

Hydrogen storage using polymer-supported organometallic dihydrogen complexes: a mechanistic study†

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The dihydrogen complex $W(CO)_5(H_2)$ can be both generated and dissociated in polymer matrices by UV photolysis at 220 K and 90 K, respectively, suggesting a potential “UV-activated” mechanism for hydrogen storage and release.

The widespread use of hydrogen as a fuel is limited by the lack of a convenient method of H_2 storage.¹ A large number of materials have been investigated as physisorptive H_2 adsorbents including carbon,² zeolites,³ metal-organic frameworks (MOFs)^{4–6} and organic polymers.^{7,8} Similarly, there has been intense interest in the chemical storage of H_2 in a wide variety of materials.⁹ None of these materials meets the criteria of size, recharge kinetics, cost, and safety required for use in transportation systems. In general, physisorptive storage in porous materials is difficult to achieve at moderate temperatures because the isosteric heat of adsorption for H_2 is much too low (5–10 kJ mol⁻¹). For this reason, H_2 physisorption is usually investigated at 77.3 K, a temperature which is commensurate with isosteric heats of adsorption in this range.¹⁰ This has prompted researchers to develop, for example, MOFs which exhibit kinetic trapping behaviour.⁵ Although promising levels of hydrogen physisorption (>6 wt%)⁴ have been attained at 77.3 K and elevated pressures (>20 bar), the associated system weight implications are major practical disadvantages. In contrast with physisorptive systems where adsorption enthalpies are generally too low, excellent gravimetric storage densities can be achieved *via* chemical storage approaches⁹ (e.g., metal hydrides) but here binding energies may be too high to allow for reversibility over a reasonable timescale.

In principle, therefore, a promising strategy for hydrogen storage is to investigate systems which have binding energies that are intermediate between conventional physisorption and chemisorption. Organometallic dihydrogen complexes, as first identified by Kubas,¹¹ exhibit binding energies in this range and are known to have M–(H_2) bond energies which may fall in the desirable range for reversible H_2 storage close to ambient temperatures.¹² Organometallic complexes such as $M(CO)_6$ ($M = Cr, W$) form “non-classical” dihydrogen complexes upon UV photolysis as demonstrated in solution studies,¹³ matrix isolation experiments,¹⁴ and in supercritical fluids.¹⁵ In principle, such complexes could serve as H_2 storage motifs if presented to the gas in sufficient concentrations in a chemically-accessible form (e.g., on a porous

support). We have developed techniques for the isolation of such metal complexes in “inert” polymer matrices^{16,17} whereby high loadings of organometallics can be obtained and where the accessible temperature range is very much broader (20–400 K). In this paper, we evaluate the potential of such polymer-supported organometallic dihydrogen complexes for reversible hydrogen storage at temperatures well in excess of 77.3 K.

As a model study, the photolytic reaction of H_2 with $W(CO)_6$ was investigated using polyethylene (PE) as the polymer “matrix”.† For all reactions involving H_2 , Hostalen Gur PE was used as the polymer support since we have shown previously^{17,18} that, unlike low density PE (LDPE), this polymer contains negligible amounts of unsaturation and therefore can function as a relatively inert matrix without competitive reactions involving alkene residues. These preliminary mechanistic studies were conducted in non-porous PE supports and at low loadings of organometallic (<10⁻³ wt%) in order to ensure isolation of the complexes and to eliminate the possibility of bimolecular organometallic reactions. First, a solid PE sample (LDPE in this case†) was impregnated with $W(CO)_6$ using a heptane solution of the organometallic. Even at these rather low loadings, the strong $\nu_{C=O}$ infrared carbonyl band for $W(CO)_6$ at 1979 cm⁻¹ was relatively intense (Fig. 1a).

The impregnated PE sample was mounted in the cryogenic cell and cooled to 21 K. UV irradiation at this temperature led to a reduction in the intensity of the band associated with $W(CO)_6$ and the growth of three new bands (1926, 1953, 2089 cm⁻¹) which can

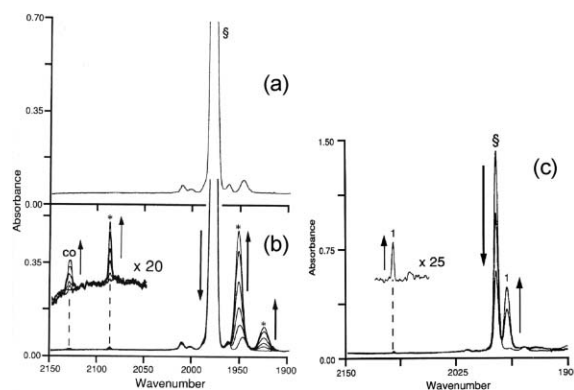


Fig. 1 (a) FTIR spectrum of $W(CO)_6$ in low density polyethylene (LDPE) at 21 K. (b) Spectra showing effects of UV photolysis at 21 K. Spectra recorded every 10 min, total photolysis time 1 h. The bands marked * correspond to PE-matrix isolated $W(CO)_5$. (c) FTIR spectra showing UV reaction of $W(CO)_6$ (band marked §) with hydrogen (220 K, 500 psi H_2) in a high density PE film to generate $W(CO)_5(H_2)$ (1). Total photolysis time = 24 min (>300 nm). (Inset scale expanded $\times 25$).

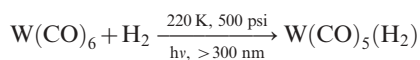
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be assigned to the a_1 , e and a_1 bands of $W(CO)_5(PE)$ by comparison with studies conducted on wax discs and poly(vinylchloride) at <20 K.¹⁹ This “naked” 16-electron species was stable indefinitely at 21 K but disappeared upon warming the PE matrix to 150 K with complete regeneration of the initial $W(CO)_6$ spectrum. It was very difficult to observe such thermal reversal reactions using inert gas matrices²⁰ due to the narrow temperature limitations of such techniques.

We next investigated the photoreaction of H_2 with $W(CO)_6$ in PE at 220 K under a constant pressure of H_2 (500 psi). We have shown previously (e.g., with complexes such as $Fe(CO)_5$)¹⁵ that, despite being non-porous, these PE samples can dissolve and trap small quantities of gases such as H_2 and N_2 under such conditions. UV irradiation of the sample at 220 K resulted in depletion of the IR band assigned to $W(CO)_6$ and the growth of new bands at 1968 and 2096 cm^{-1} (Fig. 1c). These bands can be assigned, by comparison with liquid xenon data¹³ and our previous polymer matrix studies,¹⁷ to the dihydrogen complex, $W(CO)_5(H_2)$:



This complex was found to be stable for at least 12 h at 220 K in the polymer under these conditions. Previous studies have shown that it is also possible to generate the bis-dihydrogen adduct, *cis*- $W(CO)_4(H_2)_2$, at slightly lower temperatures (190 K) and at higher H_2 pressures (2000 psi) once the $W(CO)_6$ species has been totally depleted.¹⁷ It is important to note (from a potential gas storage perspective) that one mole of CO is generated for every mole of H_2 that reacts with the metal centre (see discussion below).

After photolysis at 190 K to form a mixture of $W(CO)_5(H_2)$, **1**, and $W(CO)_6$ (§) the sample was cooled to 90 K and subjected to a further period of UV photolysis (>300 nm), again under a pressure of H_2 (500 psi). Surprisingly, there was a rapid decrease in the intensities of the carbonyl bands associated with both $W(CO)_5(H_2)$, **1**, and $W(CO)_6$, §, accompanied by the growth of a new species, **2** (Fig. 2).

The carbonyl bands associated with **2** could not be assigned to *cis*- $W(CO)_4(H_2)_2$ ¹⁷ but corresponded almost exactly in position and relative intensity to the bands observed for PE-matrix isolated $W(CO)_5$ in LDPE at 21 K (Fig. 1b). Thus, it appears that photolysis at the same wavelength and in the same sample causes

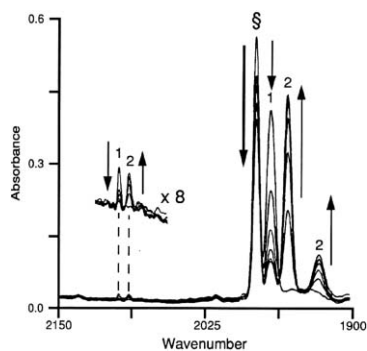
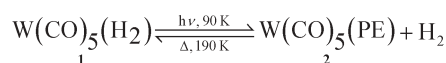


Fig. 2 FTIR spectra showing effect of photolysis at 90 K/500 psi H_2 . Total photolysis time = 24 min (>300 nm). The bands associated with $W(CO)_6$ (§) and $W(CO)_5(H_2)$ (**1**) all decrease in intensity and a new product, $W(CO)_5(PE)$ (**2**), is formed (PE = polyethylene, inset scale expanded $\times 8$).

the addition of H_2 at one temperature (220 K) but the removal of H_2 at another temperature (90 K). This is reminiscent of the reversible formation of $W(CO)_5Ar$ in solid argon (Ar) at 20 K.²¹ The apparent photoreversibility of dihydrogen addition may have broader implications in the search for mechanisms for “switchable” H_2 storage.

After photolysis at 90 K, the sample was warmed slowly to 190 K. This had two effects; first, there was a slight increase in the IR band for $W(CO)_6$ (Fig. 3) indicating a degree of thermal reaction of $W(CO)_5$ with CO, as observed for the sample which was annealed after the photolysis of $W(CO)_6$ at 21 K in LDPE (Fig. 1).

More pronounced, however, was the growth in the bands associated with $W(CO)_5(H_2)$, **1**. Indeed, a comparison of Figs. 3a and 3c indicates that the thermal reaction of $W(CO)_5(PE)$ with H_2 has generated an increased quantity of $W(CO)_5(H_2)$, **1**, at the expense of the $W(CO)_6$ complex:



This thermal reaction was not observed in argon matrices,¹⁴ perhaps because either more H_2 was trapped in our PE samples or the available temperature range in the case of the argon experiments was too low to permit this reaction. Whatever the rationalization, the generation of labile $M(CO)_n(\text{polymer})$ complexes which are stable at lower temperatures but can undergo thermal reaction with H_2 is of significant interest in terms of potential gas storage strategies.

Taken together, this study and others¹⁷ suggest that polymer-supported organometallic dihydrogen complexes could be useful for H_2 storage at modestly cryogenic temperatures (220 K) or indeed above. For example, photogenerated “piano stool” complexes of the type $(\eta^6\text{-arene})M(CO)_2(H_2)$ ($M = Cr, Mo, W$) can be stable in PE matrices even at ambient temperatures.¹⁷ It is possible to conceive of a sequence of photolytic-thermal binding and release steps, such as illustrated here, such that reversible storage could be achieved. A number of difficult challenges exist, however, in terms of implementing such strategies for practical H_2 storage. Most obviously, the loading of chemically-accessible

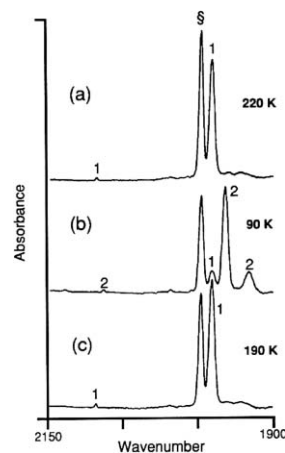


Fig. 3 (a) FTIR spectrum of PE film containing $W(CO)_6$ (§) and $W(CO)_5(H_2)$ (**1**) at 220 K. (b) Sample after 24 min. photolysis at 90 K/500 psi H_2 to form $W(CO)_5(PE)$ (**2**). (c) Sample after warming to 190 K showing thermal reaction of $W(CO)_5(PE)$ with H_2 .

	Hexacarbonyl	"Piano stool"	Polymer supported
$n = 1$	1.03 wt. %	1.06 wt. %	0.8 wt. %
$n = 2$	2.38 wt. %	2.47 wt. %	1.88 wt. %

Fig. 4 Organometallic dihydrogen complexes and the theoretical "best case" hydrogen storage capacities calculated for varying degrees of substitution. Note that a simplified scheme is used to represent the structure of the hypercrosslinked polymer, see ref. 8 for details. Theoretical storage capacities were calculated for $M = Cr$ assuming chemisorption only.

organometallic needs to be very much higher than we have used here in order to increase the storage capacity. This may be achievable, for example, in hypercrosslinked polystyrene systems⁸ which can exhibit very high apparent inner surface areas ($\sim 2000 \text{ m}^2 \text{ g}^{-1}$)^{8,22,23} and might be functionalized, as demonstrated previously for polybenzyls,²⁴ with high loadings of metal tricarbonyl functional units.²⁵ Similar strategies were invoked for polyacetylenes,²⁶ although the issue of porosity was not addressed.

Fig. 4 illustrates the hypothetical "best case" hydrogen storage capacities for a range of organometallic species. In all cases, the capacities quoted are based on chemisorption with the metal species only—that is, ignoring any additional physisorption that may occur in the case of microporous supports.⁸

The hypercrosslinked polymer-supported species in Fig. 4 (right) is a promising synthetic target,^{24,25} although even this idealized structure ($M = Cr$; 100% ring functionalization; 100% accessibility of metal sites to H_2 ; $n = 2$) falls well short of the 6.0 wt% DoE gravimetric target.²⁷ Furthermore, there is a practical requirement for systems which are reversible over multiple charge–discharge cycles.^{1,10} As such, it has to be possible both to release the H_2 (e.g., thermally or by suitable photolysis) and also to regenerate in this case the original $M(CO)_3$ functionality. In the systems proposed here, it follows that CO loss should be reversible and that the photoejected CO ligand (boiling point $CO = 81 \text{ K}$) would need to be separated and recycled in some way. As yet, therefore, organometallic complexes such as these are far from being utilized as practically-useful H_2 storage systems. Nonetheless, the results presented here suggest that polymer-supported organometallic dihydrogen complexes have a number of potential advantages over other approaches. Most notably, these compounds can be stable at temperatures well in excess of 77.3 K but are in general much less stable than metal dihydrides. As we show here for the first time, it is also possible to reverse the binding of H_2 to polymer-supported organometallic complexes by UV photolysis. UV-activated H_2 binding and release in complexes supported on high surface area hypercrosslinked polymers⁸ will be the subject of future studies.

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