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Short Communication

Synthesis and catalytic investigation of organophilic Pd/graphite oxide nanocomposites

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ABSTRACT

Low-loaded, organophilic Pd/graphite oxide (Pd/GO) nanocomposites were synthesized from different Pd complex precursors by applying graphite oxide as a host material and tetradecyltrimethylammonium bromide ($C_{14}TAB$) as a stabilizer. Structural investigation of the Pd/GO samples was performed by ICP-AES, XRD, N_2 sorption and TEM measurements. It was found that monodispersed Pd nanoparticles were formed, ranging in size between 1 and 6 nm, both on the external surface and in the interlamellar space of GO. The samples proved to be highly active and selective catalysts for liquid-phase alkyne hydrogenations. The variation in the catalytic performances was attributed to the difference in the amount of interlamellar Pd particles, which participated in the reactions as active sites.

1. Introduction

Graphite oxide (GO) is a carbonaceous layer-structured material, which may be produced by the controlled oxidation of graphite [1–4]. Since the formation of GO has been first reported [5], several preparation methods have been developed [6,7]. GO is a two-dimensional solid in bulk form, with strong covalent bonding within the layers and weaker interlayer contact between intercalated water molecules [1,3,8]. Several models have been proposed for the structure of GO [9–12]. One of the most recent models, introduced by Lerf et al. [13], describes a GO layer as a random distribution of flat aromatic regions with unoxidized benzene rings and other regions of alicyclic six-membered rings with tertiary hydroxyl and epoxide groups. The graphene oxide sheets are terminated with carboxyl groups, located only at the edges of the single GO sheets [13,14]. Unlike most lamellar compounds of graphite, GO cannot be characterized by a definite empirical formula [4], as GO is a nonstoichiomeric compound and its composition depends on the synthesis conditions [3,15]. Further, GO is strongly hygroscopic and tends to decompose above 333 K [15]. GO is a hydrophilic material, which may be readily dispersed in water to form stable colloidal suspensions [1,3]. Self-assembled films can be prepared from diluted dispersions, as the GO lamellae are capable of parallel orientation [16]. As a result of liquid sorption, GO exhibits swelling and disaggregation, similarly to clay minerals [2]. GO also possesses an excellent intercalation ability and cation exchange capacity and hence a large number of intercalated GO materials have been synthesized and investigated [8,17,18]. For the preparation of metal nanoparticles on graphite oxide or graphene-derived materials, several methods have been reported in the literature [19–22], including the photochemical loading of metal nanoparticles on reduced graphene oxide sheets [21] and a special heating procedure applied for metal complexes and GO [22]. In the present study, GO has been utilized as a host material for the formation of Pd nanoparticles of controlled particle size. The structure of the Pd/GO materials has been investigated and the samples were tested as catalysts for the liquid-phase hydrogenations of terminal and internal alkynes under standard conditions. For the latter reactions, Pd has been recognized as the most selective metal [23], and Pd nanoparticles supported on layer-structured materials have been found to be particularly efficient catalysts [24,25].

2. Experimental

2.1. Preparation of Pd/GO from $Pd(NH_3)_4(NO_3)_2$

1 g of finely powdered GO was dispersed in 100 cm^3 of distilled water. After adjusting the pH to 10, the suspension was left under stirring overnight. Pd nanoparticles were generated by using the precursor $Pd(NH_3)_4(NO_3)_2$ and the cationic surfactant tetradecyl trimethylammonium bromide ($C_{14}TAB$). In order to ensure the complete hydrophobization of GO, an excess of $C_{14}TAB$ was applied

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($n_{C14TAB}=130\ n_{Pd}$). The aqueous solution of C_{14}TAB was added to the aqueous solution of the precursor and the mixture was left under stirring for 2 h. After reduction of the precursor by an excess of $NaBH_4$, the solution was added dropwise to the GO suspension. This resulted in the formation of an organophilic Pd/GO nanocomposite material. Stirring was maintained for 48 h and then the solid was centrifuged and purified by washing with a pH = 9 NaOH solution 3 times. The sample (Pd/GO1) was dried in an oven at 333 K overnight.

2.2. Preparation of Pd/GO from K_2PdCl_4

The GO suspension was prepared in the same way as mentioned above. Pd nanoparticles were obtained by using the precursor K_2PdCl_4 and the cationic surfactant C_{14}TAB, by applying an excess of surfactant ($n_{C14TAB}=130\ n_{Pd}$). The precursor was dissolved in 10 cm^3 of distilled water and then the aqueous solution of the surfactant was added, resulting in the formation of a bright orange solution, which was left under stirring for 2 h. Reduction of the precursor was effected by $NaBH_4$, upon which a dark Pd sol was obtained. This was added dropwise to the GO suspension and then the mixture was left under stirring for 48 h. The sample (Pd/GO2) was purified and dried in the same way as described above. For a similar synthesis procedure, applied for Pd/hydrotalcites [25], it has been found that the effect of residual surfactant molecules on Pd was negligible and hence it was unlikely to affect the catalytic performance.

2.3. Structural characterization

The Pd contents of the samples were obtained from inductively coupled plasma atomic emission spectroscopy (ICP-AES), by using a Jobin Yvon 24 sequential ICP-AES spectrometer at 229.7 and 324.3 nm. The Pd contents for Pd/GO1 and Pd/GO2 (0.18% and 0.15%, respectively) were only slightly lower than the nominal Pd loading (0.20%).

The specific surface areas of the Pd/GO samples were determined by N_2 sorption measurements, performed by using a Micromeritics 2375 BET apparatus at 77 K.

X-ray diffraction (XRD) measurements were performed with a Philips PW 1820 diffractometer (40 kV, 35 mA, CuK_α radiation). The basal spacings of the samples were determined from the first-order Bragg reflections, by applying a PW 1877 software.

TEM measurements were effected by using a Philips CM10 transmission electron microscope, equipped with a LaB_6 cathode and a Megaview II digital camera. The particle size distributions and the mean particle diameters were determined as $\Sigma n_i d_i / \Sigma n_i$ ($\Sigma n_i > 250$), by using AnalySIS 3.1. software. The dispersions of the catalysts were calculated from the mean particle diameters d, as $D = 0.885/d$ [26].

2.4. Catalytic test reaction

The Pd/GO materials were tested as catalysts in an automated hydrogenation apparatus [25], for the liquid-phase hydrogenations of 1-pentyne, 1-hexyne, 3-hexyne, 1-heptyne and 1-phenyl-1-butyne. For each measurement, 5 mg of sample was used. The reactions were investigated at 298 K and 10^5 Pa, with a reactant:Pd (R:Pd) ratio of 2500. Pretreatment of the catalyst was carried out in static hydrogen at 298 K for 60 min, followed by the addition of solvent (1 cm^3 of toluene), and stirring for 45 min. All reactions were performed under vigorous stirring (1400 rpm) to eliminate mass transport limitations. The hydrogen consumption was recorded as a function of reaction time. The reaction rates were determined from the slopes and the turnover frequencies (TOF) were calculated as $TOF = 7.2538 \cdot 10^{-5}$ RS/D [s^{-1}], where RS is the initial rate and D is the dispersion of the catalyst. Quantitative analysis of the products was performed with an HP 5890 gas chromatograph equipped with a HP-I capillary column and a flame ionization detector (FID). The experimental error was ±2% for repeated runs.

3. Results and discussion

The specific surface areas of the Pd/GO samples were very low (2.5 $m^2\,g^{-1}$ and 3.5 $m^2\,g^{-1}$ for Pd/GO1 and Pd/GO2, respectively), indicating that the interlayers of organophilic GO were highly loaded with alkyl chains, as related to the intercalation of C_{14}TAB molecules, and therefore N_2 adsorption took place on the external surfaces of the GO particles.

The pore size distribution could not be determined, as GO was found to be a nonporous material.

The XRD patterns of GO and the Pd/GO nanocomposites are demonstrated in Fig. 1. For the GO host, a well-defined peak was obtained at $2\Theta = 12.9°$, which corresponds to an interplanar distance (d_L) of 0.69 nm. The characteristic d_{002} reflection of graphite at 26.6° could not be observed, which confirmed that complete oxidation took place [27]. As a result, a well-ordered, lamellar structure was formed, which was more open than that of graphite ($d_L = 0.336$ nm) and thus more susceptible to intercalation [27]. The pattern of Pd/GO1 is comprised of three peaks at $2\Theta = 7.82$, 9.08, and 18.16°. The latter peaks characterize the same basal spacing, 0.97 nm. The first reflection, appearing with smaller intensity, belongs to another phase, in which the c-axis repeat distance is 1.13 nm. These distances indicate that both phases comprise of surfactant-stuffed interlayers with slightly different amounts or conformations of the intercalated molecules. Pd/GO2 shows a similar diffractogram, but the first two reflections are markedly shifted toward lower diffraction angles (with d-values of 1.4 and 1.2 nm). On the other hand, the position of the $2\Theta = 18°$ ($d = 0.5$ nm) peak remained unchanged. Since the related distance is too low to be accounted for a first-order reflection of GO ($d_{001} = 0.66$ nm for the air-dry sample, whereas the lowest values for anhydrous Brodie-GOs are ca. 0.59 nm [15]), we still assign this peak as a second-order reflection. The fact that the peaks no longer occur at integral d-values suggests that randomly interstratified structures were formed, that is, the structure, conformation and interlayer concentration of surfactant molecules were different. Nevertheless, the relatively low interlamellar distance implies that the density of accommodated surfactant molecules is not too high and the molecules lie flat and take a monolayer arrangement [17]. The XRD patterns do not give conclusive evidence whether the Pd nanocrystals are inserted between the GO layers, because the Pd loadings are lower than the detection limit for ultrafine crystallites generally exhibiting significant broadening and concomitant intensity loss, to which interstratification may also contribute.

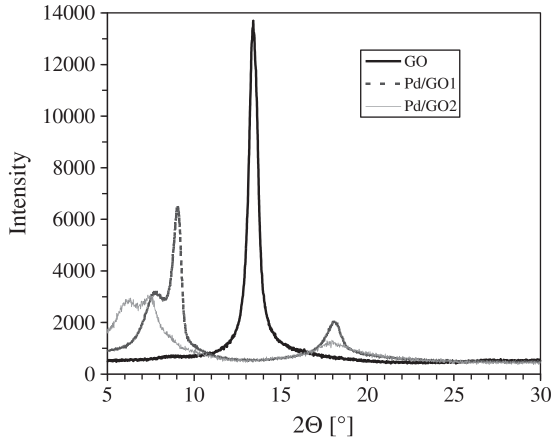

Fig. 1. XRD patterns of GO, Pd/GO1 and Pd/GO2.