsorbate) play an important role in the chemisorptive bond formation (e.g., Blyholder model for CO chemisorption [2]). The latter explains why someone can find CO to be considered either as an electron-acceptor (electrophilic) or as an electron-donor (electrophobic) adsorbate. For Pt, both considerations for the Pt-CO bond characteristic, electrophilic [3] and electrophobic [4] can be found in literature. For Ru-based catalysts, Dreyer et al. [5] reported decreasing CO coverage with the support reducibility (between γ -Al₂O₃ and ZnO supports) associated with a weaker CO adsorption in the latter, while the Ru-CO strength remained sufficiently high on Ru/CeO₂ catalyst. No relevant information for the Rh-CO bond is available in the literature.

Figure S1. HRTEM images of the fresh, treated @ 750 °C and treated @ 850 °C Rh/ γ -Al₂O₃ (a, b, c) Ru/ACZ (d, e, f) and Ru/CZ (g, h, i) catalysts, respectively. Fresh: as-produced; Treated @ 750 °C: heating in 10 NmL/min flow of 20%O₂/He for 2 h at 750 °C; Treated @ 850 °C: heating in 10 NmL/min flow of 20%O₂/He for 2 h at 750 °C + 2 h at 850 °C. Adapted from Ref. [6].

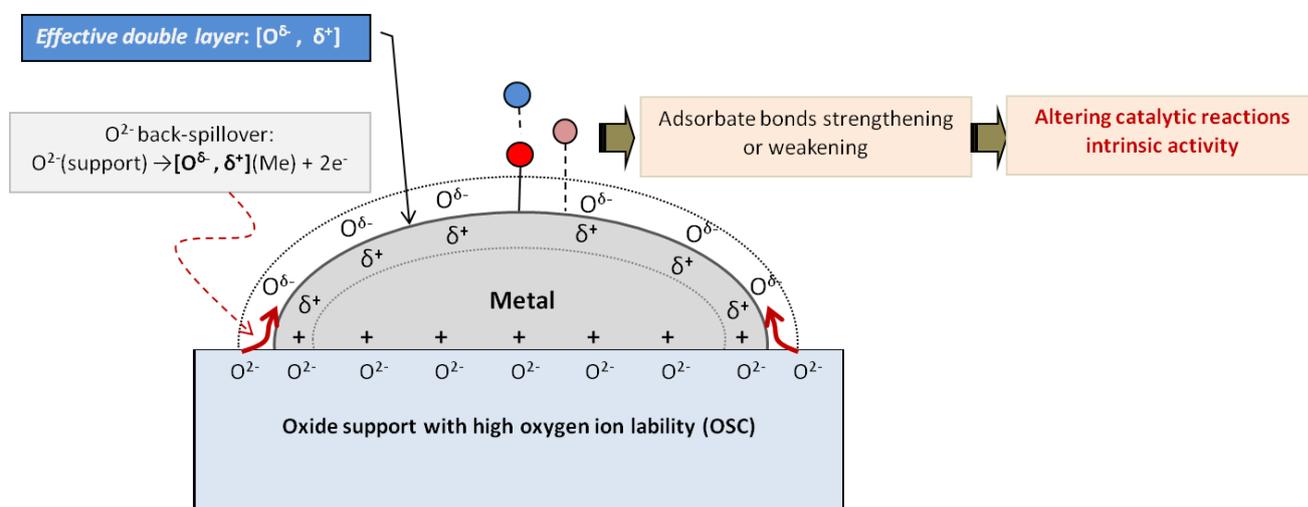


Figure S2. Schematic representation of the effective-double layer account of chemical promotion and metal support interactions: Spontaneous, thermally-driven, O²⁻ ions back-spillover from supports with high lattice oxygen ion lability and mobility on catalyst particles surface creates an electrical O^{δ-} layer, which acts as an electronic modifier of the catalytic particles by its compensating charge, δ⁺, altering their work function and chemisorptive properties and hence the intrinsic activity and/or selectivity towards catalytic reactions.

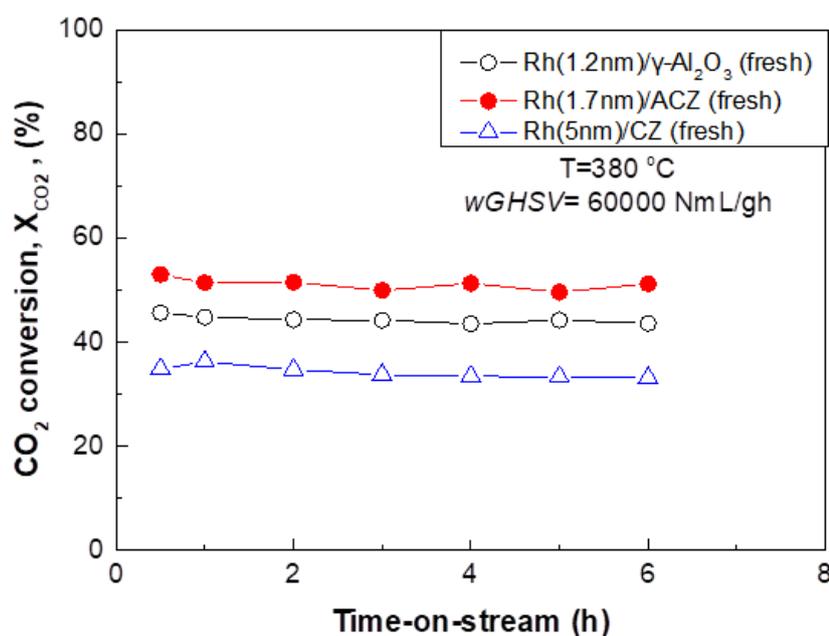


Figure S3. First 6 hours time-on-stream stability of fresh Rh/ γ -Al₂O₃, Rh/ACZ and Rh/CZ catalysts at constant feed (5% CO₂ / 20% H₂ / 75% Ar at 1 bar) and temperature (T=380 °C) conditions. Other conditions: w_{cat} = 50 mg; $wGHSV$ = 60000 N mL/g·h (total feed flow rate F_t = 50 NmL/min).

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