



Short Communication

CO₂ hydrogenation with shape-controlled Pd nanoparticles embedded in mesoporous silica: Elucidating stability and selectivity issuesJ. Martins^a, N. Batail^a, S. Silva^a, S. Rafik-Clement^a, A. Karelavic^b, D.P. Debecker^b, A. Chaumonnot^a, D. Uzio^{a,*}^a IFP Energies Nouvelles (IFPEN) – Lyon, Rond-point de l'échangeur de Solaize, BP 3, 69360 Solaize, France^b Institute of Condensed Matter and Nanoscience/MOLEcules, Solids and reactiviTy (IMCN/MOST), Université Catholique de Louvain, Croix du Sud 2 box L7.05.17, 1348 Louvain-La-Neuve, Belgium

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ABSTRACT

Shape-controlled Pd nanocubes and nanopolyhedra particles were embedded in mesoporous silica shells and their catalytic properties for the CO₂ hydrogenation were compared to a reference Pd/SiO₂ catalyst prepared by wetness impregnation. Whereas the Pd impregnated silica exhibits a strong deactivation, the activity of both embedded solids is remarkably stable. This difference is due to a significant Pd particles sintering in the reference catalyst while no increase of particle size is observed for the core@shell solids. CH₄ selectivity is shown to be correlated to the mean coordination number of surface atoms which controls the adsorption strength of CO as intermediate species.

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1. Introduction

Catalytic conversion of CO₂ has recently attracted a lot of attention because of obvious environmental issues [1–3]. As far as the mitigation of the greenhouse effect is concerned, the recycling of CO₂ in the energy production should be preferred to the synthesis of chemicals. Among the possible routes, hydrogenation of CO₂ to CH₄, also called the Sabatier reaction, is an interesting way to obtain an added value product. Most of the studies dealing with methanation have been focused at high temperature (>300 °C) in order to promote the kinetics of the reaction which is highly limited since eight electrons are involved in the process. Extensive studies have been conducted on metal based catalytic systems and supported nickel catalysts remain as the more widely used for this reaction. Nevertheless, deactivation due to metallic particle sintering and coke formation is still strongly detrimental to the performances despite many attempts made to prevent this phenomenon. One of the options is to modify the properties of the support and the interaction it creates with the active phase. Various oxide carriers have been studied, such as doped, reducible ones and even mesostructured silica [4–8]. Low temperature methanation has also been investigated on noble metals such as Ru, Rh or Pd and the former has been identified as the more active and selective to CH₄ formation [9,10].

Recently, it has been shown that core@shell solids are highly efficient systems to enhance the stability of nanoparticles [11–13]. Due to the protective effect of the porous shell surrounding the metallic core,

sintering can be almost suppressed even at very high temperature [14, 15]. Supported Pd based catalysts are among the best metallic catalysts for hydrogen activation and have been studied in the methanation of CO₂ [7,8,16]. Erdöhelyi et al. [17] observed that selectivity was highly particle size dependent and the CH₄ formation favored on small particles, whereas RWGS (Reverse Water Gas Shift) is the main reaction occurring on large particles, leading to a preferential formation of CO.

The present study focuses on the evaluation of shape-controlled Pd nanoparticles (cube and polyhedra morphologies) embedded in mesoporous silica and compared to impregnated counterparts. Such embedded nanoparticles allow evaluating the impact of the core@shell structure on the thermal sintering and the catalytic stability in the case of CO₂ methanation. Controlling the shape of Pd nanoparticle surface structure allows the preferential exposure of different crystallographic planes, mostly (100) for cubes and (111) for polyhedra, and provides a useful way to establish structure–selectivity relationships [18,19].

2. Experimental

2.1. Catalyst preparation

The Pd nanocubes (Pd_{cub}) and nanopolyhedra (Pd_{poi}) were synthesized in a degassed water under Ar atmosphere following the procedures detailed in [20] and [21]. For the Pd_{cub}, 180 ml of a K₂PdCl₄ 2.8 mM solution under moderated magnetic stirring at 80 °C under Ar atmosphere was firstly added to 150 ml of a hexadecyltrimethylammonium bromide (CTAB) 60 mM solution. Then, about 3 ml of a sodium ascorbate 185 mM solution was added and the final colloidal solution was left stirring

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at 80 °C for 3 h under Ar. In the case of Pd_{pol}, 180 ml of a K₂PdCl₄ 2.7 mM solution was firstly added to 150 ml of a CTAB 95 mM solution under moderated magnetic stirring at 30 °C under H₂ atmosphere. Then, about 6 ml of a sodium ascorbate 80 mM solution were added and the final colloidal solution was left stirring at 30 °C for 4 h under H₂ atmosphere.

For the nanoparticle encapsulation step, a solution containing 300 ml of H₂O, 260 ml of EtOH and about 3.5 ml of NH₄OH 28 wt.% aqueous solution was added to the previous colloidal solution of nanoparticles. In order to obtain core@shell Pd nanoparticles with a mesoporous silica shell (Pd@m-SiO₂), 1 g of tetraethylorthosilicate (TEOS) is added afterwards drop wise under strong magnetic stirring and the mixture is left to maturation overnight under moderate stirring at room temperature. After maturation and EtOH addition, the suspension is then centrifuged (20 min, 14,000 rpm) to recover the precipitate. The black solid is then dried under air at room temperature and finally treated in hydrogen flow at 250 °C for 12 h (heating rate of 2 °C min⁻¹).

The reference catalyst with a final Pd loading of 2 wt.% was obtained by wetness impregnation of a Pd(NO₃)₂ solution on a Grace Davison silica support (reference X254). The solid is dried in an oven overnight at 100 °C, and then calcined under dry air flow at 450 °C for 2 h. Before the catalytic test, the catalyst was reduced in hydrogen flow at 150 °C for 2 h.

2.2. Catalyst characterization

The Pd contents of the catalysts were determined by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES, Activa – Horiba Jobin Yvon).

Transmission Electron Microscopy (TEM) images were obtained with a FEI TECNAI 20F UltraTwin operated at 200 kV.

The textural properties of the catalysts were measured by N₂ physisorption at 77 K using a Micromeritics ASAP 2420 setup.

Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectra of the catalysts in the 2300–1700 cm⁻¹ range were recorded using a Tensor27 spectrometer (20 kHz scan rate, 4 cm⁻¹ resolution, 32 scans/spectrum, MCT detector) at 25 °C under Ar. The following operation conditions were applied: adsorption of CO, followed by purge with Ar for 30 min to remove the gaseous CO species. The samples were previously reduced under H₂ at 400 °C during 3 h and then cooled to room temperature under Ar for analysis.

Coke loading after catalytic tests was assessed using a Thermo Scientific FLASH 2000-CHNS/O analyzer.

CO chemisorption measurements were conducted at 35 °C using a Micromeritics Pulses Chemisorb 2700 apparatus equipped with a TCD detector. The sample (about 100 mg) was reduced at 300 °C under a pure H₂ flow (20 ml min⁻¹) for 2 h and then flushed for 1 h 30 min under He and finally cooled down to 35 °C under He. Several pulses of a known volume of CO (185 μl) are admitted sequentially. The Pd dispersion (*D*) is calculated from the cumulative amount of adsorbed CO (i.e. the sum of non-detected CO in each pulse of a known CO volume sequentially admitted) as follows:

$$D (\%) = \frac{V_T \times M_{Pd}}{V_m \times m \times (\text{Pd wt.}\%) \times n} \times 10^4 \quad (1)$$

where *V_T* stands for the total volume of adsorbed CO (NTP conditions), *M_{Pd}* is the Pd atomic weight (106.42 g mol⁻¹), *V_m* is the molar volume of an ideal gas at 25 °C and 1 atm (24,465 cm³ mol⁻¹), *m* is the sample mass, Pd wt.% is the Pd mass content and *n* is the CO/Pd_s stoichiometry coefficient (0.5 for cubic and polyhedra Pd@SiO₂, and 1 for Pd impregnated particles).

2.3. Catalytic test

Catalytic tests were carried out at atmospheric pressure in a tubular Inconel® reactor (8 mm internal diameter) equipped with a frit of the same material in order to support the catalysts (30–50 mg, 100–350 μm particle size) diluted with 1 g of quartz (315–500 μm). The catalytic testing was performed with the same exposed metallic surface loaded in the reactor based on the CO chemisorption results. The catalyst was pre-reduced in pure H₂ flow (30 ml min⁻¹) for 1 h at 400 °C (heating rate of 5 °C min⁻¹). Afterwards, the reaction mixture (30 ml min⁻¹) was admitted (CO₂ 10 vol.% and H₂ 40 vol.% diluted in He) and measurements were performed at 400 °C (7 h) and 500 °C (10 h), with a final plateau at 400 °C (3 h). We applied the criteria recommended by Vannice [22] and found that mass and heat transfer phenomena do not exert a significant influence on the measured reaction rates. Exit gases were analyzed by gas chromatography (CH₄ and CO₂ were detected using FID and TCD detectors respectively). All the lines were maintained at 120 °C to avoid water condensation. Reaction rate constants (*k*, first order assumed) are expressed as the number of mole of CO₂ converted per mole of exposed Pd atoms by second using Eq. (2):

$$k = \frac{Q_{\text{CO}_2}}{m_{\text{cat}} \times (\text{Pd wt.}\%) \times D} \times 10^4 \times \ln \left(\frac{100}{100 - X_{\text{CO}_2}} \right) \quad (2)$$

where *Q_{CO₂}* is the CO₂ mass flow, *m_{cat}* is the catalyst mass, *D* is the Pd dispersion determined using CO chemisorption (%) and *X_{CO₂}* is the CO₂ conversion (%).

3. Results and discussion

Two types of nanoparticles morphologies were prepared: Pd_{cub} exposing mostly (100) facets (Pd_{cub}@SiO₂), and Pd_{pol} with a majority of octahedra but also pyramids or icosahedra, giving a combination of (111) and (100) facets (Pd_{pol}@SiO₂). A Pd impregnated reference (Pd_{imp}/SiO₂) containing smaller nanoparticles with a higher fraction of discontinuities (corners and edges), was used for comparison. The main physicochemical characteristics of these catalysts are presented in Table 1.

3.1. Adsorbed CO DRIFT spectroscopy

The characterization of the metallic surface followed by CO adsorbed DRIFT spectroscopy in the stretching region 1700–2300 cm⁻¹ was performed at 400 °C in order to characterize the surface at the starting temperature of the catalytic test.

In the spectra of adsorbed CO (Fig. 1), two regions are observed, corresponding to two adsorption modes of CO–Pd. The first, with a more intense band in the range 1800–2000 cm⁻¹, is attributed to multi-bonded CO adsorbed. In particular, the peaks in the range 1950–2000 cm⁻¹ are assigned to bridge bonded CO species on the (100) crystallographic planes [23–25]. It is reported that the peaks in this region may also be attributed to edges and steps [24–26]. Nevertheless, in the case of our well faceted Pd_{cub} and Pd_{pol}, the proportion of these last sites may be neglected (see Fig. 2). Peaks in the range 1900–1950 cm⁻¹ or 1800–1900 cm⁻¹ are assigned to bridge bonded and threefold hollow CO species on (111) facets, respectively [23,25,27–30]. The second region, with a much less intense band, ranges between 2000 and 2100 cm⁻¹ and the peak centered at about 2075 cm⁻¹ is ascribed to linear adsorbed CO, which is mainly attributed to corners, edges and steps, but may also indicate the adsorption on (111) facets [23,25]. In the particular case of the Pd_{imp}/SiO₂ sample, the higher linear/bridge bonded CO ratio indicates a more important contribution of linear adsorbed CO on discontinuities between exposed planes [26,29,30].

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