

Solid-state solvent-free catalyzed hydrogenation: Enhancing reaction efficiency by spillover agents

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ARTICLE INFO

Article history:

Received 26 January 2013

Received in revised form 5 April 2013

Accepted 6 April 2013

Available online 15 April 2013

Keywords:

Hydrogenation
Spillover
Carbon nanotubes
Solid-state
Solvent-free
Hydrogen storage
Catalysis
Phenyl acetylene

ABSTRACT

The adsorption kinetics of hydrogen on solid support is accelerated by three orders of magnitude upon adding carbon nanotubes (CNT) to the support. The gas–solid catalytic hydrogenation is studied at ambient temperature and sub atmospheric pressure while the support consists of a mixture of nano Pd-on-carbon with unsaturated hydrocarbon H-acceptor. The addition of a small amount of pristine CNT minimizes the required Pd concentration. A similar effect is demonstrated by addition of different oxides to the composite, but at much higher additive concentrations. The addition of the spillover agent improves the transport of the hydrogen atoms in the composite to remote sites with low Pd concentration via a spillover mechanism. Therefore, it is possible to overcome the decelerating effect of inhomogeneity in the support. The irreversible gas–solid hydrogenation could serve as a simplified platform to study the slower step of hydrogen spillover, which operates also in hydrogen storage processes.

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1. Introduction

Solid phase catalyzed hydrogenation of phenyl acetylenes under low hydrogen pressure and ambient temperature is a fast, irreversible and quantitative reaction, which could reach high yields (>99%) of the hydrogenated product [1,2]. The reaction has useful applications in avoiding possible explosion or chemical damages by scavenging hydrogen in closed enclosures such as cell-phone batteries, optical fiber cables or radioactive waste containers [3–5].

Catalytic solid–gas hydrogenation mechanism involves hydrogen activation on a metallic surface, followed by atomic *hydrogen spillover* (SO), a term describing a transport (e.g., via surface diffusion) of activated hydrogen from one solid surface to another. Recently, hydrogen SO has been pointed out as a vital step in hydrogen storage processes [6–10] and in the chemistry of fuel cells electrocatalysts [11]. The well known SO phenomenon in liquid phase heterogeneous catalysis has been extensively studied during the last four decades with carbon and oxide promoters, and found to be rather complex [12,13].

The solvent-free, solid–gas hydrogenation is, however, a simpler system, which makes it an ideal platform for the study of dissociated hydrogen direct interactions with the solid surfaces.

A *primary* hydrogen SO involves transport of activated hydrogen from the metallic catalyst to the catalyst support, while a *secondary* SO relates to hydrogen transport to a third solid, such as carbon nanotubes (CNTs) [14] or zeolites [15], which “bridges” between the catalyst support and final H-acceptor [16].

The study of secondary SO effect on hydrogen storage has been performed by comparing the hydrogen uptake mediated by various substrates, e.g., multi wall CNTs (MWCNT) [17–23] and single wall CNTs (SWCNT) [24,25], graphite [26,27], activated carbon nanofiber [28,29], activated carbon [30–32] and graphene nanoplatelets [33].

Hydrogen SO step is followed either by hydrogen covalent binding (e.g., hydrogenation process) or by reversible physisorption of hydrogen to a solid support in hydrogen storage process. Therefore, it is important to isolate and to evaluate the contribution of the net SO step to the kinetics of the overall hydrogenation/adsorption process.

The objective of the present research is to study the kinetic effect originated by adding a SO agent (e.g., pristine CNTs or various oxides) to the composite to be hydrogenated. We focus on the SO in a catalytic hydrogenation reaction of an unsaturated hydrocarbon (acceptor) such as diphenyl acetylene (DPA) or di-(phenylethynyl) benzene (DEB). The overall solid phase hydrogenation process includes both a SO step (slower) and the irreversible covalent

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Table 1
Properties of the MWCNT.

	Cheaptube 20–30 nm	NC 7000
Outer diameter ^a	20–30 nm	9.5 nm
Inner diameter ^a	5–10 nm	No data
Length ^a	10–30 μm	1.5 μm
Purity (carbon) ^a	93.5 wt%	90 wt%
Surface area ^a	110 m^2/g	250–300 m^2/g
Metals ^a	5.5 wt% (Ni + Fe)	10 wt% (metal oxides)
D/G ^b	0.89	1.2

^a As specified by the supplier.^b As measured by Raman spectroscopy.

bonding of the hydrogen to the acceptor (faster). The rate-determining step is the SO process, which is the focus of this study.

2. Experimental

2.1. Materials

1,4-Di(phenylethynyl)benzene (DEB) was synthesized according to [34,35]. Diphenyl acetylene (DPA) was purchased from Aldrich and used without further purification.

Multi wall carbon nanotubes were purchased from Cheaptube (CT 20–30) and from Nanocyl (NC7000) and were used as received. The properties of the CNT are presented in Table 1.

Palladium on carbon 5%, silica fumed, silica and zirconia nanopowder were obtained from Aldrich, and Alumina nanopowder was purchased from Strem.

2.2. Preparation of a powdered sample for hydrogenation

Spillover agents, e.g. oxides (0–1500 mg) or pristine CNTs (0–150 mg) and Pd/C (60–210 mg) were grounded with hydrogen acceptors (DPA or DEB (1000 mg)) in a Pulverisette 6 milling machine (Fritsch) in an agate bowl at 600 rpm for 15 min.

2.3. Kinetic measurements of hydrogenation

The rate of hydrogenation was determined by following the decrease of hydrogen pressure during the reaction, using a home-made computer controlled Volumetric Pressure Measurement (a Sievert type apparatus) system (Fig. 1) [2].

A pyrex Reaction Chamber (RC) (Fig. 1) containing a solid mixture of an unsaturated hydrocarbon (DPA or DEB), a catalyst (Pd/C) and spillover agent (CNTs or oxides), is connected to the vacuum line. Following the evacuation, hydrogen is introduced to a calibrated volume and then transferred into the RC at the desired initial pressure. The hydrogen pressure is measured at an accuracy of ± 0.013 kPa (± 0.1 Torr).

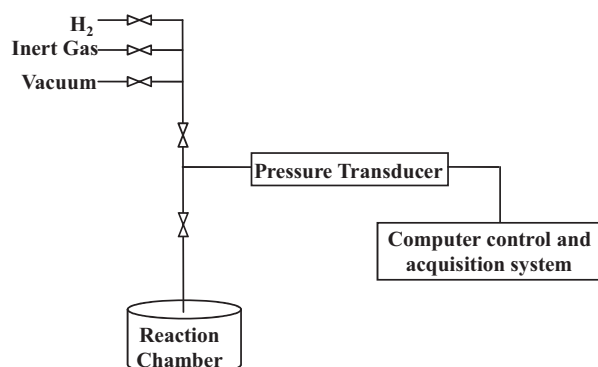


Fig. 1. Schematic description of volumetric pressure measuring apparatus.

A multistage pulse hydrogenation process is then performed. The portion of hydrogen introduced at each pulse is 5% (or 10%) of the sample theoretical hydrogen capacity, as calculated from the number of acetylene bonds in the acceptor molecule (under our experimental conditions there is no hydrogenation of aromatic rings of the DPA or DEB, as proved by GC/MS [2]). The sample weight is adjusted to match an initial hydrogen pressure of 13.3 kPa (the typical sample weight is 150–400 mg). The measurement of the pressure drop for each portion is stopped when 98% of the hydrogen is consumed, unless the reaction rate is too slow, then the experiment is stopped after 12 h. The introduction of additional hydrogen portions is finally stopped when the substrate reaches about 50% (or 80% in several experiments with DEB) of the theoretical hydrogen capacity, according to the experimental setup.

We measured in situ the temperature in the reaction vessel during hydrogenation to make sure that a gas–solid reaction takes place. For both reactions (DEB and DPA) we found that the maximal temperature was well below the melting points of all the reagents (an example of a temperature profile for DPA is shown in Fig. S1 in supplementary materials). There was no ocular evidence of liquid appearance during the reaction for both systems.

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.molcata.2013.04.007>.

A convenient measure of the reaction rate is the time needed to complete a given percent of the acceptor saturation. The cumulative time needed to reach this end point is termed t_{50} or t_{80} .

Fig. 2a presents a typical time–pressure multistage hydrogenation of the DEB acceptor (each portion is 10% of the full capacity), where t_x is an accumulative time to reach conversion of X% of hydrogenation. The first hydrogen portion (left curve) has a relatively longer initial delay due to the initial catalyst activation step. The last portion (right curve) is not completely consumed at the time scale of the experiment due to the slow rate of the reaction at this point.

The conversion vs. time presentation enables one to compare between different samples. Fig. 2b shows the time dependence of the conversion of DPA hydrogenation as a function of the concentration of CNTs (here, each portion is 5% of the hydrogen theoretical capacity). The effect of MWCNTs addition could be clearly seen. Note that the time scale is logarithmic, thus the reaction rate is increased by almost three orders of magnitude by addition of 10% of MWCNT.

Henceforth, t_{50} and t_{80} are used as the ordinate, while the abscissa will be the SO agent concentration in the sample (wt%).

2.4. Transmission electron microscope (TEM)

TEM micrographs were obtained by FEI Tecnai 12 G2 TWIN TEM, operated at 120 kV. The microscope was operated at 120 kV at a low electron-dose mode (to reduce radiation damage) and at a few micrometers under focus to increase phase contrast. Images were recorded on a Gatan 794 CCD camera and analyzed by Digital Micrograph 3.6 software.

3. Results and discussion

The hydrogen SO phenomenon was followed by tracking the kinetics of irreversible hydrogenation reaction. The influence of different types of SO agents, e.g. CNTs and oxides, at different concentrations was examined on the kinetics of two types of organic unsaturated substrates (DPA and DEB).

The general hydrogenation behavior of DPA and DEB is similar while the reaction rate of DEB is faster than that of DPA. We chose to describe the irreversible solid phase hydrogenation without a SO

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