On the nature of spillover hydrogen species on platinum/nitrogen-doped mesoporous carbon composites: A temperature-programmed nitrobenzene desorption study

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ABSTRACT

Spillover hydrogen species were generated by dissociative H_2 adsorption on Pt nanoparticles supported on nitrogen-doped mesoporous carbon. The spillover hydrogen species on the support can migrate back to the Pt nanoparticles and hydrogenate subsequently adsorbed nitrobenzene to aniline at 80 °C, which was detected during temperature-programmed desorption experiments from 80 to 300 °C in pure He. The amount of spillover hydrogen can be tuned mainly by the pre-reduction temperature rather than by other parameters. The absence of aniline formation during nitrobenzene desorption experiments in the presence of CO indicates that hydrogenation occurs exclusively on Pt and that the spillover hydrogen species are present on the carbon support in a chemically inactive state. Most likely, spillover hydrogen is reversibly stored on the carbon support as adsorbed protons on the surface and as electrons in the bulk. These findings provide a new perspective on Pt/C-based hydrogen storage materials and fuel cell catalysts.

1. Introduction

Since the first observation of hydrogen spillover effect on Pt/WO_3 catalysts [1], much attention has been devoted to studying this hydrogen activation and migration phenomenon due to its fundamental importance in heterogeneous catalysis [2,3] and hydrogen storage [4,5]. Generally, hydrogen spillover is defined as the transport of activated H species, adsorbed or formed on a surface, to another surface, which does not adsorb or form the activated H species under the same conditions [2]. A common hydrogen spillover system consists of metal nanoparticles for hydrogen activation, mostly Pd, Pt and Ru, and supports for hydrogen migration, such as transition metals [6,7], metal oxides [2,3] and carbon materials [4,5]. It is widely accepted that the spillover H species are very difficult to detect [2,4,8], and, unfortunately, some of the methods, which had been employed to investigate the mechanism of hydrogen spillover, were gradually falsified by further studies in this field [3]. Although spillover H species had been believed to

exist in the form of protons, atoms, or both protons and atoms depending on the nature of the surface for a long time [9], recent studies by means of the state-of-the-art characterization techniques provided direct experimental evidence revealing the mechanisms of hydrogen spillover and the precise assignment of the nature of spillover H species on different supports. Sykes and co-workers [6] observed the spillover H species on a well-defined Pd/Cu alloy surface by scanning tunneling microscopy. Coupled with an *in situ* temperature-programmed desorption (TPD) experiment, spillover H species were found to be H atoms, which were active for styrene and acetylene hydrogenation. Further work on a Pd alloy pointed out that the reversible spillover pathway can be controlled by selectively poisoning the Pd sites with CO [10,11]. In this way, the spillover H species were imprisoned solely on the Cu surface, where they were not able to recombine and desorb in the absence of a clean Pd surface, but were able to hydrogenate unsaturated C=C bonds [10]. In comparison, Karim et al. [12] investigated the support effect of metal oxides using reducible TiO_2 and nonreducible Al_2O_3 on hydrogen spillover by *in situ* spatially resolved X-ray absorption spectroscopy with a series of $Pt-Fe_2O_3$ nanoparticle pairs in varied distance. It was found that the spillover H species on TiO_2 reduced the remote Fe_2O_3 nanoparticles

as a function of distance via a coupled proton-electron transfer mechanism, whereas hydrogen spillover on Al_2O_3 had to be mediated by water and was about 10^{10} times slower than on TiO_2 [12].

In the last decade, hydrogen spillover on carbon materials attracted substantial interest due to the significant enhancement of hydrogen storage on carbon materials [13,14]. In contrast to metal and metal oxide supports, the spillover H species were found to not only diffuse on the C surface, but also intercalate between the layers of the graphitic structure [15]. However, the mechanism and the nature of spillover H species on carbon supports has been rarely studied in great detail due to the difficult characterization of both the carbon support and the H species. Mitchell et al. [16] attempted to experimentally clarify the nature of spillover H species on Pt/C and Ru/C fuel cell catalysts using inelastic neutron scattering (INS) spectroscopy. The INS spectra of H_2-treated fuel cell catalysts were found to be similar to coronene, leading to the conclusion that bonds were formed between spillover H species and the carbon support, as well as to the assumption that spillover H species were atoms on carbon supports according to the coronene structure. Further studies based on diffuse reflectance infrared Fourier transform spectroscopy as well as Raman spectroscopy confirmed the formation of highly reversible H-C bonds upon H_2 exposure to the catalysts with bond energies significantly lower than a typical sp^3 bond [17–19]. However, based on the assumption of spillover H species being atoms on the carbon support, several catalytic phenomena cannot be fully explained and more efforts have to be undertaken to clarify the remaining uncertainties. For instance, to the best of our knowledge, hydrogenation using spillover H species on a carbon support has not been reported so far. More importantly, the high reversibility of hydrogen spillover [20] is not in agreement with the observation that hydrogen spillover can be enhanced by a variety of functional groups [21–23], because atomic H species in a high concentration are highly reactive with respect to each other, to the defects and to the functional groups of the carbon supports [5]. Furthermore, there is an obvious discrepancy between hydrogen storage systems and proton-exchange membrane hydrogen fuel cells. In both systems hydrogen adsorption, activation and migration upon exposure to H_2 on Pt/C catalysts can occur, but the electrons are still combined with protons in a hydrogen storage system, whereas the electrons are transferred to an external circuit in a fuel cell [24–26]. These differences raise questions about the involvement of H spillover on carbon supports in catalytic processes hampering research pertaining to the spillover effect [27,28]. Therefore, more experimental evidence and a generally valid model for hydrogen spillover on carbon supports are highly desired to explain the H-C interaction in hydrogen spillover systems for different applications.

In this work, we investigate the reactivity of spillover H species on nitrogen-doped mesoporous carbon (NMC) by means of temperature-programmed nitrobenzene desorption/surface hydrogenation (NB TPD) experiments. Nitrobenzene (NB) has been selected as probe molecule, because the nitro group has been reported to be hydrogenated with high selectivity compared with other reducible groups [29] and is even reducible on metal-free catalysts [30,31]. Therefore, it can serve as a sensitive probe site for active H species. Furthermore, the aromatic ring enables a well-defined adsorption/desorption behavior via a strong π-π interaction with the carbon support [32,33]. In addition, aniline (AN) is the only product under the applied reaction conditions, which enables the continuous fast quantitative determination of the composition of the effluent [34]. The NB TPD experiments under varied conditions indicate that H species originating from dissociative adsorption on Pt can be stored on NMC, and the spillover H species can be used in NB hydrogenation due to the reversible spillover process. The CO-poisoned NB TPD experiments

confirm that the spillover H species are highly reversible and only active in the presence of non-poisoned Pt surface for NB hydrogenation. The results from the NB TPD studies suggest that the spillover H species on NMC are transported as protons on the surface, while the electrons are transported in the bulk. These findings may provide a new point of view in understanding the hydrogen activation and migration on Pt/C composites for hydrogen storage materials and hydrogen fuel cell catalysts.

2. Experimental

2.1. Catalyst preparation

The NMC support was synthesized by pyrolysis of a nitrogen-containing precursor with $CaCl_2$ as template [35,36]. The as-prepared NMC support was purified with 1.5 M HNO_3 aqueous solution at room temperature for 72 h and dispersed and filtered in deionized water several times until the pH of the waste solution became neutral. Purified NMC was dried in flowing air at 80 °C overnight and ground in an agate mortar for further use. For the deposition of Pt nanoparticles, 0.02 M chloroplatinic acid solution was prepared by dissolving chloroplatinic acid hydrate (99.9%, Sigma-Aldrich) into 25 mL ethanol. Then, the predetermined amount of solution with the nominal Pt loadings of 0.3%, 1% and 3% was added to a suspension of 1 g carbon support in 50 mL ethanol and stirred vigorously at room temperature for 2 h. Then, the suspension was dried and the resulting dark powder was reduced in a tubular furnace at 200 °C for 3 h in 100 NmL min^{-1} in 50 vol% H_2 diluted in He. Finally, the catalysts were carefully passivated and stored in air. For comparison, syntheses with the same procedure were performed using three other supports: activated carbon (AC, Norit SX2, Sigma-Aldrich), carbon black (CB, Vulcan XC72R), and MCM-41 (Sigma-Aldrich).

2.2. Catalytic tests

NB hydrogenation was carried out in a flow setup with a tubular glass reactor connected to an online gas chromatograph (GC). The setup was fully computer-controlled through mass flow controllers and pneumatic valves. For the catalytic test, 5 mg of catalyst were diluted with 1 g of quartz sand and fixed in the reactor using quartz wool. The tests were performed between 80 and 200 °C with an interval of 20 °C. At each temperature, the catalyst was pre-reduced with 10 vol% H_2/He for 30 min and then exposed to the reactant mixture containing 0.3 NmL min^{-1} of NB, 3 NmL min^{-1} of H_2 and 96.7 NmL min^{-1} of He for 4 h. The products were sampled every 30 min. Steady state at each temperature was reached after 4 h of time on stream, and then the degree of NB conversion was determined.

2.3. Temperature-programmed nitrobenzene desorption/surface reaction

NB TPD experiments were performed with 50 mg sample sandwiched in quartz wool in the same tube reactor used for the catalytic tests. Standard procedure: (a) pre-reduction at 80 °C for 30 min in 10 vol% H_2/He flow; (b) purging with pure He at 80 °C for 30 min; (c) exposure to 3000 ppm NB/He flow at 80 °C for 2 h; (d) purging with pure He at 80 °C for 2 h; (e) linearly heating from 80 to 300 °C in pure He. A total flow of 100 NmL min^{-1} was used in all the steps. The effluent gas was analyzed by GC with an injection interval of 1 min. H_2 concentration, pre-reduction time and temperature in step (a), the He purging time in step (b) and (d), as well as the linear heating rate in step (e), were systematically varied to study the effect of H spillover. For the CO poisoning experiments,