



Particle size effect in methane activation over supported palladium nanoparticles



Antje Ota^a, Edward L. Kunkes^a, Jutta Kröhnert^a, Martin Schmal^b, Malte Behrens^{a,*}

^a Fritz-Haber-Institute of the Max-Planck-Society, Department of Inorganic Chemistry, Faradayweg 4-6, 14195 Berlin, Germany

^b Federal University of Rio de Janeiro, Programa de Engenharia Química/COPPE/NUCAT, Cidade Universitária – CP: 68502, 21941-972 Rio de Janeiro, RJ, Brazil

ARTICLE INFO

Article history:

Received 8 August 2012

Received in revised form 9 November 2012

Accepted 13 November 2012

Available online 29 November 2012

Keywords:

Palladium

Hydrotalcites

Co-precipitation

Methane activation

Non-oxidative coupling

ABSTRACT

A synthesis method for producing MgAl oxide supported uniform palladium nanoparticles with varying diameters has been developed. The method consists of reductive-thermal decomposition of a PdMgAl hydrotalcite-like compound, formed via co-precipitation of metal nitrate salts and sodium carbonate. The hydrotalcite-like precursors were characterized by XRD, TG-MS and SEM, and were found to contain a well-defined crystalline structure and a uniform distribution of all constituent elements. The resulting catalysts were characterized by XRD, TEM, Chemisorption of CO and in situ IR measurements of CO, and were found to consist of partially oxide-embedded Pd nanoparticles with diameters ranging from $d = 1.7$ to 3.3 nm and correspond dispersions of 67–14%. Furthermore, the particle size was found to be inversely related to Pd loading. The palladium catalysts were studied for methane activation via chemisorption at 200 and 400 °C followed by a temperature programmed surface hydrogenation. The most disperse catalyst ($d = 1.7$ nm) possessed an intrinsic methane adsorption capacity, which was an order of magnitude larger than that of other catalysts in the series, indicating a strong structure sensitivity in this reaction. Additionally, the methane adsorption capacity of the hydrotalcite-derived Pd catalysts was nearly two orders of magnitude higher than that of catalysts derived through other synthesis pathways such as colloidal deposition or sonochemical reduction.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

In our previous work [1] we have shown that the catalytic activity in the non-oxidative coupling of methane over Pd nanoparticles strongly depends on the preparation method and the resulting particle size. A sonochemically reduced Pd/ α -Al₂O₃ catalyst and a Pd/ α -Al₂O₃ sample prepared by colloidal deposition differed in particle size of Pd, widths of their particle size distributions and amount of carbon incorporation in the Pd lattice after synthesis. PdC_x was found in the colloidal sample due to carbon incorporation from the protecting ligand shell upon thermal treatment. It was shown that a large particle size has detrimental impact on the methane adsorption property and the ability to form higher hydrocarbons from methane. To further investigate the aforementioned particle size effect, in the current work we aimed at developing a synthesis concept to obtain size controlled Pd-nanoparticles and to study their catalytic performance in non-oxidative methane coupling. In our synthesis approach, hydrotalcite-like compounds (HTlc's) are used as well-defined precursor materials, whose

general formula is $[M^{2+}_{1-x}M^{3+}_x(OH)_2](A^{n-})_{x/n} \times mH_2O$ [2,3] with $M^{2+} = Mg^{2+}$, Pd^{2+} , and $M^{3+} = Al^{3+}$. This synthesis concept has been previously applied for the preparation of oxide-supported intermetallic Pd₂Ga ($M^{3+} = Ga^{3+}$) nanoparticles [4]. Divalent and trivalent metal cations are incorporated in brucite-like layers and between these positively charged layers, charge-balancing anions, typically carbonate, maintain the electro-neutrality of the lattice. Furthermore the M^{2+}/M^{3+} ratio can be varied from approximately 0.2–0.4 to gain phase-pure materials.

Upon heating, HTlc's decompose into mixed oxides exhibiting high specific surface area, homogeneous metal distribution, and strong interaction between the individual elements. During reduction in H₂, noble metals such as Pd segregate out of the mixed-oxide matrix to form well-defined nanoparticles, whose size tends to depend on metal loading. PdMgAl hydroxycarbonates have already been studied by several groups and were found to be active in phenol hydrogenation, oxidation of toluene, acetone condensation, hydrodechlorination of 1,2,4-trichlorobenzene and total oxidation of methane [5–9].

The catalytic methane homologation into higher hydrocarbons under non-oxidative condition was proposed to be an alternative reaction to the oxidative coupling of methane, which also leads to CO₂ formation via partial combustion [10,11]. Direct conversion

* Corresponding author. Tel.: +49 30 8413 4408; fax: +49 (0) 30 8413 4405.

E-mail address: behrens@fhi-berlin.mpg.de (M. Behrens).

of methane into higher alkanes or alkenes is thermodynamically disfavored. To homologate methane it is necessary to dissociate methane by chemisorption on metal surfaces [12–14]. The adsorption and decomposition mechanism of methane on metallic surfaces is an exothermic activation process of dissociative and homolytic nature. Indeed, the kinetics of CH₄ adsorption on metallic surfaces has been studied using surface analyses, showing that atomic and electronic surface properties affect the adsorption and formation of intermediate species, and indicating that the methane dissociation is the determining step in this process [15].

The dissociation of methane on transition metals may occur directly (DDM—direct dissociative mechanism) or through a precursor mediated mechanism (PMM). In the first case the dissociation occurs during the impact at the surface while for the PMM mechanism desorption or dissociation occurs after adsorption and accommodation of the molecule at the surface. In this case, the reaction depends on the initial probability of adsorption. Most studies concluded that the DDM mechanism on transition metals is preferred [16–18]. Yang et al. [18] and Beebe et al. [19] showed that the methane dissociation on single crystal surfaces can form intermediate hydrocarbon species with one or two carbons, such as methylidene (CH), vinylidene (CCH₂) and ethylidene (CCH₃), besides graphitic carbon [20]. Lee et al. [16] observed on Ni surfaces CH fragments at very low temperatures which are recombined to C₂H₂ at temperatures around 230 K with simultaneous desorption of H₂ at 395 K. Heating favors the trimerization of the adsorbed C₂H₂ species [18].

Thus, chemisorption can lead to different carbonaceous intermediates some of which can further be hydrogenated to C₂₊ hydrocarbons. The nature and reactivity of the formed adspecies toward coupling are expected to be different dependent on the reaction conditions [21,22]. Furthermore the morphology, crystallinity, and abundance of vertices and kinks on the Pd surface may affect activity and selectivity in this reaction. For nanoparticles, these properties are closely associated with particle size, and related to the phenomenon of structure sensitivity in catalytic reactions. A straightforward correlation between single crystal surfaces and supported catalysts exists only for structure insensitive reactions, however, for structure sensitive reactions no direct correlation is possible below a certain particle size [23].

The main objective of this work is to study the influence of the particle size of nanostructured supported palladium catalysts in the activation of methane by chemisorption. Catalysts with different Pd particle sizes were prepared by co-precipitation, comprehensively characterized and their methane chemisorptions capacity was determined. The quantity and nature of methane adsorption sites were measured via adsorption followed by temperature programmed surface hydrogenation (TPSH), as outlined previously [1]. Additionally, we have compared the current results with the sonochemical and colloidal synthesis approaches reported in our earlier work [1] and the new catalysts turn out to have greater methane chemisorptions capacity. Regarding the non-oxidative coupling of methane in two steps, unfortunately no significant activity could be detected.

2. Experimental

2.1. Catalyst preparation

PdMgAl HTlc's were synthesized by controlled co-precipitation at pH 8.5 and a temperature of 55 °C by co-feeding appropriate amounts of mixed metal nitrate and sodium carbonate solutions. Appropriate ratio of magnesium nitrate hexahydrate (Mg(NO₃)₂·6H₂O), aluminum nitrate (Al(NO₃)₃·4H₂O) and palladium nitrate solution (Pd(NO₃)₂·2H₂O) were mixed with deionized

water. The Pd:Mg:Al atomic ratio was $x:70 - x:30$ ($x=0.1, 0.5, 1.0, 1.5$ and 2.5). A 0.345 M sodium carbonate solution was used as precipitating agent. Both solutions were added simultaneously dropwise into a 2 L precipitation reactor (Mettler-Toledo LabMax). After completion of addition, the mixture was kept for ageing at 55 °C and with stirring for 1 h. The precipitate was filtered and washed two times with warm deionized water in order to remove the nitrate and sodium ions. The solid was dried for 12 h at 80 °C in air. The precursor was reduced in 5% H₂ in Argon at 500 °C. A heating rate of 2 °C/min was chosen to achieve a mild reduction procedure after which the temperature was kept constant for 240 min. Precursor samples will be hereafter referred to as Pd_x, where x is the 10× nominal Pd content in mol%. A sample with a Pd loading of 0.1 mol% is for instance labeled Pd01.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns of the HTlc precursor and its decomposition products were recorded on a STOE Stadi P diffractometer in transmission geometry using a primary Ge monochromator, CuKα₁ radiation and a 3° linear position sensitive detector. The specific surface area (BET-SA) of the precursors and reduced compounds were determined by N₂ adsorption–desorption measurements at 77 K by employing the BET method (Autosorb-1C, Quantachrome). Prior to N₂ adsorption, the sample was outgassed at 80 °C (precursors)/150 °C (reduced samples) to desorb moisture from the surface and pores. Thermogravimetric analysis (TGA) was performed on a Netzsch STA449 thermobalance. The reduction process was studied in 5 vol% H₂ in Argon up to temperatures of 800 °C (2 °C/min). Inductively coupled plasma optical emission spectrometry (ICP-OES) was used for chemical analysis. Known amounts of the sample were dissolved in aqua regia and the content of the metals is determined after matrix matched calibration on a Vista RL, Varian. Scanning electron microscopy (SEM) images were acquired with a Hitachi S4800 FEG microscope equipped with an EDS system (EDAX) for elemental analysis. The samples were loosely dispersed on a conductive carbon tape to preserve the as-prepared morphology as much as possible. EDX spectra were acquired at an accelerating voltage of 15 kV. Transmission electron microscopy (TEM) images of Pd nanoparticles were acquired using a FEI TITAN microscope, equipped with a field emission gun (FEG) and operated at 300 kV. With computer assisted correction and alignment, the value of the spherical aberration constant C_s was kept below 100 nm in the present experiments. Typically, several scanning TEM (STEM) images of different regions were imaged for analysis of the particle size.

Volumetric CO chemisorption measurements were carried out in an Autosorb 1C (Quantachrome Instruments). The samples were pretreated in situ in the sample cell by heating to 500 °C for 60 min in 5% H₂ in argon flow (20 ml/min), followed by an evacuation (120 min) at pretreatment temperature. The samples were cooled down to 40 °C under vacuum and the chemisorption measurement was performed in the pressure range of 2–560 torr. The active surface area can be determined by using the Dual isotherm method. The weak isotherm curve was measured after the combined isothermal curve and contains only the physisorbed part of the CO because all adsorption sites for the chemisorbed CO are still occupied. The difference of combined and weak isotherms results in the chemisorbed amount of the CO. The metal surface area, dispersion and particle size were calculated according [24].

The infrared (IR) spectroscopy of adsorbed CO was carried out using a PerkinElmer Pe100 spectrometer equipped with a MCT detector. The spectra were recorded with a resolution of 2 cm⁻¹ and an accumulation of 64 scans. Self-supported wafers were obtained by pressing the powdery sample under a pressure of 123 MPa. The

Download English Version:

<https://daneshyari.com/en/article/40509>

Download Persian Version:

<https://daneshyari.com/article/40509>

[Daneshyari.com](https://daneshyari.com)