니오비움 함유 실리카라이트 분자체의 수열합성 및 특성연구

고용식*, 장현태[1], 안화승[2]
신성대학 신소재화학과, [1]한서대학교 화학공학과, [2]인하대학교 화학공학과
(ysko@shinsung.ac.kr*)

Hydrothermal Synthesis and Characterization of Niobium-containing Silicalite Molecular Sieves

Yong Sig Ko*, Hyun Tae Jang[1], Wha Seung Ahn[2]
(ysko@shinsung.ac.kr*)
Department of Advanced Material Chemistry, Shinsung College,
[1]Department of Chemical Engineering, Hanseo University,
[2]Department of Chemical Engineering, Inha University

Introduction

Isomorphous substitution of silicon and/or aluminum by various heteroatoms into the framework of different zeolites has received considerable attention in the utilization of zeolites as catalysts. These elements can impart catalytic properties to the zeolite for many reactions other than those catalyzed by acid sites while offering the advantages of atomic dispersion of the elements, which is difficult to achieve with traditional catalyst preparation methods. In this respect, isomorphous substitution of titanium, zirconium, or vanadium into the framework of high-silica zeolites has expanded the scope of application of these materials. Titanium silicalite-1 was found to be active in the oxidation of a variety of organic substrates in the presence of aqueous hydrogen peroxide as oxidizing agent. Much the same as titanium-substituted molecular sieves, zirconium or vanadium silicalite-1 (ZS-1 or VS-1) can be synthesized by isomorphous substitution of Zr^{4+} or V^{5+} for Si^{4+} in the MFI structure framework, and has very interesting properties towards catalytic oxidation [1].

Niobium - which belongs to the same group in the Periodic Table as vanadium (Group V) - has been reported to have the capability of the photocatalytic and selective oxidations [2]. The presence of niobium in molecular sieves has the potential of generating catalysts with shape-selective properties and acidic or redox characteristics. Only a few reports are available on porous niobium silicates; they include work on the incorporation of niobium in micro/mesoporous materials, ETS-10 [3] denoted as ETNbS-10, to MFI [4] designated as NbS-1, and also to MCM-41 [5].

In this work, we report the hydrothermal synthesis and characterization of crystalline niobium silicalite molecular sieves with the MFI structure prepared using silicon and niobium alkoxides. Results from X-ray diffraction, scanning electron micrograph, framework infrared (IR) spectroscopy, UV-vis diffuse reflectance spectroscopy (DRS), ^{29}Si MAS NMR, NH_3-TPD, nitrogen adsorption and elemental analysis are discussed to verify the incorporation of niobium in the zeolite lattice framework.

Experimental

1. Synthesis of niobium silicalite-1 catalyst

NbS-1 samples were prepared from substrates having the following composition ratios ： $SiO_2/Nb_2O_5 = 32.7 \sim 99$, $TPA^+/SiO_2 = 0.46$, $H_2O/SiO_2 = 35$. In a typical preparation, a pyrex beaker was placed in a glove box and nitrogen was flushed over to minimize the adverse effect of moisture in air. After 27.01 g of tetraethylorthosilicate (Aldrich, 99.999 %) was transferred to the pyrex beaker and vigorously stirred, 0.43 g of niobium(Ⅴ) ethoxide (Aldrich, 99.95 %) was carefully introduced into this solution, and the mixture was cooled to about 273 K. After a few minutes, 60.65 g of tetrapropylammonium hydroxide (TPAOH) aqueous solution (Aldrich, 20 %), also cooled to 273 K, was slowly added dropwise into the mixture. After addition of all TPAOH the synthesis mixture was kept for $5 \sim 6$ h at $343 K \sim 353 K$ in order to accelerate hydrolysis and to evaporate the ethyl alcohol produced. This clear homogeneous solution was then transferred to a Teflon-lined stainless steel autoclave and kept in a convection oven at 448 K under autogenous pressure. The solid

products were separated by means of suction-filtration or centrifugation, washed several times with hot deionized water and dried in an air oven at 383 K overnight.   The products were finally calcined at 823 K for 6 h.

2. Characterization

The samples synthesized were analyzed by X-ray diffraction (XRD) for both qualitative and quantitative phase identification.   The crystal size and morphology of the crystalline samples were examined using a scanning electron microscope (Hitachi, X-650) after coating with a Au-Pd evaporated film.   Framework infrared (IR) spectra of samples were recorded in air at room temperature on a Perkin Elmer 221 spectrometer with wafers of zeolites mixed with dry KBr.   The elemental analyses of crystalline samples were performed with an inductively coupled plasma (ICP) spectrometer (Jobin Yuon, JY-38 VHR) and X-ray fluorescence (Rigaku, 3070).   UV-vis diffuse reflectance spectroscopy was performed on a Varian CARY 3E double-beam spectrometer in the range 190～500 nm.   The solid-state NMR spectra were obtained with a Bruker AM 300 spectrometer at a frequency of 59.6 MHz and spinning rate of 3.5 kHz with a pulse width of 3 μs, a relaxation delay of 5 s and 100～200 acquisitions.   The nitrogen-adsorption isotherms and specific surface areas were determined by nitrogen physisorption with the Brunauer-Emmett-Teller (BET) method at liquid-nitrogen temperature using a Micromeritics ASAP 2010 automatic analyzer. Ammonia temperature-programmed desorption tests were carried out in a quartz microreactor with continuous analysis of the released NH_3 concentration via a TCD detector using a Micromeritics TPD/TPR 2900 analyzer.

Results and discussion

The isomorphous substitution of Si^{4+} by larger Nb^{5+} ions in the NbS-1 framework causes a slight expansion of the unit cell parameters and volume.   Figure 1 shows the variation of unit cell volume calculated for calcined NbS-1 samples with different niobium contents.   The unit cell volume increases linearly with increasing niobium content of the reaction mixture up to 3 mol%.   The increase in unit cell volume is due to the introduction of larger Nb^{5+} ion in the framework lattice.   A similar expansion of the lattice has also been reported for isomorphous substitution of Si^{4+} by Ti^{4+}, Zr^{4+} or V^{5+} in the silicalite framework lattice.   Again, linear increases in the unit cell volume, V, with increases in the amount (mol%) of niobium suggest the presence of niobium in the framework. Earlier studies [6] have shown that the expansion of the unit cell volume is related to the concentration of the framework vanadium in the V^{5+} containing zeolite samples.

The overall crystallization rates at constant gel composition and temperature for TS-1, Zr-containing zeolite ZrS-1 [7] and NbS-1 are compared in Figure 2.   While the crystallization time was kept to 3 or 4 days to obtain the maximum crystallinity for TS-1 or ZrS-1, it was necessary for NbS-1 sample to be kept to 10 days in order to obtain the same degree crystallinity.   The fact that a relatively longer crystallization time was necessary to maintain the same degree of crystallinity for NbS-1 may be a consequence of the radius of niobium atoms being larger than that of titanium or zirconium atoms, and consequently it is believed to be more difficult for niobium to enter the silicalite framework than titanium or zirconium.   In addition, while ZSM-5 (which has the same MFI structure) can be prepared in 1 day, it takes substantially longer when titanium, zirconium or niobium is substituted into the framework.   Such a trend is generally observed in the synthesis of metal-substituted silicate molecular sieves, but it can be also considered as a consequence of the mineralizing agent NaOH/KOH being absent in the reaction mixture in such cases.

We have synthesized a series of NbS-1 samples by varying the amount of niobium in the synthesis gel.   It is seen that the niobium content of the NbS-1 crystals obtained is linearly correlated with the niobium content of the reaction mixtures.   This indicates that varying amounts of niobium can be incorporated in the crystal by changing the niobium content at the stage of gel preparation, and most of the niobium present in the substrate can be incorporated into the zeolite framework within the range of less than about 3 mol%.

The niobium content in the substrate mixture did not lead to a significant modification in the

morphology of NbS-1.　　All NbS-1 samples were made up of uniform crystals of size about 0.13 μm and hexagonal shape.　　The transmission electron micrograph of the NbS-1 sample shows the absence of amorphous matters outside the crystals of NbS-1.
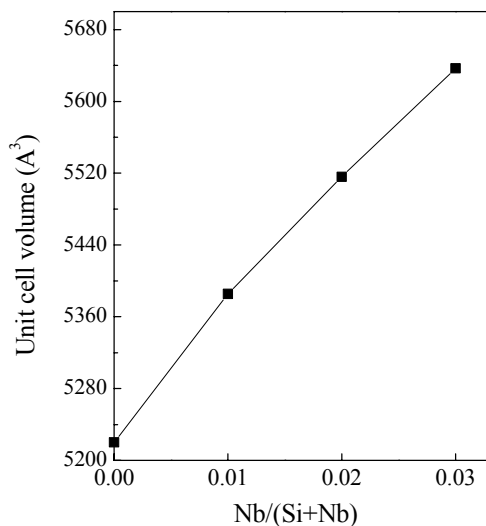
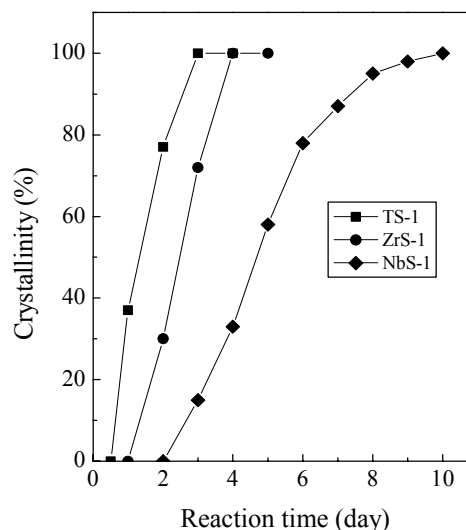Fig. 1. Unit cell volume of NbS-1 as a function of niobium content.

Fig. 2. Comparison between the crystallization rates of TS-1, ZrS-1 and NbS-1.

The IR spectrum of NbS-1 showed a characteristic absorption band at 963 cm^{-1}, which may be ascribed to Si−O−Nb stretching vibrations.　　This band was not observed in the IR spectra of calcined ZSM-5, pure silicalite-1 or in Nb_2O_5 powder.　　An absorption band near 950～970 cm^{-1} is usually known as characteristic of metal−oxygen stretching vibrations [7] or it has been interpreted to be a consequence of the Si−O^{-} vibrations [8] perturbed by metal ions nearby in the zeolite framework. Similar IR results have been reported earlier for isomorphous substitution of Si^{4+} by Ti^{4+}, Zr^{5+} and V^{5+} in the silicalite framework ; in all these cases, an IR band around 963 or 967 cm^{-1}, not present in the titanium-, zirconium- or vanadium-free analog, was observed.

The UV-vis diffuse reflectance spectrum of NbS-1 exhibited a strong transition band around 200 nm, similar to the band at ～210 nm of titanium- or zirconium-containing silicalite [8].　　The band around 210 nm is a charge-transfer band arising from excitation of an oxygen 2p electron in the valance band to the empty d orbitals of titanium [7] or zirconium ions in the framework of zeolites. In the titanium or zirconium silicalite, the band around 210 nm has been assigned to isolated titanium or zirconium in zeolite lattice framework [8].　　The pure silicalite-1 sample showed no corresponding signals.　　Thus, we suggest that the absorption band around 200 nm for NbS-1 is due to Si−O−Nb units in the framework.　　The main absorption band of Nb_2O_5 powder was observed at ～310 nm, and the absorption band of Nb/silicalite-1 (IMP) was very similar to that of the Nb_2O_5 powder.　　The absence of this band at ～310 nm in NbS-1 samples prepared further confirms the absence of occluded Nb_2O_5 in the framework.

The ^{29}Si MAS NMR spectrum of the NbS-1 was very similar to that of TS-1, ZrS-1 or VS-1 [9]. The NMR spectrum of the NbS-1 displays a resonance at about −103 ppm, a main signal at −113 ppm and a shoulder at about −116 ppm.　　Following the discussion in literature [10] the main peak at −113 ppm can be assigned to the central Si atom (in bold type) in Si(OSi)$_4$ (Q^4) sites based on the chemical shift.　　The ^{29}Si MAS NMR spectrum of NbS-1 showed a characteristic shoulder around −116 ppm which did not appear in the case of pure silicalite-1.　　In an earlier study on TS-1, this signal was assigned to (TiO)Si(OSi)$_3$ units and cited as evidence for framework substitution of

titanium [9].   Thus, we suggest that the shoulder at about -116 ppm of the NbS-1 is presumably attributed to the distorted silicon environment in tetrahedral due to Si−O−Nb bond.   Axon and Klinowski [10] reported that the signal at about -103 ppm is indicative of $Si(OSi)_3O^-$ (Q^3 unit) framework defects.   This seems reasonable in particular in the case of niobium silicalite-1 where at least a partial incorporation of the large Nb^{5+} ions should lead to structural distortions and defects of the silicalite structure.

The specific surface area of NbS-1 was about 504.5 m^2g^{-1} and remained almost constant up to 3 mol%.   Therefore, it could be speculated that no occluded niobium species are present in the samples prepared.   From the results of N_2-adsorption measurements on NbS-1 samples, it could be seen that the majority of the niobium up to 3 mol% in the reaction mixture was substituted isomorphously into the zeolite framework.

In order to study the potential development of acidity in the niobium silicalite-1 sample, NH_3-TPD tests were carried out on the pure silicalite-1, Nb/silicalite-1 (IMP) and NbS-1.   As expected, acid sites were almost absent in pure silicalite-1.   A broad NH_3 desorption peak positioned between 400 and 600 K was observed in the NbS-1 sample.   This corresponds to the weak acid sites, which may be attributed to silanol groups located near to niobium sites [Nb$\cdots$(OH)−Si].   On the other hand, the Nb/silicalite-1 (IMP) produced a far smaller desorption peak centered near $\sim$470 K, despite almost the same niobium content.   This desorption peak is probably associated with Nb−OH of the extraframework niobium oxides in the sample.   The NH_3-TPD results further prove that Nb^{5+} species in the niobium silicalite-1 sample were incorporated into the silicalite framework.

Conclusions

Niobium silicalite-1 (NbS-1) molecular sieves with the MFI structure have been synthesized hydrothermally, isomorphously substituting Nb^{5+} for the framework Si^{4+} of silicalite.   Uniform-sized (0.13 μm) and hexagonal-shaped crystals were obtained, and the unit cell volume of NbS-1 lattice was found to increase linearly with increasing niobium content of the substrate.   Framework IR spectrum showed a characteristic absorption band at around 963 cm^{-1}, probably due to Si−O−Nb linkages.   In the UV-vis spectrum, the absorption around 200 nm, which was assigned to the presence of Nb^{5+} in the zeolite framework, was observed for the NbS-1.   The ^{29}Si MAS NMR spectrum of NbS-1 exhibited a well-defined shoulder around -116 ppm due to the distorted Si environment.   Finally, NH_3-TPD studies revealed a development of mild acid sites in NbS-1.   All the diverse characterization methods employed in this study confirmed the structural incorporation of niobium in NbS-1.

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