Catalysis Letters 12 (1992) 231–238

Synthesis and characterization of niobia-containing aerogels

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Niobium ethoxide was used as a precursor either by itself to impregnate a silica aerogel or in conjunction with tetraethyl orthosilicate to produce a mixed oxide aerogel. In contrast with bulk niobia, niobia in these samples did not crystallize into the high-temperature form even after calcination at 1273 K. Niobia-silica interactions, which apparently stabilized niobia from crystallization, also introduced acidity as shown by n-butylamine titration and infrared study of pyridine adsorption. Furthermore, niobia on silica was found to have stronger Brönsted acid sites than niobia in silica, in agreement with previous observations on samples prepared with more conventional methods. All these samples were also active in the isomerization of 1-butene.

Keywords: Aerogels; niobia; silica; acidic oxides

1. Introduction

The generation of acidity when two different oxides are combined can usually be understood in terms of the charge distribution across cation-oxygen-cation linkages [1]. From an acidity viewpoint, it would thus be desirable to synthesize a mixed oxide in which the two oxides are intimately mixed. One effective way to accomplish this goal is the sol-gel process with metal alkoxides as precursors [2]. In particular, high-surface-area aerogels can be obtained by removing the solvent with supercritical extraction [3].

Aerogels of single- or multi-component oxides have in fact been synthesized as catalysts [4,5], but the acidic properties of these materials remain largely unexplored. In this paper we demonstrate that acidic, high-surface-area materials can be prepared by either using an aerogel as a support or co-gelling a mixed oxide directly. As we have previously shown that both niobia in silica and niobia

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on silica are acidic [6], we chose to work with the niobia-silica system to allow a comparison between preparation methods.

2. Experimental methods

PREPARATION OF SAMPLES

A niobia/silica mixed oxide aerogel containing 25 weight% niobia was prepared with $Nb(OC_2H_5)_2$ (Alfa) and $Si(OC_2H_5)_4$ (Aldrich) as precursors. The silica precursor was first diluted in methanol and added to a methanolic solution of doubly deionized water and nitric acid. The pH of the solution was adjusted to 6 with the addition of NH_4OH. A similar solution containing the appropriate amount of niobia precursor was then quickly added to the silica sol, resulting in a light clear-yellow niobia/silica sol. The pH of this solution was adjusted to 7 with NH_4OH and the solution turned into a firm gel upon standing for about 10 minutes. This gel was subsequently extracted with supercricial CO_2 in a commercial autoclave (Autoclave Engineers, Model No. 08U-06-60FS) at the following conditions: temperature = 343 K, $P = 2 \times 10^4$ kPa, flowrate of $CO_2 = 0.05$ SCFM. A typical extraction lasted about 2 hours for the complete removal of solvent. Once removed from the autoclave, the aerogel was ground to < 100 mesh and calcined by heating in flowing N_2 at 673 K for 2 hours and then in flowing O_2 at 773 K for 2 hours. The same extraction and calcination procedure was used for all samples in this study unless otherwise noted. The niobia/silica mixed oxide aerogel is denoted as A-NS25w.

A silica aerogel (denoted as A-SiO_2) was prepared with a two-step acid-base catalyzed procedure [3] using $Si(OC_2H_5)_4$, H_2O, and HNO_3 (in 1.0:4.0:0.15 mole ratio) in s-butanol. Niobia was then placed onto the surface of this support via incipient wetness impregnation with a hexane solution of $Nb(OC_2H_5)_5$. By assuming each $NbO_{2.5}$ unit occupies an area of 16 Å^2 [7] and adjusting the amount of niobium ethoxide accordingly, we prepared three silica-supported niobia oxides containing 0.05, 0.1 and 0.25 monolayers of niobia. The samples are denoted as A-NS(x) where x represents the monolayer coverage.

CHARACTERIZATION

Techniques for characterizing the physical and acidic properties of the samples were described in detail elsewhere [6,8]. Briefly, BET surface areas were measured with a commercial Quantasorb unit (Quantachrome Corp.). Powder X-ray diffraction (XRD) patterns were obtained with a Rigaku D/Max diffractometer using a Mo or Cu source. The acidity was determined by titrating the samples in benzene with n-butylamine following the Benesi method [9]. In order to distinguish between Lewis and Brönsted acid sites, infrared spectra of adsorbed pyridine was obtained with an IBM 98 FTIR spectrometer. In a typical experiment, the sample was exposed to pyridine at room temperature and spectra were taken after evacuation at 373, 473, and 573 K. The ratio of Lewis to Brönsted acid sites was calculated from the integrated areas of the 1450 and 1490 cm^{-1} absorption peaks by following the procedure of Basila and Kantner [10]. 1-butene isomerization was studied in a stainless-steel microreactor operated in a differential mode at 423 K and atmospheric pressure. The procedure, which has been described previously [8], involved flowing 1-butene in a helium stream (5 mol% 1-butene) through the top of the reactor and analyzing the effluent mixture with gas chromatography after steady-state activity had been reached.

3. Results and discussion

PHYSICAL CHARACTERISTICS

Table 1 summarizes the BET surface areas and XRD data of the samples as a function of heat treatment. As typical for silica aerogels, the A-SiO_2 sample had a very high surface area which persisted until 1273 K, a temperature at which silica becomes mobile [12]. The introduction of niobia onto the surface of A-SiO_2 did not significantly alter its surface area (when compared on a per gram support basis) or its thermal stability. On the other hand, the crystallization behavior of the niobia surface oxide was very different. Bulk niobia has many stable modifications; it transforms into the TT-form at 773 K and the H-form at 1273 K [11,13]. H-Nb_2O_5 was not observed in any of the silica-supported niobia samples up to a heat treatment of 1273 K for 48 hours. In fact, the

Table 1
BET surface areas and X-ray diffraction results of niobia-containing aerogels as a function of heat treatment

Heat treatment (temperature in K, time in h)	Sample				
	A-NS25w	A-NS(0.05)	A-NS(0.10)	A-NS(0.25)	A-SiO_2
(773, 2)	670 [a] (A [b])	840 (A)	800 (A)	690 (A)	920 (A)
(873, 2)	600 (A)	830 (A)	770 (A)	640 (A)	825 (A)
(1073, 2)	390 (A)	700 (A)	650 (A)	500 (TT_{vpc})	750 (A)
(1273, –) [c]	315 (TT_{vpc})	630 (A)	600 (A)	390 (TT_{pc})	700 (A)
(1273, 48)	100 (TT_{pc})	280 (A)	190 (TT_{vpc})	160 (T + M)	290 (A)

[a] Surface area is in m^2/(g sample).

[b] The notation of Shafer et al. [11] is used to describe the many modifications of Nb_2O_5: A, amorphous; TT, low-temperature form; and M, medium-temperature form. vpc = very poorly crystalline, pc = poorly crystalline.

[c] (1273, –) means the sample was ramped to 1273 K without being held at that temperature.

A-NS(0.05) sample remained X-ray amorphous at this temperature, indicative of a highly-dispersed stable surface phase. This dispersion appeared to be worse with increasing niobia surface coverage, as TT-Nb_2O_5 was observed in A-NS(0.10) at 1273 K and in A-NS(0.25) at 1073 K. Niobia was also stabilized in the mixed oxide aerogel A-NS25w, as TT-Nb_2O_5 only emerged after heating to 1273 K. After the standard calcination, this sample had a surface area which was 40% larger than a sample prepared by co-precipitation [6] and four times the pore volume [14].

ACIDIC PROPERTIES

Table 2 shows the acidity of the samples at different values of pKa. The acidity is expressed in terms of millimoles of n-butylamine adsorbed per gram of niobia. We used this basis as, to be shown later, it provided a gauge on the dispersion of the surface niobia oxide. Conversion into per gram sample or per surface area can be easily done with the weight % niobia given in table 2 and the surface area given in table 1, respectively.

The A-SiO_2 support itself was found to be weakly acidic. It only turned the methyl red indicator (pKa = +4.8) to its red acidic form and had an acidity of 0.28 mmoles/g [14]. The results in table 2 thus establish the generation of acid sites when niobia was introduced either *in* or *on* silica. For the silica-supported samples, the cumulative acidity decreased with increasing niobia coverage, as shown more clearly in fig. 1. This trend suggests that the A-NS(0.05) sample is the most dispersed in the series. In fact, 7.89 mmoles/g Nb_2O_5 corresponds to ca. 1 acid site per Nb atom, consistent with a highly dispersed surface species. Apparently surface niobia aggregates at higher coverages, resulting in a lower acidity measured on a per gram niobia basis (see fig. 1). This interpretation is consistent with our earlier observation that niobia in the A-NS(0.10) and A-NS(0.25) samples crystallized into TT-Nb_2O_5 upon treatment at high temperatures. Fig. 1 shows the decrease in acidity of these two samples which reflects a decrease in dispersion accompanying the crystallization. In contrast the acidity of A-NS(0.05) remains unchanged, indicative of a stable, highly-dispersed phase.

Table 2
Acid amounts as determined with n-butylamine titration

Sample	Weight% Nb_2O_5	Acidity (mmoles/g Nb_2O_5)					
		pKa					
		+4.8	+3.3	+1.5	−3.0	−5.6	−8.2
A-NS25w	25.0	4.08	2.40	2.04	1.92	1.80	1.36
A-NS(0.05)	5.2	7.89	3.08	2.89	2.50	2.50	0.60
A-NS(0.10)	9.6	5.31	2.60	2.29	2.19	1.77	0.70
A-NS(0.25)	23.7	2.57	1.77	1.65	1.60	1.35	0.80

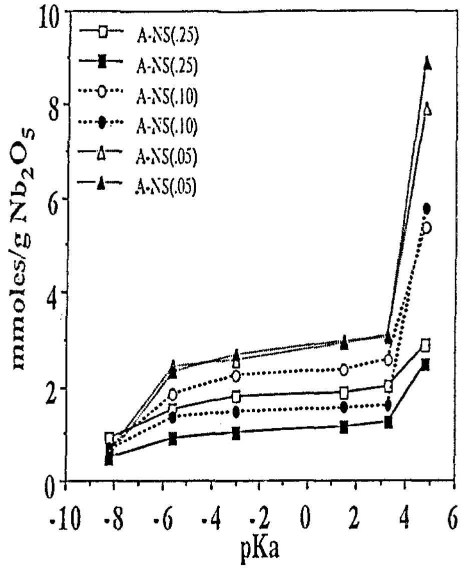

Fig. 1. Acidity of silica aerogel-supported niobia as a function of surface coverage and heat treatment (open symbols, heat treated at 773 K for 2 h; closed symbols, heat treated to 1273 K without hold).

FTIR results summarized in table 3 show that these samples possess both Lewis and Brönsted acid sites. Furthermore, the silica-supported samples have strong Brönsted acid sites as the Lewis to Brönsted ratio remained low even after evacuation at 573 K. On the other hand, pyridine adsorbed on Brönsted acid sites was preferentially removed from A-NS25w upon evacuation. These results are in good qualitative agreement with those reported for a co-precipitated Nb_2O_5/SiO_2 sample and for Nb_2O_5 impregnated onto a Davison silica support [6]. The ability of niobia to have terminal hydroxyl groups as a surface species but not as a component in the silica matrix has been used to explain the different acid site distributions [6]. The fact that similar results have been found for niobia-containing aerogels shows that the generation of acid sites when niobia is introduced on and in silica is independent of preparation methods.

Table 3
Summary of FTIR results of pyridine adsorption

Sample	Ratio of Lewis to Brönsted acid sites		
	373 K [a]	473 K	573 K
A-NS25w	2.6	9.9	27
A-NS(0.05)	6.7	10	12
A-NS(0.25)	2.9	3.6	6.5

[a] Temperature at which the sample was evacuated.

Table 4
Kinetic data of 1-butene isomerization

Sample	Activity at 423 K			cis-/trans-2-butene
	mol/h/g sample ($\times 10^{-2}$)	mol/h/g Nb_2O_5 ($\times 10^{-2}$)	mol/h/m^2 ($\times 10^{-4}$)	
A-NS25w	1.4	5.4	0.22	1.2
A-NS(0.05)	0.14	2.7	0.02	0.7
A-NS(0.10)	0.24	2.5	0.03	1.1
A-NS(0.25)	0.59	2.5	0.09	1.3

Table 4 summarizes the kinetic results of 1-butene isomerization, a common probe reaction of acidic catalysts. The activity of A-NS25w is comparable to that of niobic acid [14], a material which has been found active for many acid-catalyzed reactions [15]. The activities of the silica-supported samples are lower on per-g-sample and per-surface-area bases due to the low loadings of niobia on a high-surface-area support. Compared on a per-g-niobia basis, these samples are only a factor of two less active than the mixed oxide aerogel and have similar activities among themselves. The latter observation is different from the titration results which, as discussed above, show decreasing acidity (on a per-g-niobia basis) with increasing niobia content. However, these two trends are not inconsistent as isomerization activity is a measure of Brönsted acidity and not of total acidity. This point is supported by the selectivity data which show the ratio of cis- to trans-2-butene ranges from 0.7 to 1.3. A cis/trans ratio near unity is usually associated with a 2-butyl carbonium ion intermediate formed on Brönsted acid sites [16].

In summary, our results demonstrate that it is possible to synthesize niobia-containing aerogels which, after calcination at 773 K, are of high surface area, acidic, and active in 1-butene isomerization.

Acknowledgements

This research was supported in part by the Niobium Products Company, Inc. One of us (SMM) acknowledges the support of a U.S. Army Fellowship.

References

[1] K. Tanabe, *Catalysis Science and Technology*, eds., J.R. Anderson and M. Boudart, Vol. 2 (Springer-Verlag, Berlin, 1981) p. 231.
[2] L.G. Hubert-Pfalzgraf, New J. Chem. 11 (1987) 663.
[3] C.J. Brinker and G.W. Sherrer, *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing* (Academic Press, New York, 1990).

[4] S.J. Teichner, G.A. Nicolaon, M.A. Vicarini and G.E.E. Gardes, Adv. Colloid Interf. Sci. 5 (1976) 245.
[5] S.J. Teichner, *Aerogels*, ed. J. Fricke (Springer-Verlag, Berlin, 1986) p. 22.
[6] P.A. Burke and E.I. Ko, J. Catal. 129 (1991) 38.
[7] E.I. Ko, R. Bafrali, N.T. Nuhfer and N.J. Wagner, J. Catal. 95 (1985) 260.
[8] E.I. Ko, J.-P. Chen and J.G. Weissman, J. Catal. 105 (1987) 511.
[9] H.A. Benesi, J. Phys. Chem. 61 (1957) 970.
[10] M.R. Basila and T. Kantner, J. Phys. Chem. 70 (1966) 1681.
[11] H. Shafer, R. Gruehn and F. Schulte, Angew. Chem. Int. Ed. Eng. 5 (1966) 40.
[12] R.K. Iler, *The Chemistry of Silica* (Wiley, New York, 1979).
[13] E.I. Ko and J.G. Weissman, Catal. Today 8 (1990) 27.
[14] S.M. Maurer, Ph.D. thesis, Carnegie Mellon University, 1991.
[15] K. Tanabe, Catal. Today 8 (1990) 1.
[16] J. Goldwasser, J. Engelhardt and W.K. Hall, J. Catal. 71 (1981) 381.