



Palladium nanoparticle's surface structure and morphology effect on the catalytic activity for dry reforming of methane



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ABSTRACT

Low loaded Pd/ α -Al₂O₃ catalysts (<0.5 wt% Pd) were characterized and tested for CH₄ reforming with CO₂ at 650 °C. The catalysts were prepared by a recharging procedure, using an organometallic precursor, followed by intermediate washing and calcination steps. FTIR spectra of adsorbed CO showed that the Pd surface structure and the particle size were dependent on the number of post-impregnation washing steps. A catalyst sample with a metal dispersion of 33% showing well defined low-index planes (by FTIR) and nearly spherical particles (by TEM) was obtained using two-washing steps. In the reaction, it exhibited a high initial activity followed by a pronounced deactivation due to carbon nanofiber's formation and sintering. TEM analysis of the used catalyst revealed the presence of spherical Pd particles at the end of the fibers that were not attached to the support surface. On the other hand, a high dispersion sample (78%) with a large fraction of Pd atoms with low coordination was obtained by applying three washing steps after impregnation. The presence of small hemispherical particles and larger nearly-flat ones attached to the support were found by TEM. In this case, the catalyst initially showed a very low activity that increased slowly up to a steady value. Although sintering also occurred and the surface structure of the used catalyst resembled the one of the low dispersion catalyst, the amount of carbon formed was quite low. The observed activation under reaction conditions was associated with the slow development of a surface structure that exhibited mainly the (100) plane favoring methane dissociation. However, the initial interaction of the particles with the support suggested by TEM micrographs seems to remain unaltered despite the particle size increase. Consequently, the process of nanofiber formation and particle separation was inhibited.

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1. Introduction

The reforming of CH₄ with CO₂ remains a process of high interest for synthesis gas production due to the availability of large reserves of natural gas with high CO₂ content. Lately, the increasing amounts of landfill gas have added more potential to this process [1]. Synthesis gas derived from dry reforming may be employed for the production of oxoalcohols, dimethyl ether. Liquid fuels or methanol synthesis require proper adjustment of the H₂/CO ratio.

The main disadvantage of dry reforming is the high temperature required to reach acceptable conversion levels (>700 °C). This temperature affects catalyst performance by sintering and carbon deposition. However, laboratory studies have demonstrated that

noble metal catalysts, like Pt/ZrO₂, Rh/ZrO₂, Rh/Al₂O₃ and Rh/OMg [2–4], are active and stable for CH₄ reforming with CO₂. Wei and Iglesia [5] have compared the rate of CH₄ reforming with CO₂ as a function of dispersion over Pt, Rh, Ir and Ru, and found that Pt activity is higher and increases with dispersion. This result suggests that surface atoms of small particles are more reactive for CH₄ activation than those on low-index planes.

Less expensive metals, like Ni and Pd, have also been investigated. They are initially very active, but deactivate rather quickly mainly due to carbon buildup. Using Pd/ α -Al₂O₃ catalysts of low metal loading (<1%) with a metal dispersion below 20%, we have shown [6] that a high initial activity for CH₄ reforming with CO₂ is followed by marked deactivation. The characterization of the used catalysts demonstrated carbon accumulation and the growth of metal particles [6]. A more detailed study of the carbon material showed the formation of well-defined carbon nanofibers [7].

The carbon buildup on Pd and Ni catalysts could be controlled by the addition of promoters, like Ce or La [6,8]. However, the behavior

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of unpromoted supported Pd remains a subject of interest due to its notable high activity for C–H bond activation. It was indeed shown by Yamaguchi and Iglesia [9] that the CH₄ activation rate is much higher on Pd catalysts than on metals like Rh, Pt or Ni. This result was obtained by using samples with a Pd loading of 1.6 wt% and low dispersion (<10%) indicated the participation of large Pd particles with low-index planes in the reaction.

The effect of Pd particle size on the catalytic activity of the mentioned reaction is difficult to investigate due to metal sintering in the presence of H₂ at high temperature, particularly on samples prepared over a low surface area support. In an attempt to remove this limitation, we prepared Pd/ α -Al₂O₃ catalysts with a low metal loading (<0.5 wt%) by using a recharging procedure that included successive impregnations and washing steps to avoid or limit the formation of large Pd particles. Fresh and used samples were characterized by FTIR spectroscopy of adsorbed CO, TPR and TEM measurements. The catalytic activity for CH₄ reforming with CO₂ was measured as a function of the time-on-stream at 650 °C by using a stoichiometric feed mixture. The results showed that particles of similar size and surface structure may exhibit a different catalytic behavior. The preparation procedure seems to affect the Pd–support interaction, which in turn influence the particle shape and the carbon formation process.

2. Experimental

2.1. Catalysts preparation

Two Pd/ α -Al₂O₃ catalysts were prepared by successive wet impregnations of commercial α -Al₂O₃ using a benzene solution of Pd acetylacetonate (2×10^{-3} g Pd/ml). The support material (Rhone Poulenc, BET area = 10 m²/g), was crushed and sieved to a particle size of about 0.33 mm corresponding to a 40–50 mesh fraction and calcined at 500 °C before impregnation. The preparation procedure involved the addition of 6.5 ml of Pd acetylacetonate solution to 3 g of α -Al₂O₃. The mixtures were maintained at room temperature for 72 h with occasional stirring. The samples were then filtered, washed two or three times with 5 ml of benzene, dried in flowing nitrogen at 100 °C during 40 min and finally calcined in flowing air at 300 °C for one hour. The introduction of benzene washing steps after each impregnation allowed the removal of the solution retained on the catalyst pores and the fraction of precursor loosely bound to the support surface. In this way, the formation of large particles during drying and calcination was minimized. After calcination, the impregnation–washing procedure was repeated four times to increase the loading. The samples resulting from this recharging procedure were finally reduced in flowing H₂ at 300 °C for 1 h. Using two washings steps after impregnation, sample F with a Pd content of 0.47 wt% was obtained while performing three washing step led to sample H with a metal content of 0.37 wt%. Metal weight loadings were determined by atomic absorption spectroscopy.

2.2. Infrared spectra of adsorbed CO

Fresh catalysts were characterized by FTIR of adsorbed CO after each impregnation step. Infrared spectra were recorded on a Fourier transform spectrometer (Nicolet 20 DXB) with a resolution of 4 cm⁻¹. Catalyst samples of 30–50 mg were pressed (5 tons/cm²) to form 13 mm diameter disks that were placed in a sample holder supported in a cell with CaF₂ windows that permitted *in situ* treatments. The catalysts were reduced at 300 °C for 30 min., evacuated to 10⁻⁶ Torr and cooled slowly to room temperature under vacuum. A FTIR spectrum under vacuum was obtained and used as a reference. CO (99.99%, Matheson) was introduced at

RT at a pressure close to 5 Torr. The IR spectrum of adsorbed CO was then obtained and ratioed with the reference spectrum. The CO/Pd ratio of fresh and used samples was determined using the integrated band intensities of linear (CO_l) and multicoordinated CO (CO_b) species and the proper extinction coefficients; 2.3×10^{-17} and 1.4×10^{-16} cm⁻¹/molec. respectively [10]. The metal dispersion, Pd_s/Pd_t (surface Pd atoms/total Pd atoms), was estimated assuming H/Pd_s = 1; CO_l/Pd_s = 1 and CO_b/Pd_s = 0.5.

2.3. Temperature-programmed reduction

TPR experiments were performed in a conventional apparatus using a Pyrex glass microreactor (i.d., 4 mm; length, 20 cm). Around 0.20 mg of catalyst was first oxidized in a flow of air at 400 °C. The sample was then cooled down to –75 °C in flowing Ar, by means of a liquid nitrogen bath. Then, the carrier gas was switched to 15 cm³/min of Ar–H₂ mixture gas (5 vol.% H₂) and the bed temperature was increased at a rate of 10 °C/min up to 300 °C. The amount of H₂ consumed or released during reduction was measured with a thermal conductivity detector (TCD) cell. The effluent gas passed through a bed of molecular sieve placed before de TCD in order to remove water formed during TPR experiments. Temperature reduction profiles were measured on fresh and used samples. In order to remove carbon deposits used samples were previously calcined in air at 500 °C.

2.4. TEM measurements

Fresh and used samples of catalyst H were analyzed by transmission electron microscopy (TEM) using a FEI Tecnai F20 supertwin operating at 200 kV (Institute for Materials, Ruhr-Universität Bochum, Germany). Catalyst F was analyzed by TEM using a JEOL 100 CX instrument operated at 100 kV (CCT, Bahía Blanca, Argentina). Pre-reduced samples were suspended in distilled water and placed on holey carbon supported on a copper grid.

2.5. Catalytic activity

Catalytic tests were carried out in a horizontal tubular flow reactor at 650 °C feed with a CH₄/CO₂/Ar (25/25/50) mixture. Catalysts charges of 0.4 g diluted with an equal amount of pure alumina were located in the central section of a one meter long quartz tube (4 mm i.d.) placed in an electric furnace. A total flow rate of 200 cm³/min, was used. The samples were reduced *in situ* with pure hydrogen at room temperature and heated to the reaction temperature with pure Ar.

Reactants and products were analyzed using two on-line gas chromatographs equipped with TCD cells. One GC used He as a carrier gas and a silica gel column (6' × 1/8") held at 90 °C to separate CO₂ from the other components. Another GC used Ar as a carrier gas and a Chromosorb 102 column (14' × 1/8") at 303 K to separate H₂, CO and CH₄. A silica gel bed was set after the reactor to remove the water produced by the reverse water gas-shift (RWGS) reaction. The concentration of water in the product stream was calculated from the O₂ material balance equations.

3. Results and discussion

The effect of washing steps after impregnation on the metal loading and the surface structure of the Pd/ α -Al₂O₃ catalysts was first investigated by FTIR. Fig. 1 shows the CO adsorption spectra of samples obtained with and without washing steps. Spectrum (a) corresponds to a sample obtained by washing twice after impregnation. The metal loading was 0.1 wt%. In this case, the main band at 2087 cm⁻¹ corresponds to CO bonded to Pd atoms with low coordination indicating the presence of small crystallites, while those at

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