Synthesis of Niobium- and Tantalum-Containing Silicalite-1

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Silicalite-1 containing niobium and tantalum anchored to the zeolite framework is obtained by hydrothermal crystallization and characterized by ^{29}Si-MAS NMR and UV-Vis spectroscopy.

The isomorphous substitution of metals into the framework of molecular sieves has been studied intensely since the discovery of titanium silicalite-1 (TS-1) by researchers at EniChem.[1] TS-1 has been found to selectively catalyze a broad range of oxidations with hydrogen peroxide,[1] which is of large interest, both commercially and scientifically. The encouraging results obtained in selective oxidations by the use of TS-1 triggered studies of isomorphous substitution of other metals in silicalites such as vanadium[1] and iron.[2] To date, there have been few reports of niobium-containing and none of tantalum-containing molecular sieves in the literature. Recently, the introduction of niobium into mesoporous molecular sieves has been studied by Ziolek et al.,[3,4] while Ying et al. report the synthesis of mesoporous niobium oxide.[5] Niobium compounds and niobium materials have been show to enhance catalytic properties, e.g. in the ammoxidation of propane or the oxidative dehydrogenation of propane,[6] but have always been regarded as having little or no utility as olefin epoxidation catalysts.[7] A recent patent describes that a niobium-containing silicalite-1 has been surprisingly found to be active as an olefin epoxidation catalyst using aqueous hydrogen peroxide.[8]

The present work describes the first synthesis of niobium- and tantalum-containing silicalite-1 and its characterization by several spectroscopic techniques suggesting anchoring of niobium and tantalum to the molecular sieve framework while no evidence for true isomorphous substitution was found.

NbS-1 and TaS-1 (The samples were labeled in agreement with VS-1, although true isomorphous substitution is unlikely due to the very large size of this metal ions.) were synthesized using TEOS (Merck), a 40 wt% aqueous solution of tetrapropylammonium hydroxide (TPAOH), niobium (V) isopropoxide (Alfa, 10 wt% in isopropanole) and tantalum ethoxide (Alfa), respectively. A gel with a molar composition of y M_2O_5 (M = Nb, Ta) : 1 SiO_2 : 0.38 TPAOH : 20 H_2O was prepared. In a series of experiments, y was varied between 0 and 0.01. The synthesis mixtures were prepared as follows: 33.2 g of TPAOH were slowly added to 40 g of TEOS. The resulting mixture was stirred for 1 h and then the desired amount of niobium isopropoxide or tantalum ethoxide was added. After stirring at room temperature for another hour, 4.2 g of TPAOH were added dropwise to the gel. Finally, the gel was heated to 70 °C until complete removal of the alcohol. The resultant clear gel was loaded into a Teflon lined autoclave and heated to 175 °C for 12 days. The white solid formed was recovered by filtration, washed with water and dried at 100 °C overnight. Finally, the samples were calcined in flowing air up to 540 °C for 18 h. Aluminum-containing ZSM-5 ($n_{Si}/n_{Al} = 45$) was synthesized using the procedure described elsewhere.[9] The ^{29}Si-MAS-NMR spectra were recorded at $\omega/2\pi = 79.49$ MHz with a recycle delay of 15 s using a 7 mm rotor spun at 3.5 kHz.

Powder X-ray diffraction analysis of the as-synthesized and calcined solids confirm a crystalline MFI structure (not shown) The powder XRD pattern was substantially identical to that of silicalite-1, except that the peaks were shifted to greater d-spacing as would be expected for a larger framework substituting ion. Calcination of the as-synthesized solids in dry air did not result in any significant loss of crystallinity, which is comparable with TS-1 and VS-1 for low concentrations of niobium and tantalum, respectively. As with TS-1 splitting of some reflections (2θ = 24.4 and 29.3°) was not observed indicating a symmetry change from monoclinic to orthorhombic.[10] The results of the chemical analysis of the calcined samples are presented in Table 1. TGA of NbS-1 and TaS-1 shows a maximum weight loss at 430 °C, which is observed in silicalite-1 as well and can be ascribed to the decomposition of the template TPAOH. A shoulder is observed at 520 °C in the niobium- and tantalum-containing samples indicating a stronger interaction of the template with the sites where substitution is believed to occur. Scanning electron micrographs reveal agglomeration of rather small crystallites (d < 1 μm).

Table 1. Chemical analysis of selected samples

Sample	n_{Si} / n_M (Gel)	n_{Si} / n_M (ICP)	Water Content / wt%
NbS-1(41)	60.1	40.7	5.1
NbS-1(88)	120.3	88.4	4.8
ZSM-5(45)	45	45	5.8
TaS-1(74)	60	74	8.1
TaS-1(107)	120	107	7.1

Small distortions of the lattice effected by the presence of framework niobium and tantalum sites are also apparent from the ^{29}Si-MAS NMR spectra (Figure 1). The well resolved features of the silicalite-1 spectrum are already substantially broadened at low niobium or tantalum content. Line broadening is typically provoked by the chemical shift anisotropy of the ^{29}Si atoms and heteronuclear dipolar interactions between ^{29}Si and ^{27}Al or other NMR active nuclei, viz. ^{93}Nb and ^{181}Ta. The spectral shapes of the NbS-1 (Figure 1a) and TaS-1 (Figure 1b) are similar to those of aluminum-containing ZSM-5 with comparable n_{Si}/n_M-ratios (Fig. 1c). Three lines are observed in NbS-1 (41) whose chemical shifts are - 103, - 112 and - 115 ppm. The line around -103 ppm is due to the presence of Si(OH) groups in defect centers within the silicalite-1 structure. The other lines are attributed to Si(0Nb). The chemical shift of -103 ppm is close to the values reported for Si(1Al) and Si(1Ga), which are -106[11] and -104[12] ppm, respectively. In analogy, this signal could also be due to Si(1Nb), since the ^{93}Nb nucleus hat 100% natural abundance and a medium size quadrupole moment.[13] However, ^{29}Si Cross-Polarization (CP) MAS NMR experiments performed on these samples confirm that the signal is due to defect SiOH groups. Similar conclusions were drawn by Belussi et al. [4] for VS-1 samples and a model was put forward explaining the generation of SiOH groups upon framework incorporation of vanadium.[15]

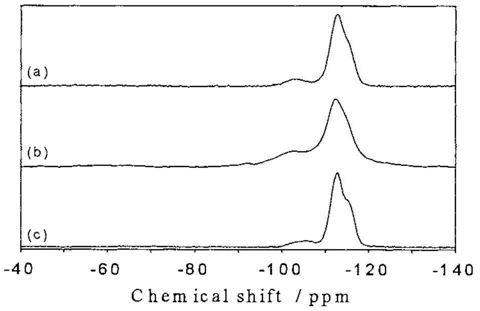

Figure 1. ^{29}Si-MAS NMR spectra of a) NbS-1 (n_{Si}/n_{Nb} = 41), b) TaS-1 (n_{Si}/n_{Ta} = 74) and c) ZSM-5 (n_{Si}/n_{Al} = 45).

Further evidence for anchoring of niobium to the silicalite-1 framework has been obtained from the respective UV-Vis spectra. The UV-Vis spectrum of NbS-1(88) (Figure 2d) shows a sharp absorption band between 200 and 300 nm with a maximum near 220 nm. The samples with the higher niobium concentration, NbS-1(41), shows a broader absorption band up to 370 nm with two maxima near 220 and 245 nm. This broadening has also been observed in Nb-containing MCM-41 and ascribed by Zhang and Ying[16] to a ligand-to-metal charge transfer. In a Nb_2O_5/SiO_2 catalyst, the charge transfer band of tetrahedral Nb(V)=O was observed at 235 nm and ascribed to NbO_4 tetrahedra.[17] In case of NbS-1 an absorption threshold is found at 360 nm, which is shorter than that corresponding to the band gap of bulk Nb_2O_5 (410 nm) (Figure 2a). The silicalite-1 impregnated with niobium isopropoxide (n_{Si}/n_{Nb} = 40) shows an absorption comparable to bulk Nb_2O_5 (Figure 2b). In contrast, the UV-Vis spectrum of NbS-1(88) show a single adsorption edge at 220 nm, which is considerably narrower than in Nb-MCM-41, where the formation of Nb-O-Si bonds is suggested.[16] Therefore, the UV-Vis spectra provide evidence for a tetrahedral niobium coordination and, hence, anchoring of niobium to the silicalite-1 framework. Analogous UV-Vis spectra were obtained for TaS-1 samples, which show an absorption band at 220 nm (Figure 3). With increasing tantalum content, the intensity increases and broadening occurs as in the case of NbS-1. Ta_2O_5 exhibits a band gap at 320 nm (Figure 3a), while silicalite-1 impregnated with tantalum ethoxide (n_{Si}/n_{Ta} = 40) shows a similiar spectrum with a band gap at 280 nm (Figure 3d).

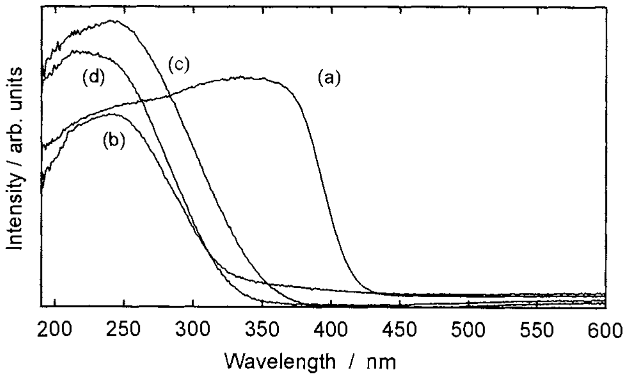

Figure 2. UV-Vis spectra of a) Nb_2O_5, b) Nb/Silicalite-1 c) NbS-1 (n_{Si}/n_{Nb} = 41) and d) NbS-1 (n_{Si}/n_{Nb} = 88).

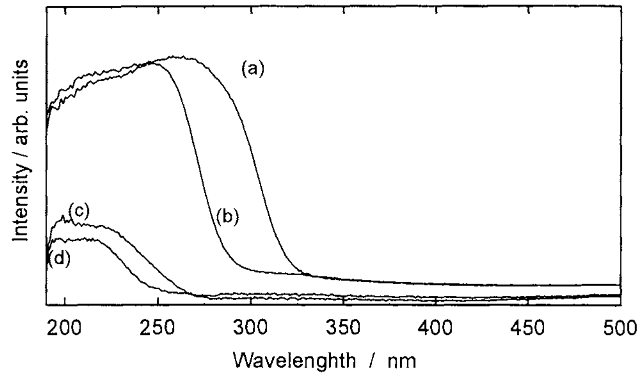

Figure 3. UV-Vis spectra of a) Ta_2O_5, b) Ta/silicalite-1 c) TaS-1 (n_{Si}/n_{Ta} = 74) and d) TaS-1 (n_{Si}/n_{Ta} = 107).

The presented results suggest that it is possible to prepare niobium- and tantalum-containing silicalite-1, in which isolated niobium or tantalum species are connected to framework defect sites. However, most likely there is no tendency for Nb(V) or Ta(V) to adopt a symmetrically binding tetrahedral coordination, which is a prerequisite for true isomorphous substitution, and one can only speculate about the nature of the defect site to which niobium or tantalum binds. Nevertheless, interesting chemical properties and catalytic performances can be expected from these systems and are subject to further studies.

References and Notes

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