

Supplementary Material: Effect of operating conditions on the performance of Rh/TiO₂ catalyst for the reaction of LPG steam reforming

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S1. Materials characterization methods: detailed information

S1.1 Specific surface area measurements

Specific surface areas of supports and catalysts were measured with the B.E.T. technique with the use of a Micromeritics (Gemini III 2375, Norcross, GA, USA) instrument, employing nitrogen physisorption at the temperature of liquid nitrogen. Prior to each measurement, the sample was dried at 120 °C under helium flow passing through the sample cell.

S1.2 X-ray diffraction (XRD) measurements

X-ray diffraction (XRD) patterns of supported Ni catalysts were obtained on a Philips P (PW 1830/40) diffractometer equipped with Cu K_α source ($\lambda = 0.15406$ nm), which operates at 40 kV and 40 mA. Scans were collected in the 2θ range of 20–80° at a scan rate of 0.025 °/s, whereas phase identification was based on JCPDS cards. The ratio (X_A) of anatase in the TiO₂ supported samples was estimated using the equation [1]:

$$X_A = [1 + 1.26 \cdot (I_R/I_A)]^{-1} \quad (S1)$$

where I_A and I_B are the integral intensities of the anatase (101) and rutile (110) reflections, respectively. The primary crystallite size of MO_x (d_{MO_x}) was calculated by means of Scherrer's equation [1]:

$$d(MO_x) = \frac{0.9 \cdot \lambda}{B \cdot \cos \theta} \quad (S2)$$

Where λ is the X-ray wavelength corresponding to CuK_α radiation (0.15406 nm), B is the line broadening (in radians) at half the maximum intensity of the peak and θ is the angle of diffraction corresponding to the peak broadening.

S1.3 Hydrogen chemisorptions measurements

The dispersion and mean crystallite size of rhodium were determined by H₂ chemisorption at 25 °C. Adsorption isotherms were obtained with the volumetric technique in the pressure range of 0–75 Torr employing a modified Fisons Instruments (Sorptomatic 1900, Glaskow, UK) apparatus. Prior to each measurement, the catalyst sample (ca 1.0 g) was pretreated by (a) dynamic vacuum at 250 °C for 1 hour; (b) reduction with 1 bar of H₂ at 250 °C for 1 hour, (c) evacuation for 30 minutes at 250 °C and (d) cooling down to the chemisorption temperature.

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When the isotherm was completed, the weakly adsorbed hydrogen was removed from the catalyst by evacuating the adsorption cell at room temperature for 10 min to a pressure of approximately 10^{-6} Torr. A second isotherm was then run to determine the reversible hydrogen uptake. The total and reversible hydrogen uptakes at monolayer coverage were obtained for each catalyst by extrapolation of the adsorption isotherms to zero pressure, accounting for possible spillover of adsorbed hydrogen from the metal particles onto the carrier surface or weak adsorption of hydrogen directly onto the carrier surface. The irreversible hydrogen uptake was determined as the difference between total and reversible hydrogen uptake.

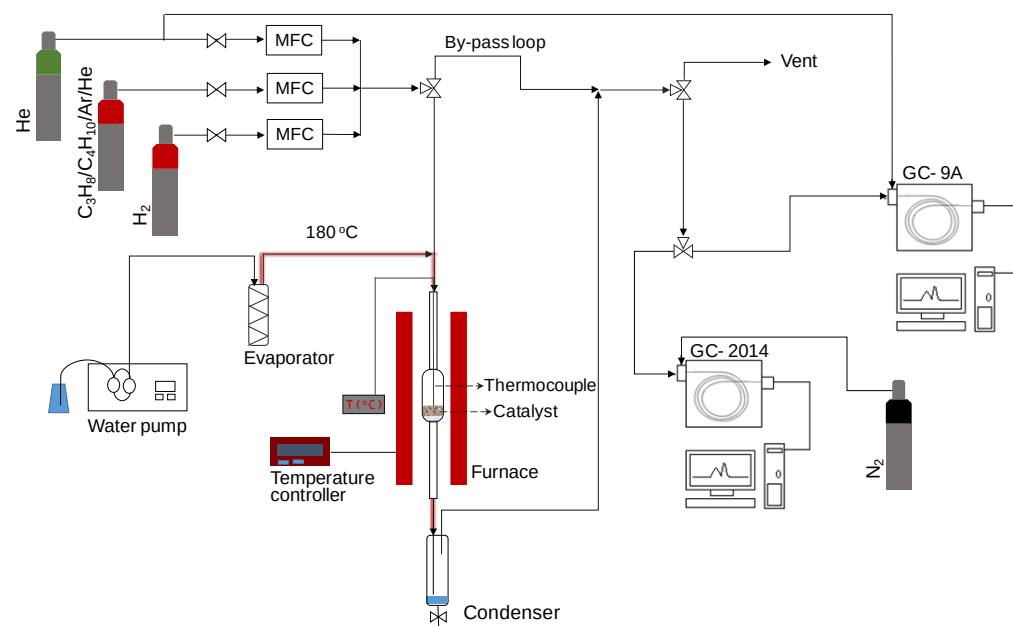
The exposed surface area of Rh was calculated assuming a H:M stoichiometry of 1:1, and an atomic surface area of $7.6 \text{ \AA}^2$. The crystallite size of the dispersed rhodium was estimated from the hydrogen chemisorption data, assuming spherical particles, using the relation:

$$d_{Rh} = \frac{60000}{\rho_{Rh} \cdot S_{Rh}} [\text{\AA}] \quad (\text{S3})$$

Where d_{Rh} is the mean crystallite diameter, S_{Rh} is the surface area per gram of metal and ρ_{Rh} ($\approx 12.4 \text{ g}\cdot\text{cm}^{-3}$) is the density of Rh.

S2. Experimental Set-up for catalytic performance tests

The experimental set-up used for the conduction of catalytic performance tests consists of (a) a flow measuring and control system equipped with a set of mass-flow controllers (M+W Instruments) for controlling the flow and composition of the inlet gases, an HPLC pump (LD Class Pump, TELEDYNE SSI) and an evaporator maintained at 180°C for feeding the water stream, (b) a quartz micro reactor placed within an electric furnace and (c) two gas chromatographs, connected in parallel through a common set of switch valves, for on-line analysis of reactor effluent. The first GC (Shimadzu GC-9A) is equipped with two packed columns (Porapak-Q, Carboxen) and two detectors (TCD, FID) and operates with He as the carriers gas, while the second GC (Shimadzu GC-2014) is solely used for the determination of H_2 in the reformate gas and is equipped with two packed columns (Porapak-Q, Carboxen) and a TCD detector, using N_2 as the carrier gas. The reaction temperature was monitored with a K-type thermocouple inserted into the reactor. The exit of the reactor is connected with a condenser in order to condensate water before entering the gas chromatographs. Steam is mixed with LPG/He mixture and is then fed to the reactor through stainless steel tubing maintained at 180°C by means of heating tapes. A by-pass loop is also available in the system in cases that the gas stream is required to be introduced to the analysis system by skipping the reactor.



Scheme S1. Experimental Set-up for catalytic performance tests.

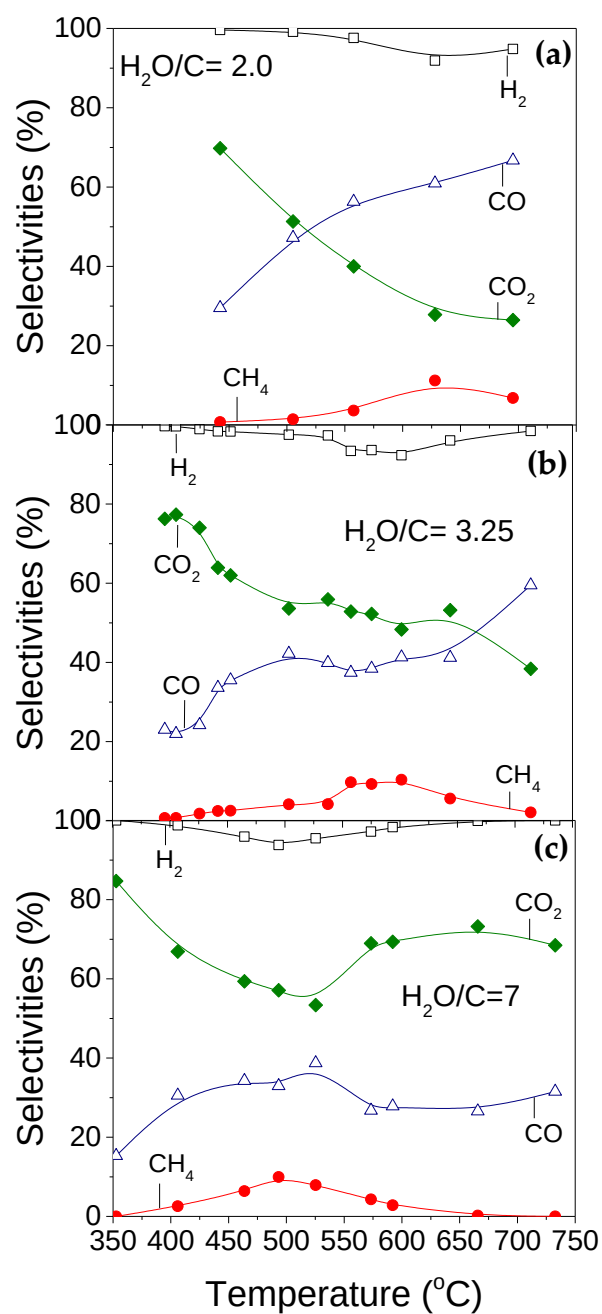


Figure S1. Effect of H₂O/C ratio on the selectivities toward reaction products obtained as function of reaction temperature over 0.5%Rh/TiO₂ catalyst. Experimental conditions: GHSV: 55,900 h⁻¹; particle diameter: 0.15<d_p<0.25 mm; Feed composition: 2.0–5.7% C₃H₈, 0.1–0.3% C₄H₁₀, 0.15–0.20% Ar, 36.8–44.1% H₂O (balance He).

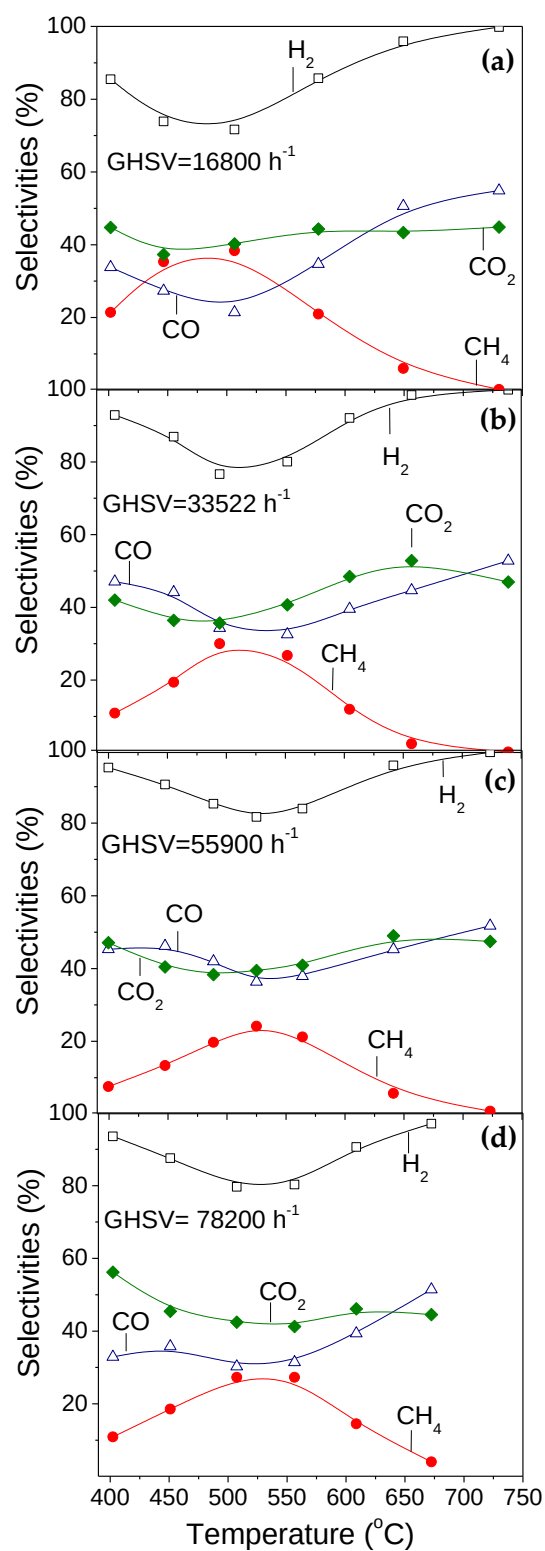


Figure S2. Effect of GHSV on the selectivities toward reaction products obtained as function of reaction temperature over 0.5%Rh/TiO₂ catalyst. Experimental conditions: H₂O/C:3.25; particle diameter: 0.15 < d_p < 0.25 mm; Feed composition: 4.5% C₃H₈, 0.15% Ar, 44% H₂O (balance He).

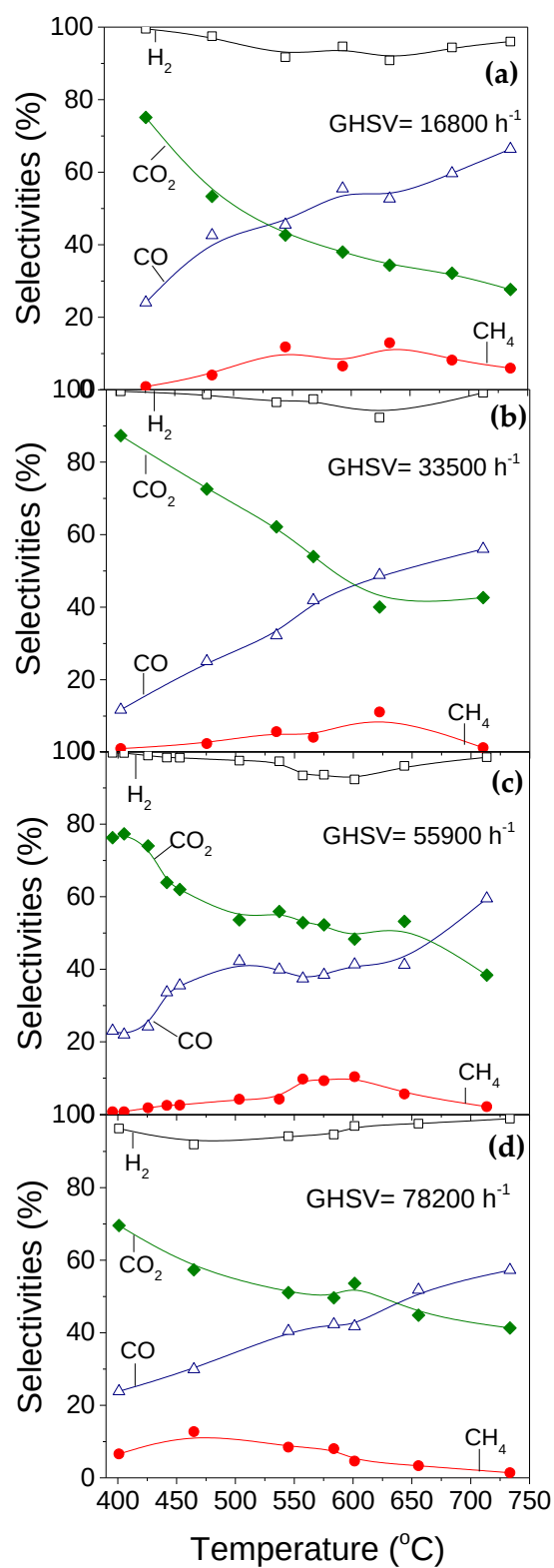


Figure S3. Effect of GHSV on the selectivities toward reaction products obtained as function of reaction temperature over 0.5%Rh/TiO₂ catalyst. Experimental conditions: H₂O/C:3.25; particle diameter: 0.15 < d_p < 0.25 mm; Feed composition: 4.27% C₃H₈, 0.23% C₄H₁₀, 0.15% Ar, 44% H₂O (balance He).

References

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