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Influence of K-doping on a Pd/SiO_2–Al_2O_3 catalyst

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ABSTRACT

This work is devoted to understand the effect of K-doping (from K_2CO_3) on the reducibility, sintering, and surface properties of Pd metal nanoparticles deposited on a peculiar high surface area SiO_2–Al_2O_3 (SA) support. The effect of K-doping on the Pd/SA catalyst is systematically investigated by means of several complementary techniques (TPR, TEM, CO chemisorption and FTIR spectroscopy), trying to separate the effects of the doping loading (spanning the large 0.25–20.3 K/Pd atomic ratio interval), of the activation temperature (up to 823 K) and of the activation atmosphere (air or H_2). It is shown that the presence of dopant, already at the lowest loading, causes an important increase of the PdO reduction temperature. The sulphur poisoning released from the support in the undoped sample during the thermal treatments in H_2 atmosphere is inhibited in the presence of K_2CO_3. The dramatic loss of metal area measured by CO chemisorption for samples H_2-treated at high temperature is not justified by the small particle sintering observed by TEM, and is assigned to the progressive particle encapsulation due to the mobilization of the support by reaction between carbonate and support itself. FTIR spectroscopy of adsorbed CO, allowing to probe the nature of the Pd surface available for adsorption, confirms the hypothesis.

1. Introduction

Palladium exhibits good catalytic properties in hydrogenation reactions that make it widely used in fine chemical synthesis [1,2]. In this context, the product selectivity is the key factor in determining the quality of a catalyst. In general, to induce selectivity other components must be added to the pristine metal catalyst, resulting in a complex nanomaterial with properties not present in the precursor [3]. A possible strategy can be a preliminary modification of the proportion of surface hydrogen species by employing bimetallic alloys (e.g. Pd–Au or Pt–Au) instead of the pure metal. The use of bimetallic catalysts can also be a way to increase the resistance to the particle sintering, and to change the geometry and the electronic properties of the active sites [4–6]. A second common practice to attain selectivity is to design a specific reaction path for the reactant/product molecules by addition of proper additives called promoters, modifiers, or dopants [7–10]. For example, Zn addition on Pd/Al_2O_3 catalyst modifies the turnover rate of the water–gas shift reaction [11], while the hydrogenation of phenol to cyclohexanone [12–15], the selective hydrogenation of acetylene to ethylene [16,17] and the conversion of syn-gas to methanol [18–20] require alkali- and alkaline earth-doped palladium catalysts. In this regard, it has been shown that modifying additives such as Ce, Zr, La and Cs oxides have influence on the electronic state of palladium supported on γ-Al_2O_3 [21].

Notwithstanding the fact that alkali metal promoters are successfully used since several decades [22], their effective overall role is still debated [13,23,24]. Together with a pure geometrical effect on the accessibility of the metal particles surface, in fact, alkali metal promoters can also influence the electronic structure of the metal particles and their mobility on the support, thus facilitating or preventing their sintering during the thermal treatments. Moreover, the contact between the doping species and the support may cause modifications to the support itself that can affect the availability of the metal particles for the catalytic process to take place. In fact, the metal particles may be covered by dissolved support material, or by the shrinkage of the porous system of the support. Furthermore, the metal particles may undergo doping by foreign species other than the added doping salt, but coming from the support [25]. It is thus clear that a complete understanding of the effect of promoters in modifying the catalyst's properties implies the investigation of all these different phenomena.

Very recently, we have investigated the morphological modifications undergone by a silicoaluminate support (SA) during all

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the steps of catalyst preparation (i.e. Pd deposition, thermal treatments and doping by K_2CO_3) [26]. In particular, it has been demonstrated that the support is highly mobilized by the addition of K_2CO_3 dopant, and that the modifications of the support increase upon increasing the dopant concentration and the activation temperature. It is expected that the processes affecting the SA support have influence also on the Pd particles, in terms of (i) Pd particle formation, (ii) Pd particle size, and (iii) fraction and properties of the available Pd surface atoms. In the present work, the effect of K-doping on the catalyst is systematically investigated by means of several complementary techniques (TPR, TEM, CO chemisorption and FTIR spectroscopy), trying to separate the effects of the activation temperature and atmosphere (H_2 and air) and of K concentration.

The system investigated here represents an example where the particle size distribution measured by TEM, often referred to as dispersion, does not match with the surface sites really available as measured by CO chemisorption. This apparent disagreement is due to the co-presence of several different effects, involving not only the Pd particles but also the support itself (such as particle sintering, lost of surface sites due to particle encapsulation, or poisoning). Most of the metal-supported real catalysts present a similar high degree of complexity which must be understood in order to determine the structure–reactivity relationship. To achieve this goal more than one technique has to be adopted, such as TEM, chemisorption and FTIR of adsorbed species. Each specific technique has its own advantages and limits; consequently, the critical use of several independent techniques is strongly recommended in order to get a complete catalyst characterization [27].

2. Experimental

2.1. Sample preparation and nomenclature

A sodium-neutralized silica–alumina (SA in the following) with a SiO_2/Al_2O_3 ratio of 5.7 was used as support. Undoped Pd catalysts (Pd_{und} in the following) was prepared by the deposition-precipitation method [28,29]. Briefly, palladium hydroxide was deposited onto the support using Na_2PdCl_4 as a palladium precursor and Na_2CO_3 as basic agent. The supported palladium hydroxide was then water-washed until residual chlorides were removed and dried at 393 K overnight. Final Pd_{und} catalyst contained 2.05% Pd and some impurities arising from SA (Na 2.64%, K 0.04%, Ca 0.05%, Mg 0.04% and S < 0.10%). It had a surface area of 141 m^2/g and a pore volume of 0.83 cm^3/g, as evaluated by N_2 adsorption measurements [26,30].

K-doped catalysts were prepared by dry impregnation of corresponding undoped catalysts with aqueous solution of dopant compounds (namely carbonate, hydroxide and chloride), followed by drying in a static oven for 16 h at 393 K. Supported metal particles were then obtained via the thermal reduction of the precursor in H_2 atmosphere, in either dynamic or static conditions, depending on the characterization technique. In order to follow the clustering of the metal particles three reduction temperatures were investigated: 393 K, 673 K and 823 K. Moreover, some doped catalysts were submitted to washing with water in order to remove the soluble fraction. Washing was done using water at 45 °C inside a sintered disc filter funnel. The investigated samples had K/Pd atomic ratios of 0, 0.25, 0.60, 1.0, 4.3, 10.0 and 20.3, hereafter labelled as Pd_{und}, PdK0.2, PdK0.6, PdK1, PdK4, PdK10 and PdK20, respectively. The adopted nomenclature allows to directly identify the approximate chemical composition of the sample. The alkali metal dopants have been introduced as carbonates unless specified, as in the case of PdK4(Cl) and of PdK4(OH) where KCl and KOH have been used as K sources, respectively.

2.2. Characterization techniques

Micromeritics Autochem 2910 instrument was used for Temperature Programmed Reduction (TPR) and CO chemisorption measurements. TPR was carried out using a heating rate of 5 K min^{-1} from 193 to 873 K in a 5% H_2 in Ar mixture at a flow rate of 50 cm^3 min^{-1}. A molecular sieve trap was put between the sample holder and the detector in order to adsorb water eventually released from the sample.

CO chemisorption experiments were performed by the dynamic pulse method at 323 K. For catalysts calcined in air, a pre-reduction treatment at 393 K was performed. In order to determine the available surface Pd atoms (surface to volume ratio, S/V_{Chemi}) a CO/Pd average stoichiometry = 1 was assumed. This assumption was verified by a parallel series of measurements performed on three different samples treated at two different temperatures with H_2–O_2 static volumetric titration, which gave a O/Pd average stoichiometry close to 1 [31]. The two methods/techniques gave a CO/O ratio in the 0.94–1.13 range, which is a strong support for the assumption of a CO/Pd average stoichiometry = 1.

High-resolution transmission electron micrographs (HRTEM) were obtained with a JEOL 3010-UHR instrument operating at 300 kV, equipped with a 2 k × 2 k pixels Gatan US1000 CCD camera. Particle size distributions were obtained counting at least 200 particles. To present the data uniformly, a class width of 1 nm was chosen for all the particle size distributions. As the sample exhibited very small Pd particles, proper contrast/sampling conditions were set by: (a) counting only Pd particles found on regions of the support thin enough to appreciate the smallest contrast differences and (b) acquiring images at a magnification of 400 k × (0.026 nm per pixel). However, it must be considered that particles with diameter below 1 nm might escape the detection by this technique. For each particle size distribution the following values were estimated: (a) the average particle diameter, $\langle d \rangle_{TEM}$; (b) the standard deviation, σ; and (c) the surface to volume ratio, S/V_{TEM}, representing the overall Pd surface sites. We adopted a cubo-octahedral model to obtain the dispersion D (defined as the number of surface atoms over the total number of atoms in cluster) as a function of the cluster diameter d [32,33]. The d vs. D relationship was then applied not simply on the average $\langle d \rangle_{TEM}$ value, but weighted according to the particle size distribution obtained from the whole TEM analysis [30].

FTIR spectroscopy of adsorbed CO was performed on self-supported pellets inside an IR quartz cell suitable for thermal treatments in vacuum and/or controlled atmosphere. The samples were heated up to the desired reduction temperature under dynamical vacuum. The reduction process consisted in three subsequent H_2 dosages (equilibrium pressure P_{H2} = 120 Torr, 1 Torr = 133.3 Pa, contact time = 5 min). After the last H_2 removal at the reduction temperature down to $P_{H2} < 10^{-4}$ Torr, the samples were cooled down to 300 K in dynamical vacuum. This procedure allowed us to obtain the reduced sample in situ inside the IR cell. All the outgassed samples were then contacted in situ with CO (P_{CO} = 50 Torr). The FTIR spectra were recorded at room temperature at 2 cm^{-1} resolution, using a Bruker IFS28 spectrometer, equipped with a cryogenic MCT detector. P_{CO} was then gradually reduced in steps from 50 to 10^{-4} Torr. After each step, the FTIR spectrum of remaining adsorbed CO species was acquired. The final spectrum corresponded to CO species irreversibly adsorbed at 300 K. All the spectra reported in this work were normalized in order to take into account the different optical thickness of the samples, i.e the quantity of Pd crossed by the IR beam. Consequently, along the whole set of samples, the apparent intensity of a given band is directly proportional to the amount of carbonyl species responsible for the component so that all the spectra are directly comparable each other.