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Preparation of Niobia/Alumina as a Mixed Oxide Aerogel

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Synopsis. A niobia (Nb_2O_5)/alumina (Al_2O_3) mixed oxide, containing 25 weight percent niobia, was synthesized as an aerogel by using alkoxides as precursors and supercritical carbon dioxide in the drying step. After calcination at 773 K for two hours, this sample had a BET surface area of 450 $m^2\,g^{-1}$ and was X-ray amorphous, and contained primarily Lewis acid sites.

Sol–gel synthesis with alkoxides is an effective way to prepare single- and multi-component oxides. The removal of solvent from a gel with supercritical drying gives an aerogel, a technique which was first introduced by Kistler.[1,2] Since materials thus prepared are of high surface area, the catalytic applications of aerogels have been widely explored as recently reviewed by Pajonk.[3] In our laboratory we have synthesized and characterized aerogels of niobia[4] and niobia/silica.[5] We report here the preparation of niobia/alumina and compare its structural and acidic properties to the other niobia-containing aerogels.

Experimental

The niobia/alumina mixed gel was prepared by first diluting niobium ethoxide (Alfa) with 2-butanol (99+% anhydrous, Aldrich) and then combining it with a solution of 2-butanol, doubly deionized water, and nitric acid (70%, Fisher). The resulting sol was stirred for 10 min (for partial hydrolysis to occur), after which the alumina precursor, aluminum 2-butanolate (Aldrich), diluted with 2-butanol, was added. Deionized water was then added to the combined solution, and a thick gel formed in about one minute. On the basis of 50 ml of 2-butanol, the following concentrations were used: 0.15 mmol of Nb (niobium ethoxide), 1.2 mmol of Al (aluminum 2-butanolate), 2.1 mols of water per mol of (Nb+Al), and 0.28 mols of nitric acid per mol of (Nb+Al). These concentrations gave a niobia/alumina mixed oxide containing 25 weight % (11 mol %) niobia.

The removal of solvent from the mixed gel and the subsequent heat treatment was done following procedures described elsewhere.[4] The gel was extracted in a commercial autoclave (Autoclave Engineers) with supercritical carbon dioxide at 2.07×10^7 Pa and 423 K for three hours in a semicontinuous fashion.[6] Subsequent to extraction, the sample was heated in a tube furnace in flowing nitrogen at 673 K for 2 h and then in flowing oxygen at different temperatures. The resulting niobia/alumina mixed oxide aerogel is denoted as A-NA25w.

Techniques for characterizing the physical and acidic properties of the samples were described in detail previously.[4] Briefly, *n*-butylamine titration with Hammett indicators was used to measure the acid site distribution and the adsorption of pyridine was used to (i) distinguish between Lewis and Brönsted acid sites and (ii) determine the heat of adsorption. The isomerization of 1-butene was studied in a stainless-steel microreactor operated in a differential mode at 423 K and atmospheric pressure.

Results and Discussion

Table 1 summarizes the physical properties of A-NA25w as a function of heat treatment. After calcination at 773 K for two hours, the sample had a BET surface area of 454 $m^2\,g^{-1}$ with a corresponding pore volume of 1.08 $cm^3\,g^{-1}$. These values are typical of an open porous network and show that the structure of the mixed oxide aerogel was indeed stabilized by the supercritical drying step. Consistent with this observation is the X-ray diffraction result, obtained with a Rigaku D/Max diffractometer, which shows that this sample remained amorphous. Heating this sample to higher temperatures and/or longer times overcame this kinetic stabilization and collapsed the pore structure. This is evidenced by the significant decrease in surface area and the accompanying crystallization of γ-Al_2O_3 and $NbAlO_4$. Apparently with enough mobility, niobia reacted with alumina to form $NbAlO_4$, as reported by Layden,[7] and the remaining Al_2O_3 (the major component) crystallized into the γ-phase.

We next characterized the acidic properties of the A-NA25w sample which had been calcined at 773 K for two hours. Figure 1 shows the results obtained with *n*-butylamine titration using Hammett indicators.[4] Most of the acid sites of the samples were at either high ($pK_a=-8.2$) or low ($pK_a>+1.5$) acid strengths; the number of acid sites at $pK_a=-8.2$ was 4.1×10^{-4} mmol m^{-2}.

Figure 1 also shows the acid site distributions of a niobia aerogel,[4] denoted as A-Niobia, and a niobia/silica mixed oxide aerogel containing 25 weight % niobia,[5] denoted as A-NS25w. On a per-surface-area basis, the A-Nb_2O_5 sample has the highest acid site density be-

Table 1. Physical Properties of A-NA25w as a Function of Heat Treatment

Heat treatment (temperature/K, time/h)	BET surface area / $m^2\,g^{-1}$	X-Ray diffraction results
(773,2)	454	Amorphous
(1273,—)[a]	130	γ-Al_2O_3 Poorly crystalline $NbAlO_4$
(1273,48)	28	γ-Al_2O_3 $NbAlO_4$

a) (1273,—) means the sample was ramped to 1273 K without being held at that temperature.

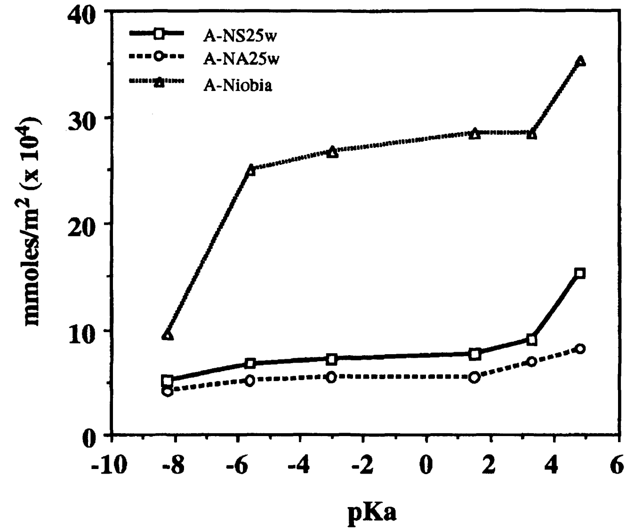

Fig. 1. Acid site distributions of aerogels of niobia, niobia/silica and niobia/alumina as determined by *n*-butylamine titration. All samples were calcined at 773 K for two hours.

cause its surface area is a factor of two to three less than those of the other two samples. Since A-NS25w and A-NA25w contain only 7 and 11 mol % of niobia, respectively, they have more acid sites per gram of niobia. The important point is that all three aerogels have acid sites at the acid strength of $\mathrm{p}K_\mathrm{a}=-8.2$.

Since *n*-butylamine titration measured only total acidity, we studied the adsorption of pyridine on these aerogels with FTIR. Specifically, we determined the ratios of Lewis to Brönsted acid sites after the sample had been evacuated at 373, 473, and 573 K.[4,8] As shown in Table 2, the A-NA25w sample contained mostly Lewis acid sites. The small amount of Brönsted acid sites appeared to be weak, as pyridine was preferentially evacuated from these sites at higher temperatures. The other two aerogels contain proportionally more Brönsted sites at all evacuation temperatures.

The lack of Brönsted sites in the A-NA25w sample was also confirmed by 1-butene isomerization. Table 3 shows that all three aerogels have a *cis-/trans*-2-butene ratio of about one which is characteristic of a 2-butyl carbonium intermediate formed on Brönsted acid sites.[9] However, the activity of the A-NA25w sample at 423 K is a factor of 30—100 lower. We have thus demonstrated that our high-surface-area niobia/alumina aerogels contain mostly Lewis acid sites.

Table 2. Summary of FTIR Results of Pyridine Adsorption

Sample	Ratio of Lewis to Brönsted acid sites		
	373 K[a]	473 K[a]	573 K[a]
A-NA25w	18	47	150
A-NS25w[b]	2.6	10	27
$\text{A-Nb}_2\text{O}_5$[c]	3.3	7.7	25

a) Temperature at which the sample was evacuated. b) Taken from Ref. 5. c) Taken from Ref. 4.

Table 3. Kinetic Data of 1-Butene Isomerization

Sample	Activity at 423 K $\mathrm{mol\,h^{-1}\,m^{-2}}$, $\times10^{-4}$	*cis-/trans*-2-Butene
A-NA25w	0.007	1.0
A-NS25w[a]	0.22	1.2
$\text{A-Nb}_2\text{O}_5$[b]	0.71	1.6

a) Taken from Ref. 5. b) Taken from Ref. 4.

We have found that an alumina aerogel, prepared from aluminum 2-butanolate, also contained Lewis acid sites after heat treatment that was identical to that used for the A-NA25w sample.[10] It is thus difficult to ascertain whether the incorporation of niobia into alumina generates additional acid sites, since the models of Tanabe[11] and Kung[12] both predict such sites, if they exist, to be of the Lewis type. On the other hand, we have evidence that niobia does not enhance the acid *strength* of alumina. Figure 2 shows the heat of adsorption of pyridine as a function of coverage measured with the method of Deeba and Hall.[13] We previously showed that heat of adsorption data obtained with this method have an uncertainty of about ±10%.[14] Thus, within the accuracy of the measurement, the addition of niobia to alumina did not change the acid strength as probed by pyridine adsorption. The decline in the heat of adsorption with increasing pyridine coverage was also similar in these two samples. The similarity between the aerogels of alumina and niobia/alumina is significant in showing that niobia–alumina interactions, while keeping niobia as X-ray amorphous after calcination at 773 K (see Table 1), do not stabilize niobia in a structure that would give rise to a stronger acid strength. We showed earlier that on a silica-stabilized niobia sample, the heat of adsorption of pyridine can be as high as

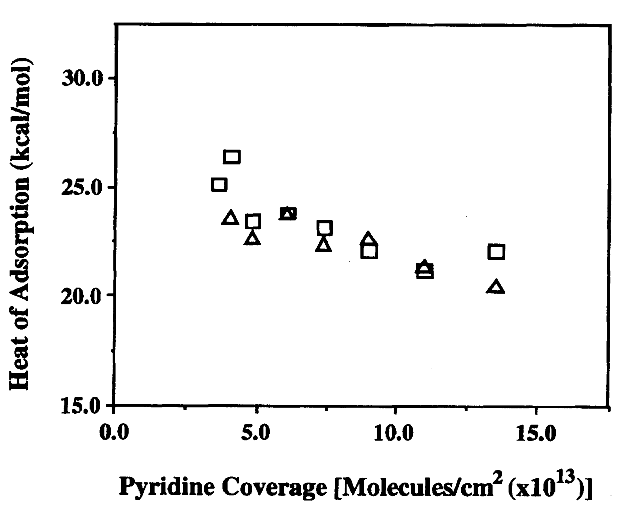

Fig. 2. Heat of adsorption of pyridine on aerogels of alumina (△) and niobia/alumina (□).

about 40 kcal mol^{-1}.[14] Thus, the actual structural environment of an oxide (e.g., niobia) as it is added as a minor component to another oxide (e.g., silica versus alumina) is an important factor in determining the acidic properties of the resulting mixed oxides (e.g., A-NS25w versus A-NA25w).

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