

# EFFECT OF METAL ADDITIONS ON THE HYDROGEN UPTAKE OF MICROPOROUS CARBON AT NEAR-AMBIENT TEMPERATURE

Cristian I. Contescu, Nidia C. Gallego, and Vinay V. Bhat\*

Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

\* Wildcat Discovery Technologies, Inc., San Diego, CA

## Introduction

Enhancing the hydrogen sorption capacity of microporous carbon materials at near-ambient temperature continue to be a challenge and the subject of intense research. Physisorption alone on microporous carbons is not strong enough to provide the desired levels of hydrogen uptake. Modifying carbons with small amounts of metals has been proven effective to increase the amounts adsorbed. However, very different mechanisms may be involved when the promoters are transition metals or alkali metals. In this presentation we compare the effect of additions of palladium and/or alkali metals on the hydrogen uptake of microporous carbons, in an attempt to differentiate between the possible mechanisms leading to enhanced hydrogen capacity and fast kinetics.

## Experimental

A developmental sample of ultramicroporous carbon (UMC) was provided by MeadWestvaco Corporation (Charleston, SC). It was prepared by a secondary-stage chemical activation with KOH of a wood-based carbon activated with phosphoric acid. Prior to hydrogen adsorption measurements, the carbon was extensively washed with hot deionized water to remove soluble impurities. This procedure lowered carbon pH from 9 to 8. The main impurities revealed by elemental analysis were K (1200 ppm) and Na (540 ppm) residual after chemical activation. Also present were Fe, Cr and Ni in ppm amounts. Gas adsorption analysis of UMC indicated high surface area (2450 m<sup>2</sup>/g) and high pore volume (1.19 cm<sup>3</sup>/g), with large contributions from micropores (0.83 cm<sup>3</sup>/g at < 2 nm) and ultramicropores (0.63 cm<sup>3</sup>/g at < 0.7 nm). A second sample labeled **UMC-Pd** was prepared by physically mixing UMC with 10 wt% Pd nanoparticles (40-60 m<sup>2</sup>/g; Sigma Aldrich). Hydrogen adsorption on UMC and UMC-Pd samples was measured at several temperatures (between 2 and 60 °C) using both volumetric (Autosorb 1C at P<sub>H<sub>2</sub></sub> < 0.1 MPa) and gravimetric (IGA-1 at P<sub>H<sub>2</sub></sub> < 2 MPa) methods. Special care was taken in order to eliminate all sources of experimental errors that may affect adsorption measurements. A research-grade H<sub>2</sub> gas (99.9999 % Matheson) was used; the gas was passed over a cold trap at 77 K to remove water traces and other condensable vapors.

## Results

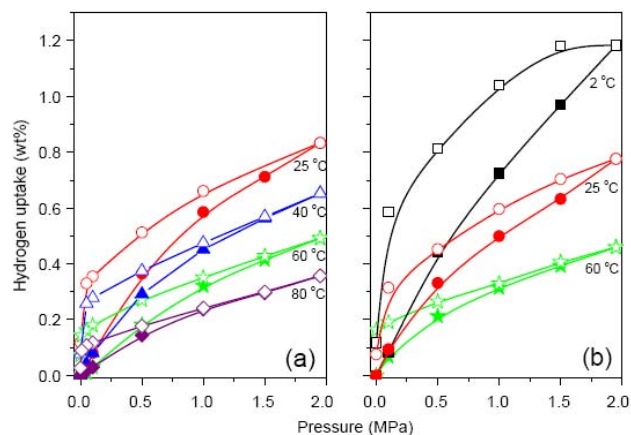
For UMC, volumetric H<sub>2</sub> adsorption measurements at sub-atmospheric pressure showed that, after a fast adsorption stage, H<sub>2</sub> uptake continues to increase slowly at longer equilibration [1]. The effect of temperature on H<sub>2</sub> adsorption is typical for exothermal physisorption, but the slow adsorption

process is unusual for physisorption at near-ambient temperatures. Gravimetric measurements with real-time analysis confirmed that H<sub>2</sub> adsorption is extremely slow on UMC, different from the known behavior of other adsorbents. In order to achieve equilibrated adsorption conditions, all gravimetric data were collected at very long equilibration times (10-15 hours).

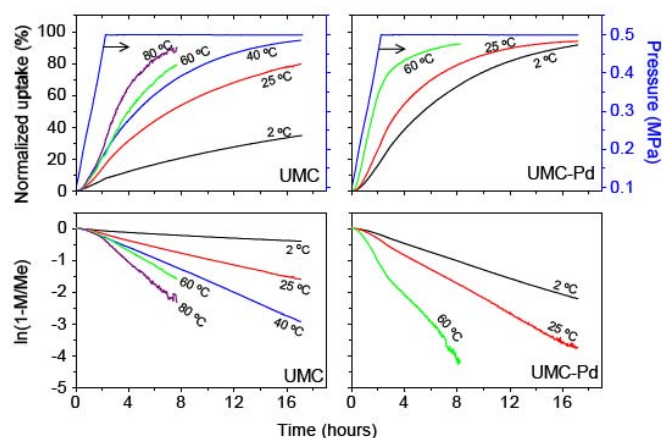
Adsorption measurements were repeated with the physical mixture containing UMC and 10 wt % Pd [2]. In order to properly characterize adsorption on the ultramicroporous carbon component in the mixture, all results for UMC-Pd were corrected by subtracting the amount of H<sub>2</sub> needed to totally convert Pd nanoparticles into saturated Pd hydride, β-PdH<sub>0.66</sub>. Different from adsorption on UMC sample, it was found that the time needed to reach adsorption equilibrium on the UMC-Pd mixture was much shorter.

## Discussion

Figure 1 compares the effect of temperature on adsorption/desorption isotherms on UMC and the carbon component of UMC-Pd. On both samples desorption isotherms show strong hysteresis, which is atypical for H<sub>2</sub> physisorption on microporous materials. The hysteresis loop diminishes as adsorption temperature increases. As expected for exothermic adsorption, the amount adsorbed decreases with increasing temperature. At equal temperatures the uptake on UMC-Pd is very close to that on UMC. In addition, adsorption levels on the ultramicroporous carbon (e.g. up to 0.8 wt % at 25 °C and 2 MPa) are much higher than what is usually reported for H<sub>2</sub> physisorption on best chemically activated carbons [3]. Note that the estimates in Fig. 1-b are conservative, i.e. they do not account for the fact that full hydrogenation of Pd nanoparticles may actually occur at H/Pd < 0.66, and therefore the amount adsorbed on the carbon component of UMC-Pd might in reality be slightly higher.



**Fig. 1** Effect of temperature on hydrogen adsorption isotherms on (a) UMC and (b) carbon component in UMC-Pd (after subtracting contribution due to formation of Pd hydride). Full symbols: adsorption; open symbols: desorption [2].



**Fig. 2** Kinetic data for  $H_2$  adsorption on UMC and the carbon component in UMC-Pd at constant pressure increment (0.1 to 0.5 MPa) and various temperatures (upper panels) and linearization of data in the LDF model (lower panels) [2].

Although the hydrogen capacity of the carbon component is not enhanced by addition of Pd nanoparticles to UMC (Fig. 1), Pd has a strong accelerating effect on kinetics. Figure 2-a shows examples of normalized kinetic data for UMC and UMC-Pd recorded after equal pressure increments during adsorption. The data were linearized (Figure 2-b) using  $M/M_e = 1 - \exp(-kt)$ , the linear driving force model for mass transfer, and the rate constants  $k$  were calculated at different temperatures. Arrhenius analysis of temperature variation of  $k_{ads}$  and  $k_{des}$  allowed calculation of activation energy for adsorption,  $E_{ads}$ , and desorption,  $E_{des}$ , of  $H_2$  on the microporous carbon component, pure or physically mixed with Pd. It was found that addition of Pd lowers  $E_{ads}$  from 25 kJ/mol for UMC to 14 kJ/mol for UMC-Pd. In contrast,  $E_{des}$  is almost constant (24-28 kJ/mol) between samples.

The isosteric heat of adsorption,  $\Delta H_{ads}$ , calculated from van't Hoff plots was in the range of 17-20 kJ/mol for UMC and 11-17 kJ/mol for UMC-Pd (depending on the amount of uptake). These values are higher than expected (4-8 kJ/mol) for  $H_2$  physisorption on activated carbon [3].

In summary,  $H_2$  adsorption on UMC is characterized by adsorption levels and large heat of adsorption, above what is usually reported [3] for  $H_2$  physisorption on most chemically activated carbons, slow kinetics, and strong adsorption hysteresis. These features suggest that the high level of hydrogen uptake on the microporous carbon component is caused by a mechanism different than physisorption. The microporous carbon structure alone cannot explain the large heat of adsorption and the high uptakes resulting in the slow adsorption stage. Based on the presence of K and Na traces in UMC, it is possible to hypothesize that the large  $H_2$  capacity is caused by polarization-enhanced adsorption on isolated alkali metal atoms. It was theoretically predicted [4,5] that low concentrations of alkali metals in carbon induce strong physisorption of hydrogen through charge transfer and local polarization in the carbon structure, followed by attractive

electrostatic interactions with  $H_2$ . This results in binding energies of up to 21 kJ/mol for Li and 11 kJ/mol for K [4,5]. Alkali intercalation structures are not uncommon in chemically activated carbons. They may contribute to enhanced  $H_2$  uptake, strong bonding, and desorption hysteresis. The slow adsorption may indicate that the tortuous labyrinth of micropores in UMC makes difficult the access of molecular  $H_2$  to these intercalated alkali atoms. The acceleration of adsorption in presence of Pd, which is similar with the increase of reaction rates in hydrogenation reactions on Pd catalysts, indicates the occurrence of hydrogen spillover during adsorption in UMC-Pd mixtures. With smaller size than  $H_2$  molecules, H atoms released by saturated Pd hydride particles are mobile, in weakly physisorbed states, on carbon. If they escape chemisorption, some of these H atoms may recombine and bind to polarization sites near alkali atoms. Consequently, adsorption on UMC-Pd is faster, and needs lower  $E_{act}$  than on UMC, where the only player is molecular  $H_2$ . In contrast, desorption occurs with almost equal  $E_{des}$  on both UMC and UMC-Pd. This fact suggests that the species desorbed from UMC-Pd have similar nature with species involved in both desorption and adsorption on UMC, namely they are molecular  $H_2$ . Reverse spillover is not confirmed on UMC-Pd probably because adsorbed  $H_2$  is not in direct contact with Pd particles.

## Conclusions

Enhancement of hydrogen adsorption on microporous adsorbents is possible by adding small amounts of either transition or alkali metals as modifiers. Residual amounts of alkali metals in chemically activated carbon may cause strong physisorption through polarization and electrostatic attraction of  $H_2$  molecules. On the other hand, transition metals able to catalytically activate molecular  $H_2$  induce kinetic effects that can be recognized in the spillover mechanism. The two mechanisms seem to produce additive effects when both types of modifiers are present in the microporous adsorbent. The work in this direction continues in our laboratory.

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