J Mater Sci (2008) 43:1155–1158
DOI 10.1007/s10853-007-2377-0

LETTER

Hydrogen storage in highly microporous solids derived from aluminium biphenyldiphosphonate

Ernesto Brunet · Carlos Cerro · Olga Juanes ·
Juan Carlos Rodríguez-Ubis · Abraham Clearfield

Received: 18 September 2007 / Accepted: 3 December 2007 / Published online: 16 December 2007

Introduction

Hydrogen may become a major energy vector in the near future because of its virtual inexhaustibility and clean combustion [1]. Yet, as important as its environmental-friendly production may be, the handling of this tiny molecule through efficient storage-release processes is a second, not secondary problem to be urgently tackled. To this concern, the seeking of porous matrices to accomplish efficient hydrogen physisorption is a very active area of research. The goal is the tight packing of H_2 molecules to achieve the maximum volumetric density with the less feasible amount of porous material. However, the attained levels of hydrogen uptake (77 K, 760 Torr) in materials well above 2000 m^2/g are seldom higher than 2 wt.% probably because of the feeble interaction between the nearly empty scaffold and the hydrogen molecules [2]. Hence, a proper balance between available volume accessible to hydrogen, high contact surface, and strong interaction with polarizing centers are the necessary features for more efficient H_2 storage [3]. Our recent research efforts are directed along these lines [4]. We hereby report the incorporation of rigid 4,4′-biphenyldiphosphonic (BPDP) and phosphorous acids (H_3PO_3) into aluminium salts with the aim of building microporous materials which would fulfill the above conditions. Precedents in the literature about the preparation of related materials were few and the obtained substances were never tried for hydrogen storage [5].

The hydrothermal treatment for 7 days in autoclave (185 °C) of a solution in a 1:1 mixture of acetone/water of $AlCl_3$ (3 eq), BPDP and H_3PO_3 acids in different ratios rendered materials designated as **UAM-150** (BPDP 0.5 eq; H_3PO_3 0 eq), **UAM-151** (BPDP 0.25 eq; H_3PO_3 0.5 eq) and **UAM-152** (BPDP 0.125 eq; H_3PO_3 0.75 eq).

Figure 1 presents the adsorption data of hydrogen as measured in an ASAP2020 apparatus (Micromeritics Co.) after degassing the samples at 300 °C for at least 16 h. It may be seen that hydrogen intake (wt.%) at 77 K and 760 Torr increased almost two-fold from 0.93 for material **UAM-150** (no H_3PO_3) to 1.10 and 1.64 for its counterparts **151** and **152**, respectively, where the amount of H_3PO_3 in the reaction mixture was progressively augmented. No hysteresis was detected in the desorption processes.

The H_2 intake displayed by material **UAM-152** is close to the highest reported for organic-inorganic materials at 77 K and atmospheric pressure. Moreover, the steep slope of the curve from 200 to 760 Torr indicates that the adsorption process is far from saturation.

The NMR spectra and the powder XRD of materials **UAM-150**, **151** and **152** were akin to those recorded for $Al_2(RPO_3)_3 \cdot 2H_2O$ [6]. Their "non-CP" MAS ^{27}Al-NMR spectra (Fig. 2) displayed three signals of 2:1:1 intensity, suggesting the co-existence of metals with two different coordination patterns in a 1:1 ratio: tetrahedral (-46.9 ppm) and two slightly different octahedral (21.9 and 33 ppm) [7].

Figure 3 shows the MAS ^{31}P-NMR spectra of the studied materials with (a) and without (b) applying CP. The "non-CP" spectrum of material **UAM-150** (no H_3PO_3) is relatively complex. However, material **UAM-151** (0.5 eq of H_3PO_3) displayed a much simpler "non-CP" MAS ^{31}P-NMR spectra showing two groups of signal in *ca.* 3:1

E. Brunet (✉) · C. Cerro · O. Juanes · J. C. Rodríguez-Ubis
Departamento de Química Orgánica, Facultad de Ciencias C-I,
Universidad Autónoma de Madrid, Madrid 28049, Spain
e-mail: ernesto.brunet@uam.es

A. Clearfield
Texas A&M University, College Station, TX, USA

ratio. In going to material **UAM-152** (0.75 eq of H_3PO_3), the intensity of the most shielded signal increased at the expense of that at −6.9 ppm.

Figure 4 shows that the XRD patterns were very similar despite H_3PO_3 incorporation suggesting that the latter occurs without altering the main structure of the phase, probably by taking the places of some phosphonates without changing the metal scaffolding, as supported by the small changes observed in NMR spectra (*vide supra*). Unfortunately we have not been able for the time being to achieve the level of crystallinity adequate to either Rietveld or single crystal refinements. However, their general molecular formula $Al_2(HPO_3)_x(C_{12}H_8P_2O_6)_{1.5-x/2} \cdot 2.7H_2O$ ($x = 0, 0.2, 0.35$) inferred from elemental analysis and TGA (Table 1), is alike to that of AlMepO-β [7] [$Al_2(CH_3PO_3)_3$] whose higher crystallinity allowed for single crystal refinement. AlMepO-β showed a microtubular structure with cylindrical pores of ca. 0.6 nm in diameter, a size compatible to the calculated pore distribution for our materials (*vide infra*). Table 1 shows that, compared to material **UAM-150**, the corresponding **151** and **152** showed lower C% contents and inferior TGA losses at high-temperature which strongly support that phosphorous acid did incorporate into the organic–inorganic matrix. It should be noted that the TGA losses occurring at low temperature (ca. 10%) could only be adjusted to the proposed molecular formulae considering the presence of small amounts of acetone (0.1–0.15 eq. per 2 eq. of Al) which were barely detected if at all by CP-MAS ^{13}C-RMN (see the small signal at 29.3 ppm in Fig. 5 expected for acetone methyl groups).

Brunauer-Emmett-Teller (BET) measurements rendered type Ib isotherms (Fig. 6) compatible with the adsorption in wide micropores and on external surface [8]. Hysteresis was almost negligible suggesting that the materials do not have mesopores. The pertinent numerical analysis of the

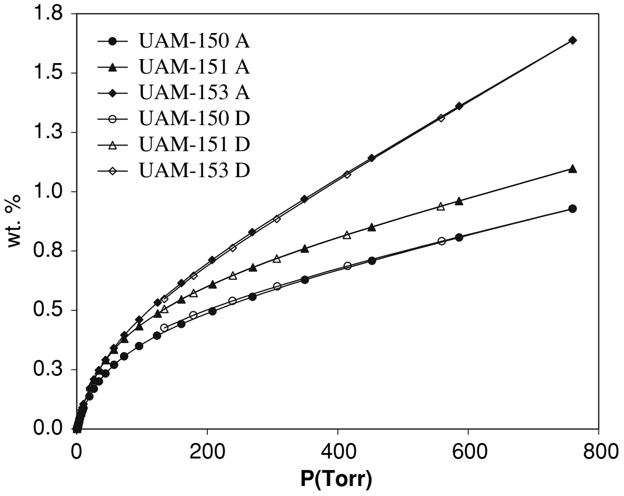

Fig. 1 Hydrogen adsorption (A), desorption (D) curves at 77 K of materials **UAM-150**, **151** and **153** of Table 1

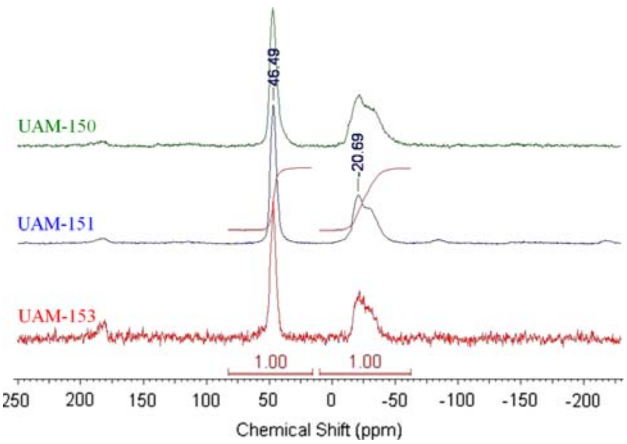

Fig. 2 “Non-CP” MAS ^{27}Al-NMR spectra of the indicated materials

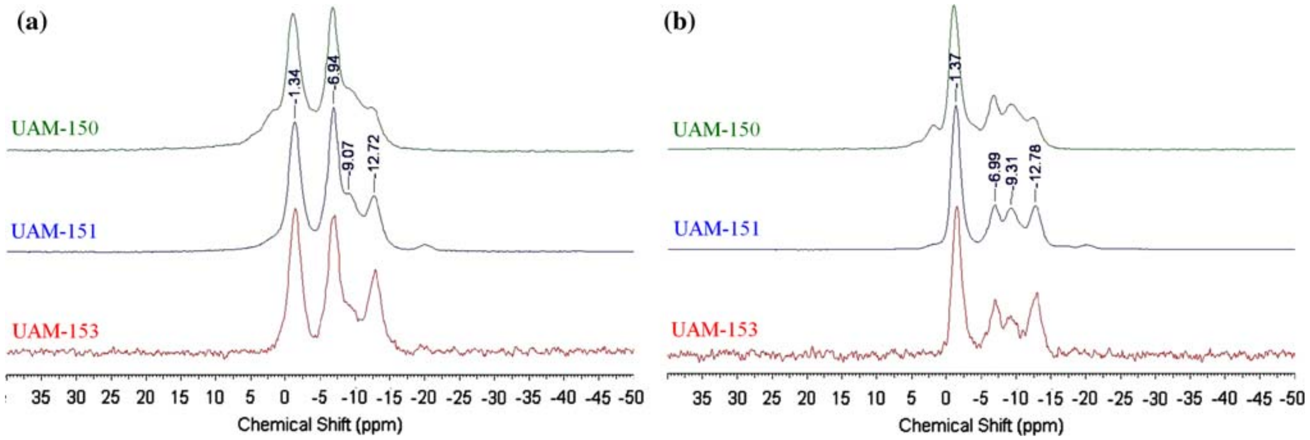

Fig. 3 “Non-CP” (**a**) and CP (**b**) MAS ^{31}P-NMR spectra of the indicated materials

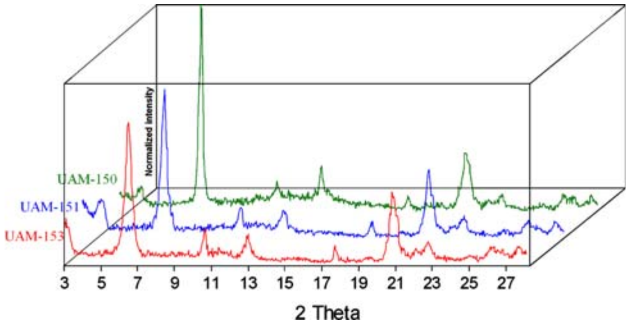

Fig. 4 Powder XRD patterns for the materials under study

curves (Table 2) using ASAP2020 software evidenced that the incorporation of H_3PO_3 to the crystals led to a substantial increase in porosity whose major contribution was internal.

Pore size distribution analysis [9] for material **UAM-150** showed mainly micropores (1.5 nm) and ultra micropores (0.6 nm) and only the latter for material **UAM-152**, that with the highest H_3PO_3 content. From ca. 2 nm the nearly porosity continuum observed could be attributed to the interstices left by particle aggregation which may be responsible for the external surface measured in Table 2.

It should be remarked that the hydrogen isotherms of Fig. 1 displayed steep births (ca. 0.25 wt.% at 10 Torr) which are indicative of strong interactions between the H_2 molecules and the material. For example, similar initial slopes were detected in MOFs derived from Mn salts of 1,4-benzeneditetrazolate [10], where the interaction energy was measured to be ca. 8.5 KJ/mol at low H_2 coverage. This high energy was attributed to the presence of unsaturated metal centers after removal of solvent molecules (DMSO). This mechanism of interaction should be less probable in our materials because of the low content of acetone and its lower coordinating ability as compared to DMSO. Therefore, the strong interactions between H_2 and **UAM-152** material might be solely attributed to increased van der Waals contact areas associated with very small pore sizes.

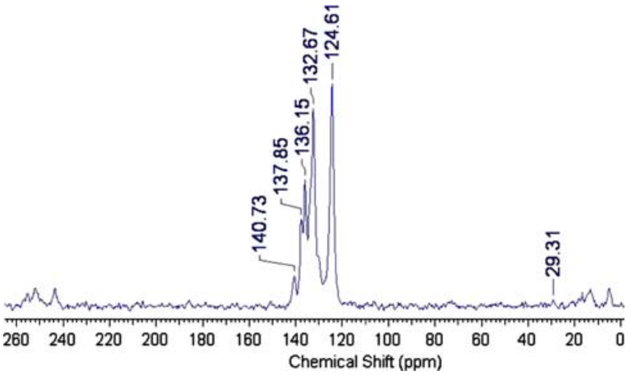

Fig. 5 CP-MAS ^{13}C-RMN spectrum of **UAM-151** as a representative example, showing aromatic signals (124–141 ppm) and traces of acetone methyl groups (29.3 ppm)

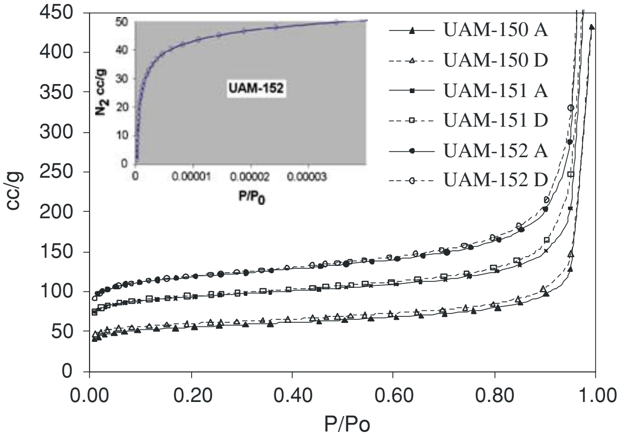

Fig. 6 Nitrogen adsorption isotherms for the indicated materials (A: adsorption; D: desorption). Inset shows nitrogen isotherm of **UAM-152** at very low P/P_0 values

Not less remarkable is the fact that **UAM-152** adsorbed 1.6 wt.% H_2 bearing a relatively limited surface area (<400 m^2/g; cf. Table 2). A thorough revision of the literature shows that most of the molecular systems adsorbing this amount of H_2 or even lower have areas well above this

Table 1 Elemental analysis, TGA losses and calculated formulae for the studied materials

Material UAM	Elem. Anal. (% C, %H)		TGA(°C) (Weight loss %)			
	Exp.	Calc.^{a,b}	Exp.		Calc.^{a,b}	
			30–70	400–900	30–70	400–900
150	38.4, 3.3	38.1 (38.4), 3.1 (3.2)	9.9	36.0	8.5 (9.8)	36.0
151	36.7, 3.3	36.5 (36.8), 3.1 (3.1)	9.5	34.2	8.8 (9.8)	34.2
152	35.9, 3.4	35.2 (35.6), 3.0 (3.2)	9.4	32.0	9.0 (10.3)	32.8

[a] Calculated for **UAM-150**: $Al_2(C_{12}H_8P_2O_6)_{1.5} \cdot 2.7H_2O$; **UAM-151**: $Al_2(HPO_3)_{0.2}(C_{12}H_8P_2O_6)_{1.4} \cdot 2.7H_2O$; **UAM-152**: $Al_2(HPO_3)_{0.35}(C_{12}H_8P_2O_6)_{1.3} \cdot 2.7H_2O$

[b] Values in parenthesis adding acetone to the molecular formulae (see text). **UAM-150**: $Al_2(C_{12}H_8P_2O_6)_{1.5}(C_3H_6O)_{0.13} \cdot 2.7H_2O$; **UAM-151**: $Al_2(HPO_3)_{0.2}$ $(C_{12}H_8P_2O_6)_{1.4}(C_3H_6O)_{0.1} \cdot 2.7H_2O$; **UAM-152**: $Al_2(HPO_3)_{0.35}(C_{12}H_8P_2O_6)_{1.325}(C_3H_6O)_{0.14} \cdot 2.7H_2O$

Table 2 Results of the BET analysis of the materials under study

Material UAM	Surface (m^2/g)		
	Microporous	External	Total
150	96.0	71.8	167.8
151	187.3	107.1	294.4
152	211.4	153.8	365.2

value [11]. Metal nitroprussides [12] (1.6 wt.%, 523 m^2/g) and prussian blue analogues [13] (1.4–1.8 wt.%, 560–870 m^2/g) may be the closest examples to the results hereby accounted for. Therefore, a large specific surface area is not necessarily a must in the design of porous materials for efficient hydrogen storage.

In conclusion, we have prepared for the first time a series of microporous Al materials derived from 4,4′-biphenyldiphosphonate (BPDP) of formula $Al_2(BDPD)_{1.5}$ in which the incorporation of a relatively small amount of H_3PO_3 $[Al_2(HPO_3)_{0.35}(BDPD)_{1.3}]$ led to an almost two-fold improvement of H_2 intake up to ca. 1.6 wt.% at 760 Torr, which appeared to be far from saturation and may thus reach DOE-required values at relatively limited pressures.

Acknowledgements Financial support (MAT2006-00570) from the Ministry of Science and Education (MSE) of Spain and FYSE-ERCROS S.A. is gratefully recognized. C.C. is grateful to the MSE for a research fellowship and for financing short stays in Texas A&M University.

References

1. Kennedy D (editorial) (2004) Science 305:917 and the following articles
2. See for example: El-Kaderi HM, Hunt JR, Mendoza-Cortés JL, Côté AP, Taylor RE, O'Keeffe M, Yaghi OM (2007) Science 316:268
3. Zecchina A, Bordiga S, Vitillo JG, Ricchiardi G, Lamberti C, Spoto G, Bjørgen M, Lillerud KP (2005) J Am Chem Soc 127:6361
4. Brunet E, Alhendawi HMH, Cerro C, Mata MJ, Juanes O, Rodríguez-Ubis JC (2006) Angew Chem Int Ed 45:6918
5. El Haskouri J, Guillem C, Latorre J, Beltrán A, Beltrán D, Amorós P (2004) Eur J Inorg Chem 9:1804
6. Maeda K, Akimoto J, Kiyozumi Y, Mizukami F (1995) Angew Chem Int Ed Engl 34:1199
7. Cabezas A, Aranda MAG, Bruque S, Poojary DM, Clearfield A, Sanz J (1998) Inorg Chem 37:4168
8. Rouquerol F, Rouquerol J, Sing K (1999) Adsorption by powders and porous solids. Academic Press, p 219
9. Evans R, Marconi UMB, Taraz P (1986) J Chem Phys 84:2376
10. Dinca M, Yu AF, Long JR (2006) J Am Chem Soc 128:8904
11. See for example: Wong-Foy AG, Matzger AJ, Yaghi OM (2006) J Am Chem Soc 128:3494
12. Culp JT, Matranga C, Smith M, Bittner EW, Bockrath B (2006) J Phys Chem B 110:8325
13. Kaye SS, Long JR (2005) J Am Chem Soc 127:6506