

SYNTHESIS AND CHARACTERIZATION OF ZIRCONIUM SILICALITE-1

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Abstract – Zirconium silicalite-1 (ZS-1) catalysts with MFI structure were prepared using a hydrothermal synthesis method. XRD, SEM, IR, ^{29}Si MAS NMR, UV-VIS DRS, physical adsorption of nitrogen, and elemental analysis were then performed to evaluate its physico-chemical properties, and evidences of Zr^{4+} incorporation into the zeolite framework were provided: The unit cell volume of zirconium silicalite-1 increased linearly with increases in zirconium content, and the characteristic framework i.r. spectra shifted to lower frequencies as Zr^{4+} was incorporated into the silicalite-1 lattice. For its catalytic reaction test, liquid phase 2-butanol oxidation using hydrogen peroxide as an oxidant was carried out. All of the zirconium silicalite-1 samples synthesized were active for the 2-butanol oxidation, but activities obtained using ZS-1 catalysts were lower than TS-1 catalyst. Zirconium in the zeolite framework was found to be the active site for the 2-butanol oxidation.

Key words : Zirconium Silicalite-1, Hydrothermal Synthesis, IR, UV-VIS DRS, 2-Butanol Oxidation

INTRODUCTION

The framework substitution of silicon and/or aluminum by various hetero-atoms into the framework of different zeolites has received considerable attention in the utilization of zeolites as catalysts. In this respect, isomorphous substitution of titanium, vanadium, or zirconium into the framework of high-silica zeolites has expanded the scope of application of these materials. These isomorphously substituted zeolites are reported to be very promising in the liquid phase catalytic oxidation of hydrocarbons. Taramasso et al. [1983] first reported the hydrothermal synthesis of a titanium-containing zeolite, denoted as titanium silicalite-1 (TS-1). 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, i.e., hydroxylation of aromatics and phenol [Kraushaar and van Hooff, 1989], epoxidation of olefins [Clerici and Ingallina, 1993], oxidation of paraffins to the corresponding alcohol and ketones [Tatsumi et al., 1990; Huybrechts et al., 1990], and oxidation of alcohols and amines [Esposito et al., 1984; van der Pol and van Hooff, 1993]. In all cases, high activities, selectivities and high efficiency of H_2O_2 consumed were reported. After the explosive studies on TS-1, TS-2 [Perego et al., 1986] and other titanium silicates such as $\text{Ti}-\beta$ [Blasco et al., 1993; Huybrechts et al., 1990], TS-48 [Serrano et al., 1992], and recently mesoporous catalysts Ti-MCM-41 [Correa et al., 1994; Boccuti et al., 1989] and Ti-HMS [Reddy et al., 1990] have been reported.

Much the same as titanium substituted molecular sieves, zirconium silicalite-1 (ZS-1) can be synthesized by isomorphous substitution of Zr^{4+} for Si^{4+} in the framework of silicalite-1,

and has very interesting properties toward catalytic oxidation [Dongare et al., 1991]. Though synthesis of zirconium silicalite-1 has been reported in open literature [Dongare et al., 1991; Fricke et al., 1993; Wang et al., 1993], its physicochemical properties have not been as extensively investigated as the titanium silicalite molecular sieves, and this justifies the need for further investigation concerning the synthesis of zirconium silicalite-1 with detailed characterization and evaluation of its catalytic property.

In this work, we report the hydrothermal synthesis of zirconium silicalite-1 using silicon and zirconium alkoxides. Results from X-ray diffraction, scanning electron microscopy, UV-VIS diffuse reflectance spectroscopy, ^{29}Si MAS NMR, nitrogen adsorption, and elemental analysis were discussed to verify the incorporation of zirconium in the zeolite framework. 2-Butanol oxidation over ZS-1 using hydrogen peroxide as an oxidant also carried out to evaluate its catalytic property.

EXPERIMENTAL

1. Synthesis of Zirconium Silicalite-1 Catalyst

ZS-1 samples were prepared from substrates having the following composition ratios : $\text{SiO}_2/\text{ZrO}_2=32.7$, $\text{TPA}^+/\text{SiO}_2=0.46$, $\text{H}_2\text{O}/\text{SiO}_2=35$. A pyrex beaker was placed in a glove box and nitrogen was flushed over to minimize the adverse effect of moisture in air. After a calculated amount of tetraethylorthosilicate (Aldrich, 98 %) was transferred to a pyrex beaker and vigorously stirred, zirconium (IV) propoxide (Fluka, -70 % in propanol) was carefully introduced into this solution, and the mixture was cooled to about 0 °C. After a few minutes, TPA-OH aqueous solution (Aldrich, 20 %), also cooled to 0 °C, was slowly added dropwise into the mixture. Stirring and cooling was maintained during this process. After addition of all TPAOH the synthesis mixture was kept for 5-6 hours at 70-

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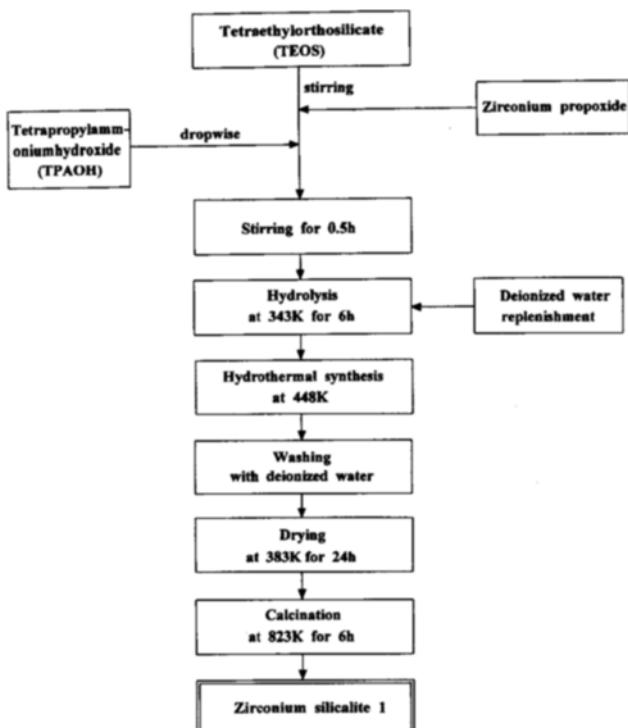


Fig. 1. Schematic diagram for the synthesis of Zr-silicalite 1.

80°C in order to accelerate hydrolysis and evaporate the ethyl/propyl alcohols which were released. Deionized water was then added to increase the volume of the mixture to its original value. This clear homogeneous solution was then transferred to a teflon-lined stainless steel autoclave and kept in a convection oven at 175°C under autogenous pressure. In order to investigate the crystallization process, autoclaves were taken out from the oven at different time intervals and were quenched immediately in cold water for sample identification. 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 110°C overnight. The products were finally calcined at 550°C for 6 hours. The synthesis procedure of zirconium silicalite-1 catalyst is schematically represented in Fig. 1.

2. Characterization

The synthesized samples were analyzed by X-ray diffraction (XRD) for both qualitative and quantitative phase identification. The unit used was a powder X-ray diffractometer (Philips, PW-1700) with a scintillation counter and a graphite monochromator attachment, utilizing Ni-filtered CuK α radiation (40 kV, 25 mA). Unit cell parameters were obtained by a least-squares fit to the interplanar spacings measured in the 5-45° (2θ) angular region, using silicon as an internal standard. 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 IR spectra of samples were recorded in air at room temperature on a Perkin Elmer 221 spectrometer (in the range of 400-4,000 cm^{-1}) with wafers of zeolites mixed with dry KBr. Elemental analyses of crystalline samples were performed with an ICP spectrometer (Johin Yuon JY-38 VHR)

and XRF (Rigaku, 3070). The nitrogen adsorption isotherms and specific surface areas were determined by nitrogen physisorption with the BET method at liquid nitrogen temperature using a Micromeritics ASAP 2000 automatic analyzer. UV-VIS Diffuse reflectance spectroscopy was performed on a Varian CARY 3E double beam spectrometer and dehydrated MgO was used as a reference in the range of 190-500 nm. 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 μsec , a relaxation delay of 5 sec and 100-200 acquisitions. The chemical shift was referenced with respect to the ^{29}Si signal of tetramethylsilane (TMS).

3. Catalytic Reaction Test

For a catalytic activity test of zirconium silicalite-1 catalyst, the oxidation of 2-butanol with aqueous H_2O_2 as oxidant was carried out using a 125 ml Pyrex reactor fitted with reflux condenser and a magnetic stirrer. In a typical run, 10 g of 2-butanol (Junsei, 99 %) and 10 g of H_2O_2 aqueous solution (Junsei, 35 %) were mixed in the reactor and heated to the desired temperature under vigorous agitation. Then, 0.1 g of ZS-1 catalyst was added to the reaction mixture, and the reaction was conducted at 50°C for 3 hours with vigorous stirring in the reactor immersed in a constant temperature sand bath. The catalyst and reaction mixture were separated and the reaction products were analyzed by gas chromatography (Shimastu, GC-14A) equipped with a 25 m capillary column (Supelco, CBP-M25-25) using a FID detector.

RESULTS AND DISCUSSION

The X-ray diffraction patterns of the ZS-1, ZSM-5 and silicalite-1 synthesized hydrothermally are shown in Fig. 2. The X-ray diffraction pattern of the calcined ZS-1 zeolites was similar to that of ZSM-5 zeolite. The symmetry of the cal-

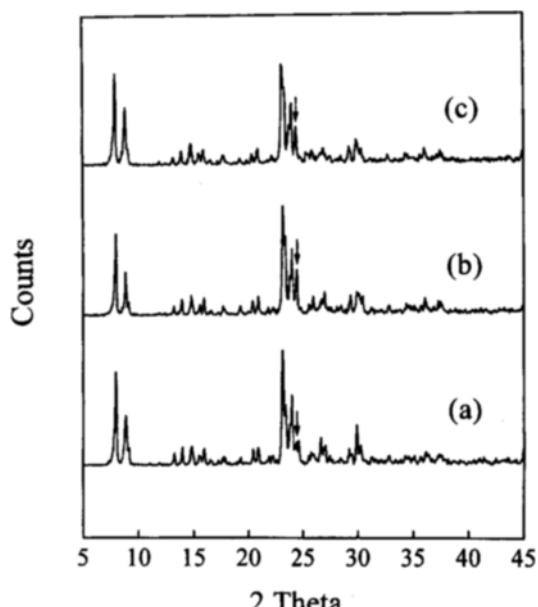


Fig. 2. XRD patterns of Zr-silicalite 1 and silicalite-1: (a) silicalite-1, (b) ZSM-5, (c) ZS-1 (3 mol% Zr).

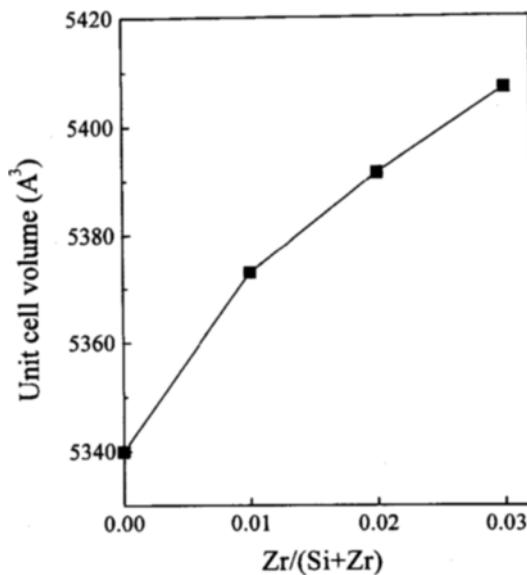


Fig. 3. Unit cell volume of ZS-1 as function of zirconium content.

calcined ZS-1 was orthorhombic, which comprises single reflections around 24.5° and 29.2° for 2θ . As expected, calcined silicalite-1 had monoclinic symmetry which presents double reflections at the same 2θ . The persistence of the orthorhombic symmetry in the calcined state in the zirconium silicalites is indicative of the location of Zr in the zeolite framework [Dongare et al., 1991].

The isomorphous substitution of Si^{4+} by the larger Zr^{4+} ions in the ZS-1 framework causes a slight expansion of the unit cell parameters and volume. Fig. 3 shows the variation of unit cell volume calculated for calcined ZS-1 samples with different zirconium content. The unit cell volume increased linearly with increases in zirconium contents of the reaction mixture up to 3 mol%. The increase in unit cell volume is due to the introduction of larger Zr^{4+} ion (0.73 \AA) in the framework lattice. A similar expansion of the lattice has also been reported for isomorphous substitution of Si^{4+} by Ti^{4+} in the silicalite-1 framework lattice [Taramasso et al., 1983]. Again, linear increases in the unit cell volume, V , with the increases in the mole% of Zr suggest the presence of zirconium in the framework.

The overall crystallization rates at constant gel composition and temperature for ZS-1 and TS-1 are compared in Fig. 4. While the crystallization time was kept to 3 days in order to obtain the maximum crystallinity for the TS-1, in order to obtain the same degree crystallinity, it was necessary for ZS-1 sample to be kept to 4 days. The fact that relatively longer crystallization time was necessary to maintain the same degree of crystallinity for ZS-1 may be a consequence of the radius of zirconium atom being larger than that of titanium atom. Consequently, it is believed to be more difficult for zirconium to enter the silicalite-1 framework than titanium. In addition, while the ZSM-5 which has the same MFI structure can be prepared in 1 day, it takes substantially longer when the zirconium or titanium is substituted into the framework. Such a trend is generally observed in the synthesis of metal-

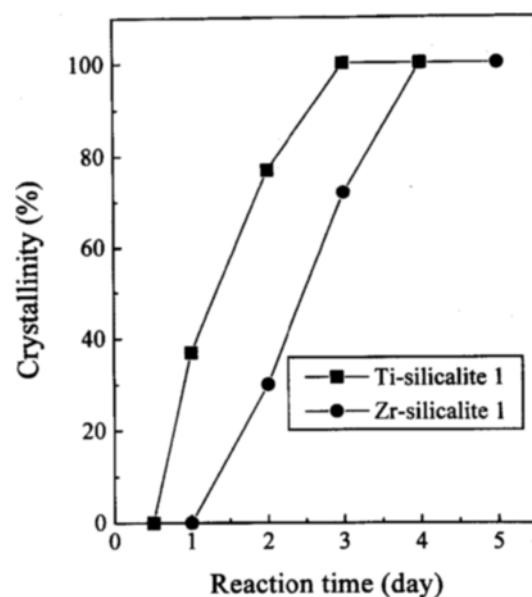


Fig. 4. Comparison between crystallization rates of TS-1 and ZS-1.

substituted silicate molecular sieves, but it can also be 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 ZS-1 samples by varying the amount of zirconium in the synthesis gel. Fig. 5 shows the bulk zirconium contents of ZS-1 crystals plotted against the zirconium content of their reaction mixtures. It is seen that the zirconium contents of ZS-1 crystals obtained are linearly correlated with the zirconium contents of the reaction mixtures. This indicates that varying amounts of zirconium can be incorporated in the crystal by changing the zirconium contents at the stage of gel preparation, and most of the Zr present in the substrate can be incorporated into the

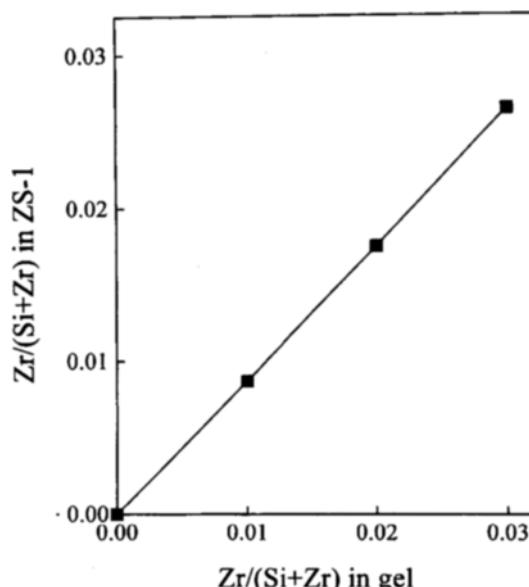


Fig. 5. Relationship between the zirconium content of the ZS-1 samples and of the gel mixtures.

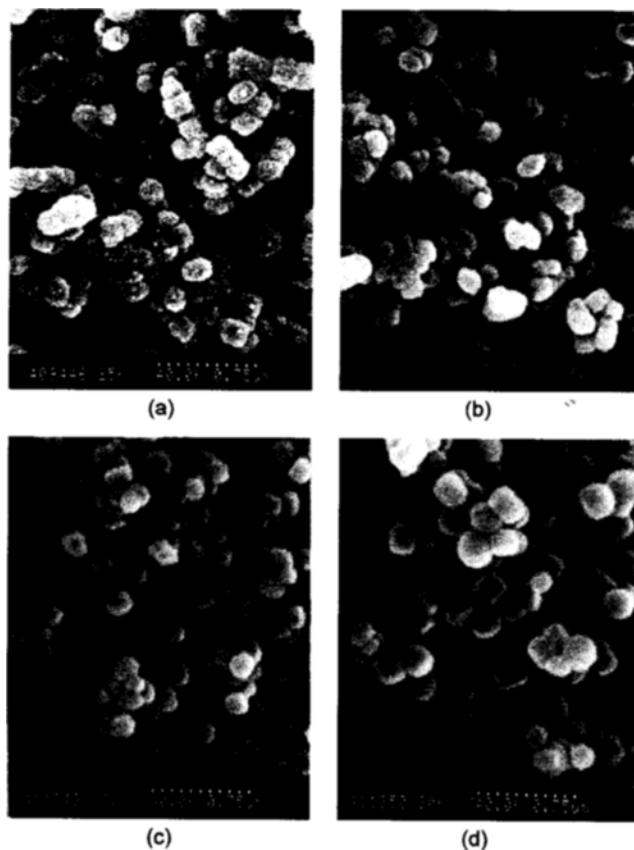


Fig. 6. SEM photographs of Zr-silicalite 1 synthesized with different zirconium content: (a) silicalite-1, (b) 1 mol%, (c) 2 mol%, and (d) 3 mol%.

zeolite framework within a range of less than about 3 mol%.

The scanning electron micrographs of ZS-1 samples with different zirconium contents are presented in Fig. 6. As can be seen from the micrographs, the zirconium content in the substrate mixture did not lead to significant modification in the morphology of ZS-1. All ZS-1 samples were made up of uniform crystals of about $0.2\text{ }\mu\text{m}$ and cuboid in shape. The scanning electron micrographs also confirmed the absence of amorphous matters outside the crystals of ZS-1.

IR spectra of the calcined silicalite-1 and ZS-1 sample are compared in Fig. 7. As is known, the IR spectra in the mid-infrared region can provide an evidence of the isomorphous substitution of large hetero-atoms ions into the framework of zeolites [Boccuti et al., 1989; Ko and Ahn, 1997b]. The band around $1,100\text{ cm}^{-1}$ corresponds to asymmetric vibrations of internal tetrahedra, and the symmetric stretching of a T-O is found around $820\text{-}780\text{ cm}^{-1}$ [Breck, 1974]. In these spectra, the absorption bands originating from zirconium hydroxides and zirconium oxides were not observed. When the zirconium was incorporated into the silicalite-1 lattice, IR absorption bands around $1,115\text{ cm}^{-1}$ shifted progressively towards the lower frequency region. The shift of the spectra to the lower frequency is due to increases in unit cell parameters caused by Zr^{4+} existing in tetrahedral sites. Our IR observation for ZS-1 did not agree with the results of Dongare et al. [1991] who claimed a presence of a characteristic absorption band

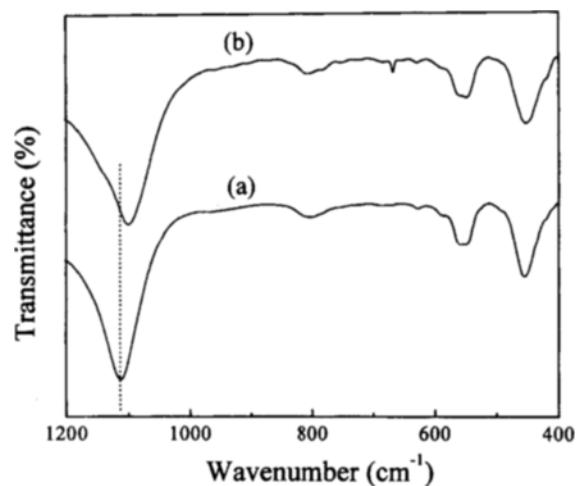


Fig. 7. IR spectra of (a) silicalite-1 and ZS-1 (3 mol% Zr).

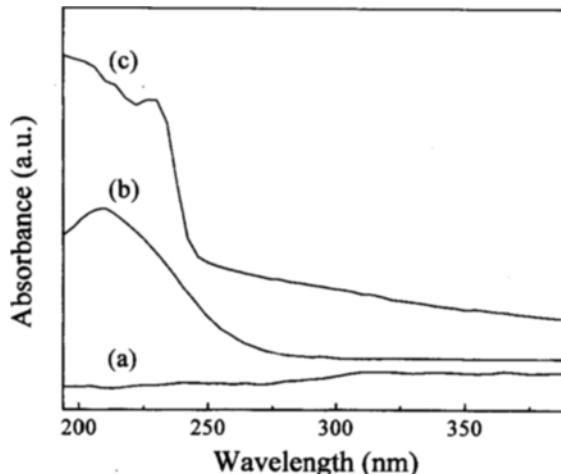


Fig. 8. UV-vis diffuse reflectance spectra of (a) silicalite-1, (b) ZS-1, and (c) ZrO_2 powder.

at 963 cm^{-1} . Fricke et al. [1993], on the other hand, could not detect the 963 cm^{-1} band and report virtually the same IR spectrum as ours. Further study seems necessary to clarify this difference.

The UV-VIS diffuse reflectance spectra of the calcined pure silicalite-1, ZrO_2 , and ZS-1 are shown in Fig. 8. Quite similar spectra were obtained among ZS-1 samples with zirconium content up to 3 mol%. The UV-VIS diffuse reflectance spectrum of ZS-1 exhibited a strong transition band around 210 nm, same with TS-1 [Boccuti et al., 1989]. The band around 210 nm has been assigned to isolated framework zirconium in tetrahedral coordination [Wang et al., 1993]. The pure silicalite-1 sample showed no corresponding signals. The main absorption band of ZrO_2 powder was observed at 230 nm. The absorption band of ZS-1 sample was significantly different from the band pattern of ZrO_2 powder. The absence of this band in ZS-1 samples prepared further confirms the absence of occluded ZrO_2 in the framework.

Fig. 9 shows the ^{29}Si MAS NMR spectra of the calcined ZS-1 and silicalite-1 samples. ^{29}Si MAS NMR spectrum of ZS-1 was very similar to that of TS-1 [Reddy et al., 1990; Kraushaar

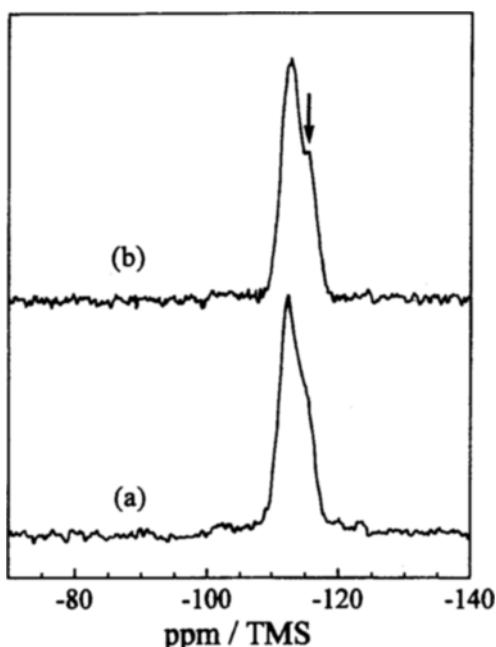


Fig. 9. ^{29}Si MAS NMR spectra of the calcined (a) silicalite-1 and (b) ZS-1.

and van Hooff, 1988]. They consist of a main signal at -113 ppm and a shoulder at about -116 ppm. It is reported in the literature that the main signal at -113 ppm can be assigned to $\text{Si}(4\text{Si})$ coordination [Engelhardt and Michel, 1987]. The ^{29}Si MAS NMR spectrum of ZS-1 showed a characteristic shoulder around $\delta = -116$ ppm which did not appear in the case of pure silicalite-1. In the ZS-1, the shoulder at -116 ppm is presumably attributed to arise from the distorted silicon environment in tetrahedra due to $\text{Si}-\text{O}-\text{Zr}$ bond.

Fig. 10 shows the nitrogen adsorption-desorption isotherms of ZS-1 and pure silicalite-1, which were calcined at 550°C in N_2 , at liquid nitrogen temperature (77 K). As can be seen, the nitrogen adsorption capacity of ZS-1 was similar to that of the pure silicalite-1. The shapes of the two isotherms were also similar except for the presence of a large high-pressure

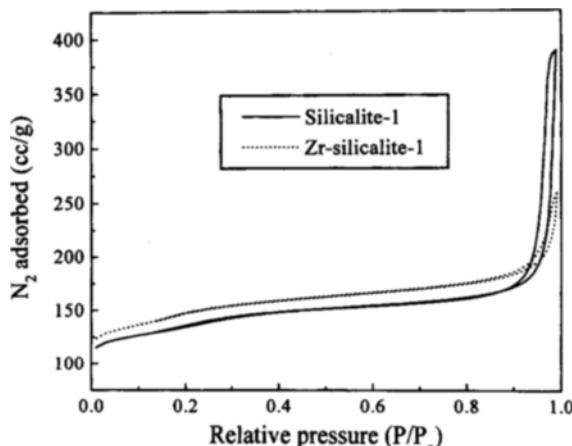


Fig. 10. N_2 adsorption isotherms of the calcined (a) silicalite-1 and (b) ZS-1.

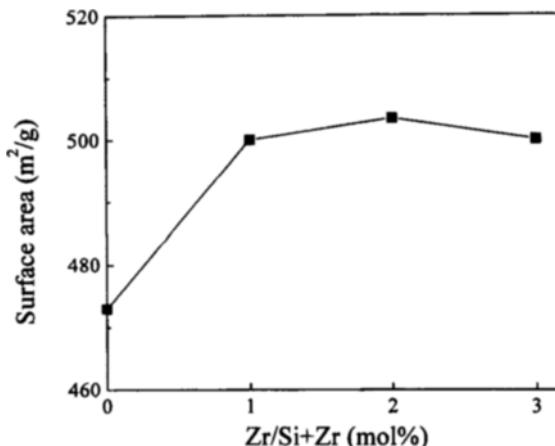


Fig. 11. Specific surface area (BET) of ZS-1 with different zirconium content.

hysteresis loop in silicalite-1. Both isotherms were of type I frequently found in zeolitic sorbents.

Fig. 11 shows the specific surface area (BET) of ZS-1 with different mole% of Zr in the reaction mixture. The specific surface area of ZS-1 was about $500\text{ m}^2/\text{g}$ and remained almost constant up to 3 mol\% . Therefore, it could be speculated that no occluded zirconium species are present in the samples prepared.

It is currently accepted that the zeolites with zirconium only in the framework can be catalytically active for partial oxidation of organic compounds in the presence of H_2O_2 [Dongare et al., 1991]. If zirconium is not in the zeolite framework, the material is reported to be inactive as oxidation catalysts, regardless of the other positive physicochemical evidences.

Table 1 shows the results of the oxidation of 2-butanol with H_2O_2 over silicalite-1, HZSM-5, ZrO_2 , ZS-1 with varying amounts of zirconium. The only product of the reaction was found to be 2-butanone. All of the ZS-1 samples synthesized were active for the 2-butanol oxidation. The conversion of 2-butanol to 2-butanone increased with increasing the zirconium content of ZS-1 up to 3 mol\% . The high conversion of 17.5% was obtained over ZS-1 with zirconium con-

Table 1. Oxidation of 2-butanol with hydrogen peroxide over various catalysts

Samples	Zr or Ti mol % in ZS-1 or TS-1	Conversion (%)
ZS-1	0.01	7
ZS-1	0.02	11
ZS-1	0.03	18
TS-1	0.01	39
TS-1	0.02	46
TS-1	0.03	54
Silicalite-1	$\text{Si}/\text{Zr}=\infty$	No reaction
HZSM-5	$\text{Si}/\text{Al}=75$	No reaction
ZrO_2	—	No reaction
No catalyst	—	No reaction

Reaction conditions: 10 ml 2-butanol and 10 ml H_2O_2 mixed with 0.1 g catalysts at 50°C for 3 hours.

tent of 3 mol%. However, their catalytic activity was not as good as the corresponding TS-1 catalysts [Ko and Ahn, 1997a]. Pure silicalite-1, HZSM-5 and ZrO_2 also examined as catalysts were found inactive for the oxidation of 2-butanol. These results over ZS-1 suggest that the Zr^{4+} present in ZS-1 framework is indeed the active site for the oxidation of 2-butanol.

CONCLUSIONS

Zirconium silicalite-1 (ZS-1) has been synthesized hydrothermally, isomorphously substituting Zr^{4+} for the framework Si^{4+} of silicalite-1. Uniform size of 0.2 μm and cuboid shaped crystals were obtained, and the unit cell volume of ZS-1 was found to increase linearly following the increases in the zirconium content of the substrate. The framework IR spectra showed a band shift to lower frequencies as zirconium was incorporated into the silicalite-1 lattice. The results of UV-VIS DRS, nitrogen adsorption, and ^{29}Si MAS NMR analysis were also indicative of the isomorphous substitution of Zr^{4+} ions into the silicalite-1 framework. ZS-1 samples synthesized were active for the 2-butanol oxidation using hydrogen peroxide as an oxidant, and the activity increased with the zirconium content up to 3 mol%. Isolated tetrahedral Zr^{4+} species in the framework of MFI structure were found to be the active sites for the 2-butanol oxidation with hydrogen peroxide.

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