

Testing in annular micro-reactor and characterization of supported Rh nanoparticles for the catalytic partial oxidation of methane: Effect of the preparation procedure

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Abstract

This work extends a previous study on the conditioning of Rh/Al₂O₃ during CH₄-CPO experiments at high space velocity. The effect of the preparation procedure was investigated by comparing well-known preparation techniques such as incipient wetness impregnation and grafting, and a novel CVD technique. Catalysts prepared by impregnation of the support with a solution of Rh(NO₃)₃ showed a very slow activation process, starting from an initially poor syngas activity and ending up to outstanding performances. Catalysts prepared by grafting of Rh₄(CO)₁₂ onto alumina showed a similar behaviour, but the initial activity was closer to final activity (similarly high). Catalysts prepared by CVD of Rh(acac)(CO)₂ showed very good and stable performances from the very initial CPO run. To better understand the morphological changes which occur during reaction conditions, H₂ chemisorption, CO chemisorption, CO-DRIFT and HRTEM were applied in concert to analyze the surface of samples prior and after catalytic testing. Characterization results support the hypothesis that the conditioning process is related to a reconstruction of the Rh particles which tends to eliminate small defective clusters and particles, wherein C-forming reactions are presumably highly favoured. The extent of reconstruction is thus strictly related to the heterogeneity of the surface, which is affected by the preparation procedure; heterogeneity is high over samples prepared *via* impregnation and grafting, low over sample prepared by CVD.

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1. Introduction

In previous studies we have reported that highly dispersed Rh/α-Al₂O₃ catalysts at low Rh loads undergo an activation process during repeated CH₄ partial oxidation runs, with progressive enhancement of the syngas yield in the temperature range 500–850 °C. The conditioning proceeds until reaching of extremely high performances, close to thermodynamic equilibrium, even operating at few ms contact times [1,2]. Several studies suggest that CH₄ partial oxidation over Rh and other metals (that is the combined activation of CH₄ by O₂, H₂O and CO₂) involves a network of structure sensitive reaction steps

(including C–H and C–O bonds breaking) [3–7], so that the observed activation was interpreted as the chemical effect of a surface reconstruction (with loss of defects), driven by the high reaction temperature and the adsorption of gas-phase species. Indeed, changes of the surface Rh species were observed by FT-IR on Rh/α-Al₂O₃ and Rh/ZrO₂ catalysts after treatments in several gaseous mixtures, representative of the CPO reaction process [8].

In this work, the research was extended and efforts were spent to better comprehend the nature of the Rh species on highly dispersed systems and the effect of their changes on the syngas catalysis.

Rh/α-Al₂O₃ catalysts obtained by different preparation procedures, including incipient wetness impregnation, grafting and chemical vapor deposition, were analyzed. The adopted methodologies were expected to produce different interactions

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with the support and consequently different particle distributions. The study consisted of a comparative analysis of the catalytic performance (during conditioning and at steady-state) and of the surface properties of the different materials. CH₄-CPO experiments were performed in an annular wall reactor at high space velocity, under kinetically controlled conditions which enable to investigate the initial reaction transients. HRTEM, IR-spectroscopy, chemisorption of H₂ and CO, well established techniques for the characterization of highly dispersed Rh-catalysts [8–23], were applied to compare the surface properties of samples before and after the catalytic testing. In a forthcoming paper the effect of Rh loading will also be addressed by the same techniques and, additionally, by EXAFS and XPS.

2. Experimental

2.1. Catalyst preparation

α -Al₂O₃ (12 m²/g) was used as a thermally stable support. It was obtained by calcination in air at 1100 °C for 10 h of a commercial γ -Al₂O₃ (Puralox Sba-150, Sasol). Phase composition was verified by XRD. BET surface area amounted to about 12 m²/g, with a pore volume of 0.4 cm³/g.

Rh (0.5 wt.%) was deposited by three different techniques: grafting of the alumina surface with Rh₄(CO)₁₂, impregnation with Rh(NO₃)₃ and chemical vapor deposition (CVD) of Rh(acac)(CO)₂. In the following, the labels Rh/Al₂O₃(CB), Rh/Al₂O₃(NT) and Rh/Al₂O₃(CVD) will be used for catalysts prepared by Rh₄(CO)₁₂, Rh(NO₃)₃ and CVD of Rh(acac)(CO)₂, respectively.

The grafting procedure was described in detail elsewhere [2,24]. Briefly, the powders of α -Al₂O₃ were added to a solution of Rh₄(CO)₁₂ (Strem Chemicals) in excess *n*-hexane at room temperature, under magnetic stirring and inert N₂ atmosphere. The reaction was complete when the solution turned transparent (within 30 min). Catalyst powders were filtered under vacuum and dried at 60 °C for 2 h.

Rh(NO₃)₃ (a 14.68 wt.% solution in water, Chempur) was deposited onto α -Al₂O₃ via the incipient wetness technique. The impregnated support material was dried at 110 °C for 3 h.

Rh(acac)(CO)₂ precursor (Strem Chemicals) was purified by sublimation and stored under Ar before use. CVD was performed in a home-made rotary-bed CVD apparatus [25]. About 10 g of support were calcined 3 h at 500 °C under air, then were evacuated overnight at the same temperature. After cooling down to RT, 1/3 of Rh-precursor amount needed to obtain 0.5% loading was sublimed under Ar flow (10 mL/min of carrier and 10 mL/min of make-up) at 70 °C until complete sublimation has occurred. Then the sample was reduced at 500 °C under H₂ flow. This procedure was repeated twice in order to obtain the desired Rh loading.

For catalytic testing, the catalysts were deposited in the form of thin layers on ceramic tubular supports (O.D. = 4 mm); a dip-coating technique, illustrated in detail in a previous work [1,2], was applied at this scope. Briefly, a slurry is prepared by adding the catalyst powders to an acidic solution

(HNO₃/powder = 1.7 mmol/g; H₂O/powder = 1.7 g/g) and is ball-milled for 24 h. Finally, ceramic tubes are coated on their terminal portions by dipping into the slurry and extraction at constant velocity. The coated tubes are then dried at 280 °C for a few minutes (flash-drying). Well adherent catalyst layers (5–6 mg, 10 to 20- μ m thin, 22-mm long) were obtained.

Rh loadings were verified by atomic absorption and ICP-MS (Plasmaquad 3 VG ELEMENTAL) on solutions obtained after microwave dissolution of reduced catalysts in 2 mL of 1:1 HCl/HF mixture followed by residual HF elimination by gently boiling after adding HCl (3 mL \times 1 mL). The measurements largely confirmed the nominal loads.

2.2. Testing apparatus

Reaction tests at high space velocity were carried out in a structured reactor with annular configuration. The reactor consists of an inner catalyst-coated ceramic tube, coaxially inserted into an outer quartz tube (I.D. 5 mm), giving rise to an annular duct through which the gas flows in laminar regime. The reactor was designed and the range of space velocities was chosen in such a way that the importance of mass transfer limitations was reduced and that the reactor operated far from equilibrium conditions, thus extending the useful temperature range for the kinetic investigation. Given the thermal equilibrium across the section of the ceramic tube, the temperature on the profile of the catalyst surface can be measured by sliding a thermocouple inside the internal ceramic tube [26]. Notably, effective dissipation of the heat of reaction by radiation allows realizing tests under quasi-isothermal conditions, as illustrated in [27].

A micro-GC (3000A by Agilent Technologies) was used to measure the inlet and outlet gas compositions. At each temperature, conversions and selectivities were estimated by repeated analyses, showing stable performances within 15–20 min.

Reference tests were performed at atmospheric pressure and at a gas hourly space velocity (GHSV) of 8×10^5 NI/(kg_{cat} h). The feed mixture consisted of CH₄, O₂ and N₂ with composition: CH₄ = 4 vol.%, O₂/CH₄ = 0.56, N₂ to balance. During a typical run, the reactor temperature was increased from 300 °C up to 850 °C in step-wise increments of 10–50 °C. Blank experiments verified that homogeneous gas-phase reactions did not occur under these conditions.

Since only small amounts of powders could be recovered from the annular reactor after testing, insufficient for the characterization analyses, samples of the dried slurries, representative of the deposited layers, were also aged in a conventional packed-bed reactor, wherein the reaction was carried out at increasing temperature up to 850 °C (with a final hold of 4 h) with a standard feed mixture. The packed-bed reactor operated at much lower GHSV than the annular reactor (10,000 vs. 800,000 NI/(kg_{cat} h)); however, this favoured the attainment of thermodynamically controlled conditions at 850 °C (complete conversion of reactants and over 95% selectivity of synthesis gas), that is the same conditions which established in the annular reactor after conditioning.

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