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CRYOGENIC ADSORPTION OF HYDROGEN ISOTOPES OVER NANO-STRUCTURED MATERIALS

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Porous materials such as zeolites, activated carbon, silica gels, alumina and a number of industrial catalysts are compared and ranked for hydrogen and deuterium adsorption at liquid nitrogen temperature. All samples show higher D_2 adsorption than that of H_2, in which a HY sample has the greatest isotopic effect while 13X has the highest hydrogen uptake capacity. Material's moisture content has significant impact to its hydrogen uptake. A material without adequate drying could result in complete loss of its adsorption capacity. Even though some materials present higher H_2 adsorption capacity at full pressure, their adsorption at low vapor pressure may not be as good as others. Adsorption capacity in a dynamic system is much less than in a static system. A sharp desorption is also expected in case of temperature upset.

I. INTRODUCTION

Hydrogen adsorption at cryogenic temperature has wide potential applications in fusion technology development, ^{3}He purification and hydrogen isotope separation. Cryogenic adsorption is effective to completely remove low concentration of hydrogen isotopes from bulk helium gas. At low temperatures, many porous materials present isotopic effects that can be used to separate hydrogen isotopes.

The adsorption of zeolite has been well studied,[1] largely in the petrochemical industry. Due to their crystalline structure, zeolites have uniformly nanostructured pores instead of a distribution of pore sizes such as in silica gel or activated carbon. Despite being well studied, information was scattered in pieces and sometimes confusing related to application in cryogenic adsorption. For example, the kinetic dimensions of zeolite pore opening and gas molecule diameter are temperature dependent. A 3A zeolite does not adsorb H_2 molecules at liquid nitrogen temperature (77K or -196°C) due to its pores being too small, while studies indicate that H_2 adsorption takes place at 140 K or higher temperature.[2] Similarly, a 4A zeolite does not adsorb N_2 molecule at liquid nitrogen temperature, but significant adsorption was reported at 195 K (-78°C).[1] Table 1 lists adsorption characteristics of various zeolites for commonly used adsorbents at liquid nitrogen temperature. The precision of pore diameter within a partial angstrom makes great difference for the exclusion of large gas molecules.

Table 1: Adsorption at Liquid Nitrogen Temperature

	H_2O	N_2	H_2	Ar
3A	Yes	---	---	---
4A	Yes	---	Yes	---
5A	Yes	Yes	Yes	Yes
13X	Yes	Yes	Yes	Yes
Activated Carbon	Yes	Yes	Yes	Yes
Alumina	Yes	Yes	Yes	Yes
Silica Gel	Yes	Yes	Yes	Yes

Recently natural mordenite was reported to have higher H_2 and D_2 uptakes than 5A zeolite at liquid nitrogen temperature.[3] The H_2 uptake correlates with micropore surface area but not meso pores in various materials,[4] in which an activated carbon sample with over 2,000 m^2/g surface area adsorbed three times as much H_2 as the best Zeolite. Langmuir (mono layer adsorption) constants were found well correlated with molecular weight of H and D hydrogen isotopes over various zeolites and activated carbons.[5] Further, adsorption constants for H, D, and T hydrogen isotopes are all consistent with their respective molecular weights; only two of six species of hydrogen isotopes need to be obtained experimentally to predict all of them.[6] Model expressions were developed for multi-component adsorption of 6 species of hydrogen isotopes on zeolite 5A and 13X (Ref. 7). The performance of a 5A zeolite bed for ITER application was found to be in agreement with the adsorption capacity measured by volumetric method.[8] These studies have potential to improve existing technology such as ^{3}He purification, or to develop new technologies such as for isotope separation.

II. EXPERIMENTAL

Zeolite, activated carbon, silica gel, alumina and commercial catalyst samples were obtained from Zeolyst, UOP, Grace Davison, Sud-Chemie, Sasol and Sigma Aldrich. H_2 and D_2 adsorption isotherm data were collected using static-volumetric techniques at liquid nitrogen temperature with Micromeritics ASAP 2020 unit. The sample's BET surface area and porosity data were also collected from the same unit but using N_2 as adsorbent. For convenience, most of H_2 and D_2 uptakes are compared at 800 torr vapor pressure. All samples were degassed for 10 hrs under vacuum or when it reached 4 umHg pressure prior to measurement. Additional cryogenic adsorption/desorption tests were also studied at flow-dynamic conditions using Micromeritics AutoChem II 2920 unit. The methods are commonly known as pulse chemical adsorption and temperature programmed desorption (TPD).

III. RESULTS AND DISCUSSION

III.A. Effect of Moisture Level to H_2 Adsorption

The moisture content has significant impacts to the zeolite H_2 adsorption capacity. Fig. 1 shows the relation between moisture level (or drying temperature) of a 4A zeolite and its H_2 uptake at liquid nitrogen temperature. Different color/shape data points represented different samples. Each sample was initially saturated with room moisture (>50% RH), then progressively dried from low to high temperatures under vacuum.

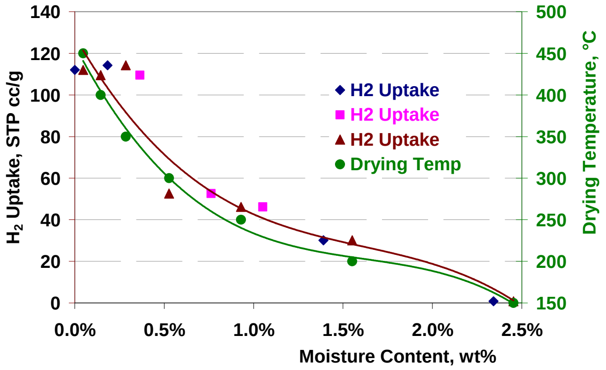

Fig. 1: Hydrogen Uptake as a Function of Sample Drying (4A Zeolite from Aldrich).

The moisture level as low as 0.5 wt% on zeolite would reduce the zeolite capacity to about half for H_2 adsorption. At 2.3 wt% moisture (dried at 150°C), the sample adsorbed only 0.8 scc/g H_2, comparing to 114 scc/g H_2 when moisture was about 0.3 wt%. When the sample was continuously dried above 350°C, the H_2 adsorption reached a plateau of 109-114 scc/g despite its weight loss continued. Note that the moisture content is based on sample weight relative to zeolite being dried at 450°C under vacuum (4 umHg). Based on the above study, all samples were dried at 350°C until reaching 4 um Hg vacuum for the following studies.

III.B. D_2 and H_2 Adsorption Measurement Accuracy

Since the difference between H_2 and D_2 adsorption is relatively small, measurement accuracy of adsorption isotherm was tested. Fig. 2 shows reproducibility of D_2 and H_2 adsorption/desorption isotherms over a UOP 13X Zeolite sample at liquid nitrogen temperature. The two H_2 isotherms were almost identical, and the two D_2 isotherms were almost identical, while the difference between H_2 and D_2 adsorption had a clear margin. The excellent precision of the instrument differentiated the small but real isotopic effect very well. Each respective adsorption and desorption curve overlapped completely without hysteresis. The D_2 uptake was slightly higher than that of H_2 in all pressure range.

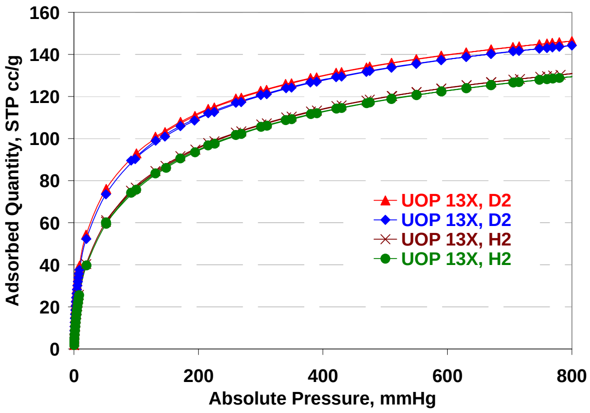

Fig. 2: Repeat D_2/H_2 Isotherms over UOP 13X Zeolite.

III.C. Comparison of Adsorption Material Types

Table 2 compares H_2 and D_2 adsorption quantity over various materials at liquid nitrogen temperature, along with each material's BET surface area measured by N_2 adsorption. As expected, 3A zeolite did not adsorb hydrogen or deuterium, and 4A zeolite adsorbed hydrogen and deuterium but not nitrogen due to pore size restriction. The 4A, 5A, 13X zeolites and activated carbon all had over 100 scc/g of hydrogen uptake at 800 torr pressure, with 13X the most H_2 uptake while activated carbon the greatest isotopic effect expressed as D_2/H_2 ratio. The performance of a Pd modified 4A zeolite was very similar to that of 4A. This is an indication of unchanged porosity. Due to ion exchange, the Pd/Z is expected to have both Pd^{2+} and Na^+ (4A) cations. Introduction of a nobel metal catalyzes hydrogen oxidation reaction for application in, e.g., tritium removal, and also converts HD with H_2/D_2, which is of interest for future study. Various commercial catalysts from Zeolyst and Sud-Chemie were also tested. All of them adsorbed higher amount of D_2 than H_2, of which a HY sample presented the highest D_2/H_2 ratio at 118%. The quantity of hydrogen uptake was still good although lower than A and X types of zeolites. X and Y zeolites share the same framework structure but Y has higher Si/Al ratio. The higher the Si/Al ratio, the smaller the unit cell constant, thus slightly smaller the pores. The smaller pore of Y zeolite is likely responsible for higher isotopic effect, however, also decreases the hydrogen uptake to about a third of the value by 13X. Another sample with nobel metal and base metal modified ZSM-5 (Zeolyst Sample A) also showed good isotopic effect, at 115% D_2/H_2 ratio. Different grades of silica gels presented isotopic effect comparable to zeolites but the hydrogen uptakes were much lower. The Sasol alumina sample adsorbed even smaller amount of hydrogen. Hydrogen is a non-condensing gas at liquid nitrogen temperature. The micropore portion was reported to be responsible for hydrogen adsorption, not mesopores or macro pores.[4] The alumina sample has majority of mesopores with an average pore diameter of about 100 Å. It lacks the micropores to capture hydrogen molecules.

Table 2: Cryogenic Adsorption of Various Materials

Material	BET m^2/g	H_2 scc/g	D_2 scc/g	D_2/H_2 ratio
3A MS, UOP	---	0.9	1.1	---
4A MS, UOP	---	113	121	107%
5A MS, UOP	447	102	111	109%
13X MS, UOP	592	131	140	107%
AC, Darco	682	117	135	115%
Pd/Z	---	112	119	107%
Sud-Chemie ZeoSorb® T-2921 (Pt/Mord.)	442	89.8	96.2	107%
Zeolyst CBV600 (HY)	502	46.4	54.6	118%
Zeolyst Sample A (Noble metal/Base metal /ZSM-5)	308	42.3	48.5	115%
Zeolyst Sample B (Noble metal/Mord./ZSM-5)	387	75.6	81.6	108%
Zeolyst Sample C (Noble metal/Mord.)	454	99.2	106	107%
Zeolyst CBV2314 (ZSM-5)	350	71.3	77.0	108%
SG, Davisil 646	316	23.3	24.9	107%
SG, Davisil 636	459	32.3	35.6	110%
SG, Merck 10181	595	37.9	42.7	113%
Alumina, Sasol 604130	204	15.4		---

MS – zeolite (Molecular Sieve); AC – activated carbon; SG – silica gel; BET surface area based on N_2 adsorption data; H_2 and D_2 uptake was at 800 torr, all at liquid nitrogen temperature.

III.D. 4A Zeolites from Different Batches

Table 3 shows some difference among 4A samples obtained from different vendors and lots on H_2 and D_2 adsorption data. The 4A zeolite sample from Aldrich (Lot# 05529KH) was proven to double TCAP efficiency for H_2 an D_2 separation when used in an inverse column,[9] while the sample's isotopic effect was the lowest among 4A samples compared. The result is encouraging since further improvements are very likely using samples with higher isotopic effects.

Table 3: Different Batches of 4A Zeolites

4A Zeolite	H_2 scc/g	D_2 scc/g	D_2/H_2 ratio
4A MS, Grace Davison Lot#1000103855	115.2	128.9	111.9%
4A MS, UOP Lot#2007007429	107.9	120.4	111.6%
4A MS, UOP Lot#2007009256*	113.2	121.4	107.3%
4A MS, Aldrich 334308 Lot# 05529KH	114.5	116.9	102.1%

III.D. Low Pressure vs. Full Pressure H_2 Adsorption

Fig. 3 compares H_2 adsorption/desorption isotherms at liquid nitrogen temperature for 4A, 5A, 13X zeolites and activated carbon. All samples had significant H_2 adsorption. The isotherms indicated that 13X zeolite adsorbed 30% more H_2 than 5A zeolite (131 vs. 102 scc/g). However, a closer look of the "zoom-in" of low pressure range indicated that the isotherm slope of 13X is not as steep as that of "A" type zeolites, as seen in Fig. 4. The 4A zeolite has the steepest slope of low pressure H_2 adsorption, followed by 5A zeolite and activated carbon. At 0.5 torr vapor pressure, for example, 13X zeolite only adsorbed 3.4 scc H_2 /g while 4A, 5A and activated carbon adsorbed about 7.3 scc H_2/g. On the other hand, at 5 scc H_2/g adsorption, the vapor pressure of 13X is then 0.75 torr comparing to 0.3 torr for other materials. The comparison at low pressure is important for trace tritium removal such as in ^3He purification or radio active material confinement processes, while full pressure uptake is related to the material capacity for hydrogen isotope as a major component.

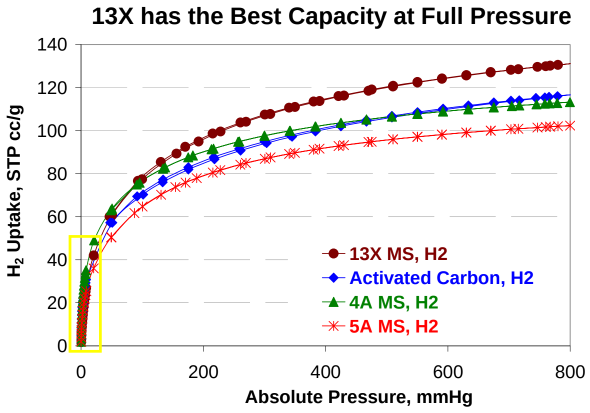

Fig. 3: H_2 Adsorption Isotherm Comparison.

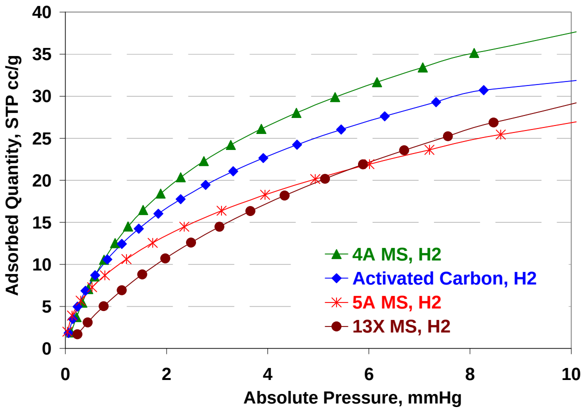

Fig. 4: Low Pressure H_2 Adsorption Isotherm.

III.E. Flow Dynamic Adsorption and Desorption

The Darco activated carbon was tested with H_2 pulse chemi adsorption followed by desorption with temperature increases. As seen in Fig. 5, breakthrough started at about 30 minutes after 7 doses were completely adsorbed. Additional doses resulted in continuous ramp of hydrogen concentration, as opposed to individual peaks normally observed at ambient conditions. The pulse chemi was stopped after 15 total doses, in which the sample had a cumulative adsorption of 55.5 scc/g. This was less than 117 scc/g from static measurement at 800 torr, because hydrogen partial pressure is lower in a flow dynamic system. When the liquid nitrogen Dewar was removed, H_2 desorbed immediately with a sharp peak at 3 minutes (-78°C), followed by a smaller peak at 6 minutes (-18°C). The desorption signal after 45 minutes was due to initial sample dry out at 350°C.

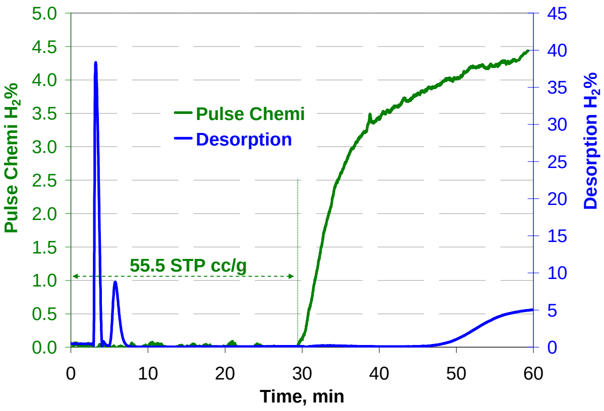

Fig. 5: Cryogenic Pulse Chemi and Desorption of Darco Activated Carbon.

IV. CONCLUSIONS

Porous materials such as zeolites, activated carbon, silica gels, alumina and a number of industrial catalysts all show higher than unity D_2/H_2 isotopic effect at liquid nitrogen temperature, in which a HY sample has the greatest isotopic effect while a 13X has the highest hydrogen uptake. A material without adequate drying could result in complete loss of its H_2 adsorption capacity. Material presenting higher H_2 adsorption capacity at full pressure may not be a good candidate at low pressure. Adsorption capacity in a dynamic system is less than in a static system. The same type of material from different vendors or lots may behave differently.

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