Synthesis of Niobium Pentoxide Aerogels

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Niobium pentoxide (Nb_2O_5) was successfully synthesized as an aerogel which, after calcination at 773 K for 2 h, had a Brunauer–Emmett–Teller (BET) surface area of 190 m^2 g^{-1} and acidity comparable to that of niobic acid.

Subsequent to the pioneering work of Kistler,[1] there have been many studies on the preparation of aerogels of inorganic oxides.[2,3] In a typical procedure, an appropriate precursor is hydrolysed to form first a sol and then a gel. The term aerogel refers to a sample obtained from drying the gel under supercritical conditions. In this article we report on the successful synthesis of an aerogel of niobium pentoxide (Nb_2O_5) by following the semicontinuous extraction procedure of Cheng *et al.*[4]

In our method the precursor, niobium ethoxide [$Nb(OEt)_5$; Alfa], was dissolved in s-butyl alcohol and then quickly added to a well mixed solution of s-butyl alcohol, deionized water, and nitric acid. The resulting solution turned into a clear gel upon standing under the following conditions: $Nb(OEt)_5$/Bu^{s}OH 0.50 mmol/ml; water/Nb 10 mol/mol; HNO_3/Nb 1.0 mol/mol. The gel was extracted in a standard autoclave (Autoclave Engineers, model 08U-06-60FS) with supercritical CO_2 (Airco) at *ca.* 343 K and 2.07 × 10^7 Pa for 2—3 h, resulting in a dry, granular solid. This solid was heated in flowing nitrogen at 673 K for 2 h, and then in flowing oxygen at 773 K for 2 h to give a sample denoted as A-Nb_2O_5.

Table 1. Physical characteristics of niobium pentoxides.

Sample	BET surface area/m^2 g^{-1}	Nb_2O_5 phase[a]
A-Nb_2O_5	190	Amorphous
P-Nb_2O_5	50	TT
X-Nb_2O_5	70	TT

[a] Determined by *X*-ray diffraction.

Two other Nb_2O_5 samples were prepared for comparison. A precipitated sample, denoted as P-Nb_2O_5, was made by adding ammonium hydroxide to a methanolic solution of niobium ethoxide. A xerogel, denoted as X-Nb_2O_5, was made by bypassing the supercritical extraction step in the synthesis of the aerogel. Instead the gel was dried by heating in an oven at 383 K for 3 h. The surface area and *X*-ray diffraction results of these three samples after the same heat treatment as used for the aerogel are shown in Table 1. After being calcined at 773 K, the Nb_2O_5 aerogel had a Brunauer–Emmet–Teller (BET) surface area which was 3—4 times larger than that of the two samples prepared by conventional methods and remained *X*-ray amorphous. To our knowledge this is the highest surface area ever reported for niobium pentoxide.

A-Nb_2O_5 was also acidic as determined by the Benesi method with n-butylamine titration.[5] As shown in Table 2, its acidity was significantly higher than that of the other two

Table 2. Acidity distributions from n-butylamine titration.

		Acid amount/mmol g^{-1}					
Sample	pK_a	−8.2	−5.6	−3.0	+1.5	+3.3	+4.8
A-Nb_2O_5		0.20	0.44	0.45	0.47	0.52	0.74
P-Nb_2O_5		0.00	0.01	0.01	0.04	0.05	0.10
X-Nb_2O_5		0.00	0.02	0.03	0.04	0.04	0.06
Niobic acid[a]		0.00	0.40	0.48	0.60	0.62	—
A-Nb_2O_5[b]		0.00	0.10	0.10	0.12	0.18	0.26

[a] Taken from ref. 7 for a sample calcined at 393 K. [b] Sample calcined at 873 K for 2 h.

Nb_2O_5 samples and, in fact, comparable to that of niobic acid which has been found active for isomerization and dehydration.[6] One final observation is that the acidity of A-Nb_2O_5 decreased upon heating at 873 K for 2 h, concurrent with the appearance of weak diffraction features of TT-Nb_2O_5. This interesting structure–acidity relationship is under investigation in our laboratory.

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