

## Supplementary Material

# The Mitigation of CO Present in the Water–Gas Shift Reformate Gas over IR-TiO<sub>2</sub> and IR-ZrO<sub>2</sub> Catalysts

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**Abstract:** CO hydrogenation and oxidation were conducted over Ir supported on TiO<sub>2</sub> and ZrO<sub>2</sub> catalysts using a feed mimicking the water–gas shift reformat stream. The influence of the support interaction with Ir and the catalysts' redox and CO chemisorption properties on activity and selectivity were evaluated. Both catalysts oxidised CO to CO<sub>2</sub> in the absence of H<sub>2</sub> and a conversion of 70% was obtained at 200 °C. For the CO oxidation in the presence of H<sub>2</sub> over these catalysts, the oxidation of H<sub>2</sub> was favoured over CO due to H<sub>2</sub> spillover occurring at the active metal and support interface, resulting in the formation of interstitials catalysed by Ir. However, both catalysts showed promising activity for CO hydrogenation. Ir-ZrO<sub>2</sub> was more active, giving 99.9% CO conversions from 350 to 370 °C, with high selectivity towards CH<sub>4</sub> using minimal H<sub>2</sub> from the feed. Furthermore, results for the Ir-ZrO<sub>2</sub> catalyst showed that the superior activity compared to the Ir-TiO<sub>2</sub> catalyst was mainly due to the reducibility of the support and its interaction with the active metal. Controlling the isoelectric point during the synthesis allowed for a stronger interaction between Ir and the ZrO<sub>2</sub> support, which resulted in higher catalytic activity due to better metal dispersions, and higher CO chemisorption capacities than obtained for the Ir-TiO<sub>2</sub> catalyst.

**Keywords:** iridium; preferential oxidation; hydrogenation; spillover; isoelectric point

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## Electronic Supplementary information

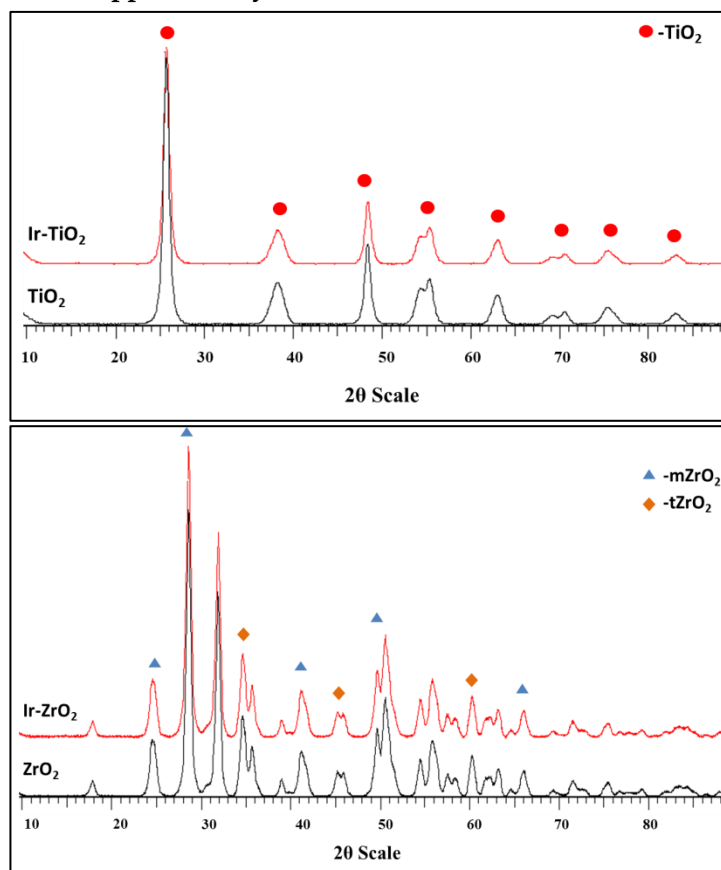
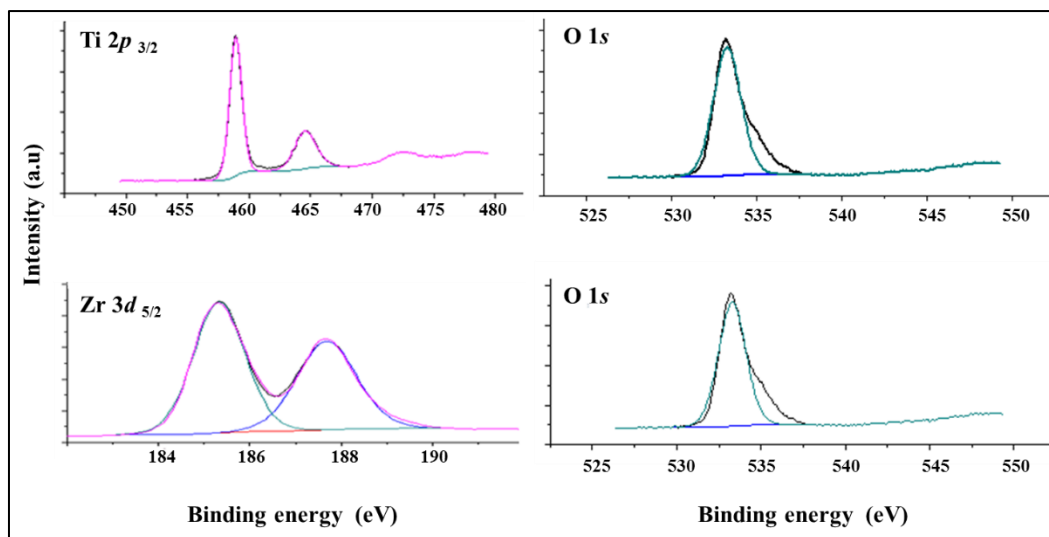


Figure S1. XRD diffractograms of the supports and catalysts.

Figure S2. XPS spectra showing the Zr 3d<sub>5/2</sub>, Ti 2p<sub>3/2</sub> and the O 1s levels for the catalysts.

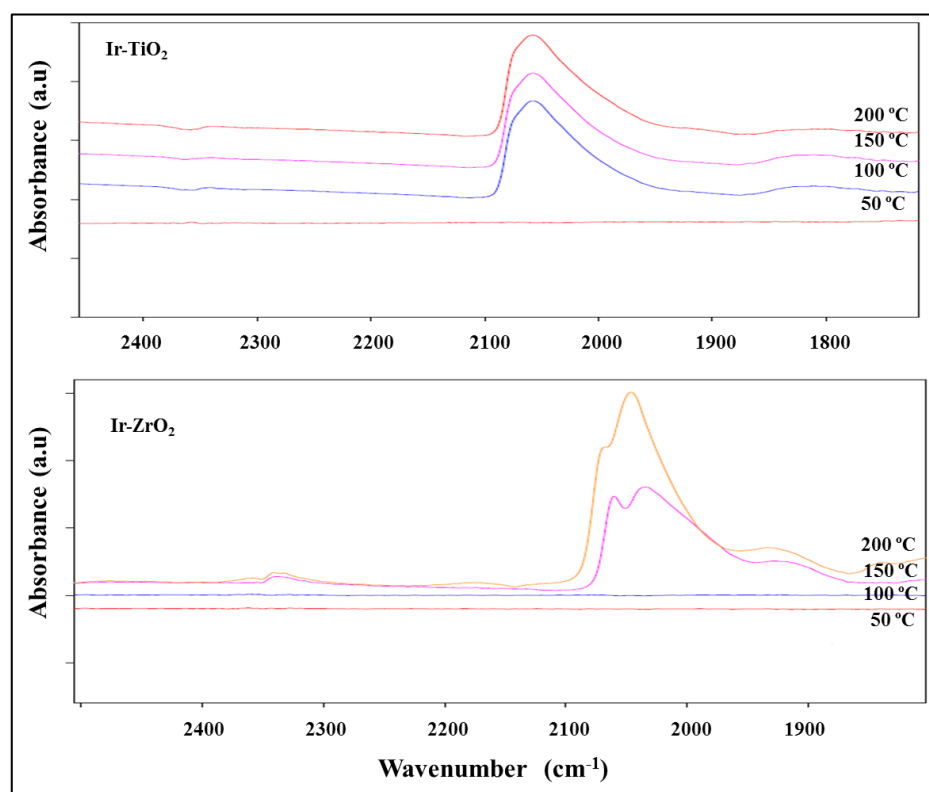


Figure S3. FTIR-CO analyses of the catalysts with increasing temperatures.

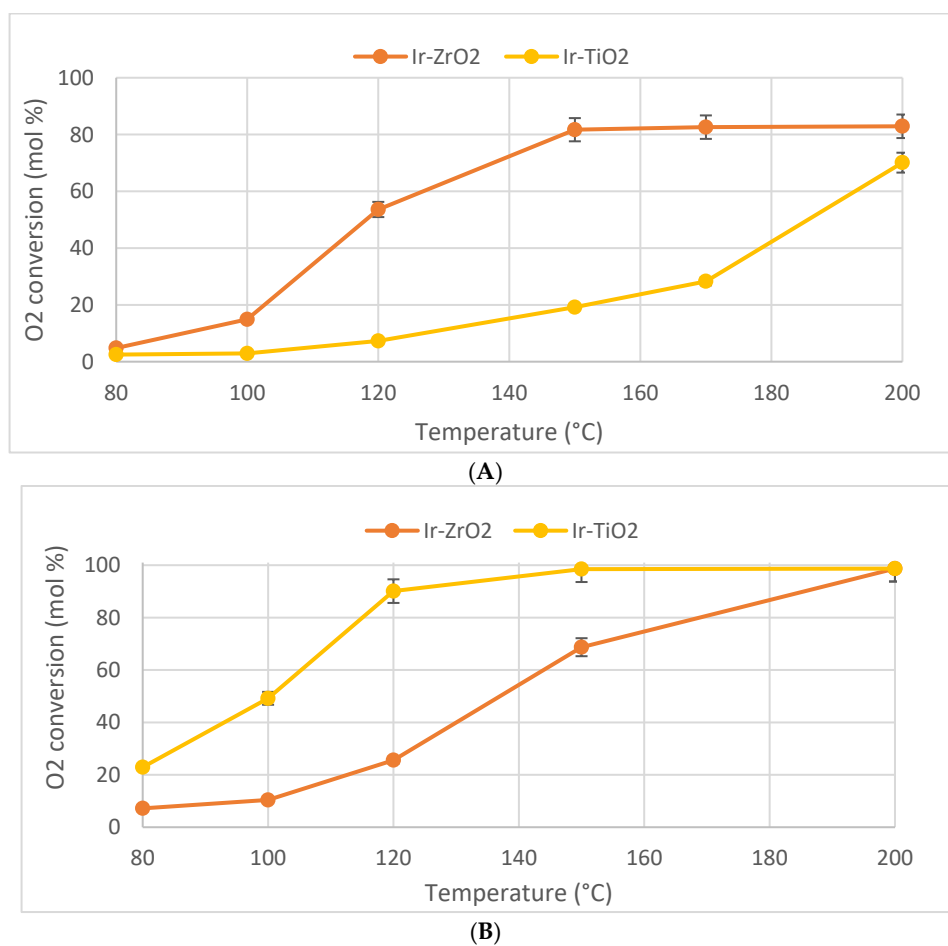
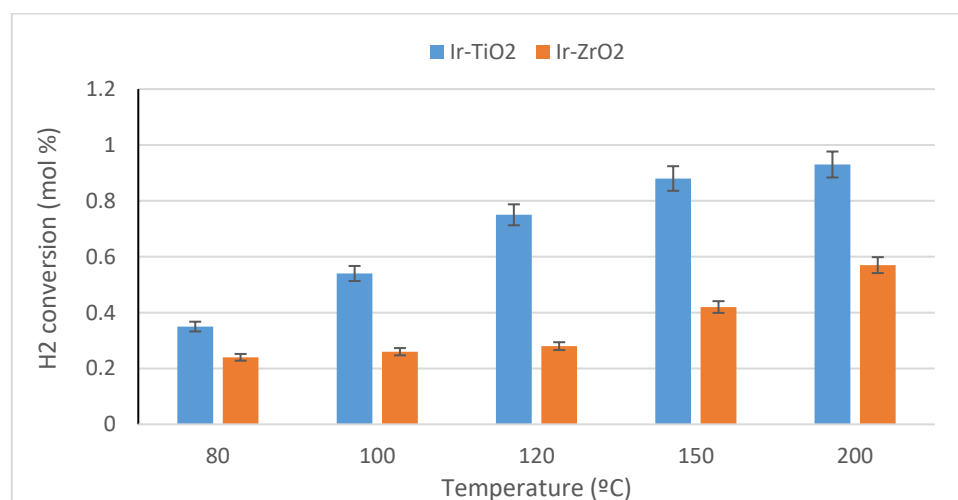


Figure S4. O<sub>2</sub> conversions of the supported Ir catalysts for (A): Total oxidation and (B): PROX.



**Figure S5.** H<sub>2</sub> conversions of the supported Ir catalysts for the PROX reaction.

### S1. Catalyst Preparation

Commercial Titania (99.7% metal basis, Alfa Aesar) and Zirconia (99.7% metal basis, Alfa Aesar) were used in this study. All catalysts were prepared by the deposition–precipitation technique [1, 2]. A 1 wt.% of Ir loading was attempted using an aqueous solution of IrCl<sub>3</sub> (Sigma-Aldrich, USA). The metal salt was dissolved in the minimal amount of deionized H<sub>2</sub>O and added to a slurry of the support (ZrO<sub>2</sub> or TiO<sub>2</sub> in 250 mL H<sub>2</sub>O), with the pH maintained between 7 and 7.5 using aqueous NH<sub>3</sub> (10%). The mixture was aged for 2 hours with constant stirring at 65 °C, filtered, and washed repeatedly with hot water (65 °C) to remove any traces of Cl<sup>−</sup>. The precipitate was oven-dried overnight at 110 °C, and calcined at 400 °C for 4 h under a steady flow of air. The materials were denoted as Ir-TiO<sub>2</sub> and Ir-ZrO<sub>2</sub>.

### S2. Catalyst characterization

Using an Optima 5300 DV PerkinElmer Optical Emission Spectrometer, the active metal contents of the samples were determined by ICP. Approximately, 0.50 g of sample (accurately weighed) was digested using 5 mL H<sub>2</sub>SO<sub>4</sub> on a hotplate. The ICP standards were prepared ranging from 0 to 50 ppm from a stock standard of Ir 1.000 µg/mL in HCl (10 wt.%, Fluka Analytical, USA). The specific surface areas of the catalysts were measured by N<sub>2</sub> physisorption using a Micromeritics TriStar II 3020 (Micromeritics, Norcross, GA, USA). Prior to the analysis, the samples (~0.2 g) were degassed under N<sub>2</sub> at 200 °C overnight. X-ray diffractograms (XRD) of the materials were recorded using Diffracplus XRD Commander Software and a Bruker VANTEC detector on a Bruker D8 Advance instrument (Karlsruhe, Germany). Scans of the materials were obtained within a 2θ range of 10–90 ° (0.5 °/min) using a Cu Kα (λ 0.1540 nm) radiation source that was operated at 40 kV and 40 mA, respectively. Temperature programmed reduction and oxidation (TPR and TPO) studies were conducted using a Micromeritics Autochem II Chemisorption Analyzer 2920 (Micromeritics, Norcross, GA, USA). The samples (± 0.05 g) were pre-treated at 80 °C under He (10 mL/min) for 30 min and then cooled to 35 °C. The reduction (5 vol% H<sub>2</sub> in Ar) and oxidation (5% O<sub>2</sub> in Ar) studies were conducted using a flow rate of 30 mL/min from 35–500 °C with a ramp rate of 10 °C/min.

Using a Bruker Tensor 27 (Karlsruhe, Germany), with a Harrick DRIFTS accessory fitted with a Harrick high-temperature reaction chamber (Pleasantville, NY, USA), the FTIR-CO spectra of the catalysts were obtained. Prior to the analyses, the samples were reduced for 3 h at 200 °C under H<sub>2</sub>. Ar was used to flush out residual H<sub>2</sub> over the samples, and CO was then pulsed through a 100 µL VICI loop using a flow rate of 25 mL/min. X-ray photon spectroscopy (XPS) scans of the materials were obtained using a Kratos Axis

Ultra DLD spectrometer (Manchester, UK). An achromatic Al K source was used and operated at 120 W while maintaining the pressure of the samples in the chamber at  $1 \times 10^{-9}$  mbar. For the regional scans, pass energies of 160 eV and 40 eV were used. Binding energy calibrations were done against the standard C 1s peak of contaminant carbon as a reference at a binding energy of 284.7 eV [3]. Using fresh catalyst samples ( $\sim 0.05$  g) that were degassed under  $N_2$  overnight (200 °C), and then placed under vacuum for 12 h prior to the analyses, CO chemisorption experiments were carried out (Micromeritics ASAP 2020, Norcross, GA, USA). The samples were housed in a quartz tube and reduced under  $H_2$  at different temperatures (200, 370 and 500 °C) for 2 h prior to the analyses. Data were recorded at 200 °C within a pressure range of 100–700 mmHg. The CO chemisorption capacities were determined by extrapolation of the CO uptake to zero pressure. Accordingly, the crystallite sizes, metal dispersions (percentage of active metal on the catalyst), metallic surface areas, and ratios of CO chemisorption capacities (ratio between the moles of CO adsorbed to moles of metal present on the surface the catalyst), were calculated using a stoichiometric ratio of 1 for CO:Ir [4].

### S3. Catalytic Testing

The catalytic testing was carried out with catalyst (75 mL) diluted with 24-grit carborundum (1:1) using a custom-built, stainless steel fixed bed reactor, at atmospheric pressure. Catalysts were pre-treated for 2 h at 200 °C under  $H_2$ . Activity measurements were recorded from RT–200 °C (oxidation reactions), and from RT to 370 °C (hydrogenation reactions). The reactant mixture for CO oxidation was 1% CO, 0.5%  $O_2$ , balanced with  $N_2$ ; for “dry” PROX it was 1% CO, 0.5%  $O_2$ , 50%  $H_2$ , balanced with  $N_2$ , and for “dry” SMET it was 1% CO, 70%  $H_2$  with balance  $N_2$ . The GHSV was kept at 12 000  $h^{-1}$ . The effluent gaseous products were analyzed using an online Agilent Micro-GC CP-4900 TCD housing 3 channels. The amount of CO and  $H_2$  converted during the reaction was calculated on the basis of inlet and outlet gas concentrations [5]. Data were recorded in triplicate (standard deviation  $\pm 1\%$ ), with  $O_2$ , C, and  $H_2$  balances ranging between 95 and 105% for all the reactions. Only  $CO_2$ ,  $H_2O$ , and  $CH_4$  were found under the conditions tested. No deactivation was observed during the reactions, and the catalysts were run for up to 96h in a hysteresis process.

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