

Synthesis, characterization, and catalytic properties of [Zr]-ZSM-5

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Crystalline, microporous, zirconium silicas have been synthesized. XRD and selected area electron diffraction revealed their MFI structure with orthorhombic symmetry. Absence of other crystalline or amorphous phases was also confirmed by electron microscopy. Uniform spherical crystallites of 0.2 μm size were observed by electron microscopy. The samples were substantially free from aluminum ($\text{Si}/\text{Al} > 2000$). An increase in unit cell volume from 5294 (\AA)³, for pure [Si]-ZSM-5, to 5402 (\AA)³, for [Zr]-ZSM-5 ($\text{Si}/\text{Zr} = 24$), was observed, suggesting isomorphous substitution of Si^{4+} by Zr^{4+} in the lattice framework. On calcination of the as-synthesized sample in air, there was a change in crystalline symmetry from orthorhombic to monoclinic. This change in symmetry could, however, be prevented by carrying out the calcination carefully, first in N_2 and then in air. Framework i.r. spectra exhibited a band at 963 cm^{-1} , probably due to Si-O-Zr linkages, in addition to other bands characteristic of the MFI structure. [Zr]-ZSM-5 is active in the hydroxylation of benzene to phenol and phenol to dihydroxy benzenes.

Keywords: [Zr]-ZSM-5; isomorphous substitution; zirconium molecular sieves; zirconium silicates

INTRODUCTION

The synthesis of crystalline zirconium silicas with zeolitic properties has been claimed.¹⁻⁴ However, the details of the synthesis and characterization of such material are not available in the literature. Specifically, no structural data indicating the presence of zirconium in the pentasil framework is available. We now report the synthesis of crystalline zirconium silicas having the MFI type of structure. Results from X-ray and electron diffraction, framework i.r. spectroscopy, electron microscopy, and adsorption and catalytic studies suggest the incorporation of zirconium in the MFI lattice.

EXPERIMENTAL

Synthesis

A solution containing zirconium isopropoxide (1.09 g) in 50 ml of isopropyl alcohol was added dropwise to a solution of tetraethyl orthosilicate (20.8 g) in 50 ml of isopropyl alcohol and stirred vigorously. To this, an aqueous (40%) solution of tetrapropylammonium hydroxide (25 g) and 50 ml of deionized water was added. Stirring was continued till the gel became homogeneous. The gel, thus formed, was heated in an autoclave at 453 K for 48 h. After

crystallization, the product was washed with H_2O and dried at 393 K for 6 h in air. This as-synthesized sample was further calcined at 673 K first in nitrogen and then in air at 673 K for 6 h.

Characterization

The crystallinity of the samples was recorded using a Philips 1730 X-ray diffractometer using nickel-filtered $\text{CuK}\alpha$ radiation. The XRD powder pattern was recorded at a scanning rate of $2\theta = 0.5^\circ/\text{min}$ with silicon as an internal standard. The elemental analyses were performed using plasma emission spectroscopy (Jobin Yvon) and wet chemical methods. Sorption measurements were carried out at 298 K on a McBain-type gravimetric unit connected to a vacuum/gas handling system. Prior to adsorption, the samples were outgassed in vacuum (10^{-6} Torr) at 674 K for several hours. Sorption of water, *n*-hexane, and cyclohexane was carried out at a relative pressure, P/P_0 0.5. For transmission electron microscopic (TEM) study, the sample powder was ultrasonically dispersed in isopropyl alcohol for a few seconds. A drop of this suspension was then placed on a carbon film supported over the TEM specimen grid. The specimen was examined with an electron microscope (model 1200, Joel, Japan, 120 kV). Lattice parameter calibrations with gold films showed the accuracy of measurements to be better than $\pm 1\%$. The i.r. framework spectra ($200\text{--}1300\text{ cm}^{-1}$) of the samples (Nujol mull technique) was recorded with a Pye unicam SP-300 spectrophotometer. The catalytic reactions were carried out in a batch reactor (100 ml

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capacity) at 333 K. The benzene (Merck, 99.9% GC pure) to hydrogen peroxide (30% aq. sol.) ratio was 8. The products were analyzed using g.c. and HPLC (Water Associates). Good agreement was found in all cases.

RESULTS AND DISCUSSION

X-ray and electron diffraction

Three samples of zirconium silicas with Si/Zr molar ratios of 100, 60, and 24, respectively, were synthesized, (samples I, II, and III, respectively). The XRD patterns of the as-synthesized samples are compared with that of silicalite-I in *Figure 1*. All the three samples are highly crystalline and possess orthorhombic symmetry. On calcination in air around 773 K, [Zr]-ZSM-5 transforms to a monoclinic form (*Figure 2*, curve B). However, when the sample was calcined initially in a nitrogen atmosphere for 10 h at 673 K and then in air at 673 K, this change in symmetry from orthorhombic to monoclinic does not occur (*Figure 2*, curve C). The selected area electron diffraction pattern and brightfield electron micrograph of sample III are shown in *Figure 3A* and *B*, respectively.

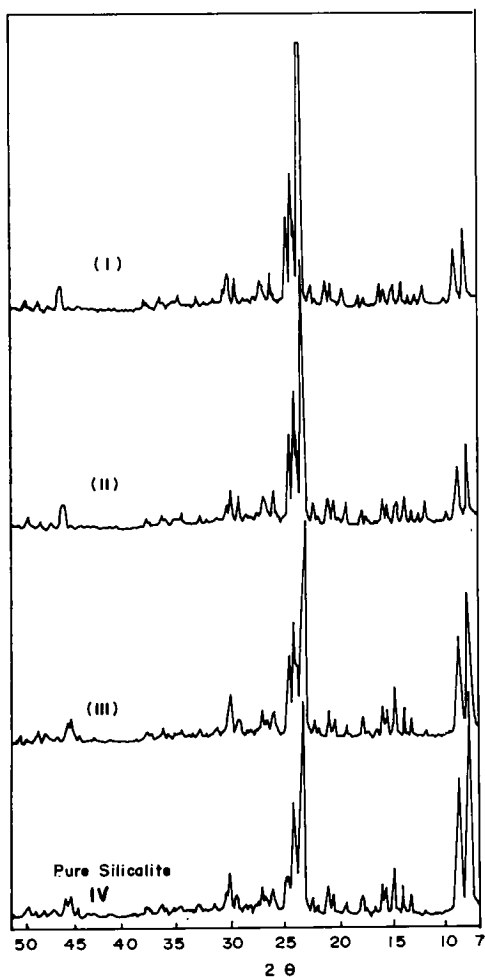


Figure 1 XRD pattern of [Zr]-ZSM-5 (samples I, II, III) and [Si]-ZSM-5 (curves I-IV, respectively), in the as-synthesized form

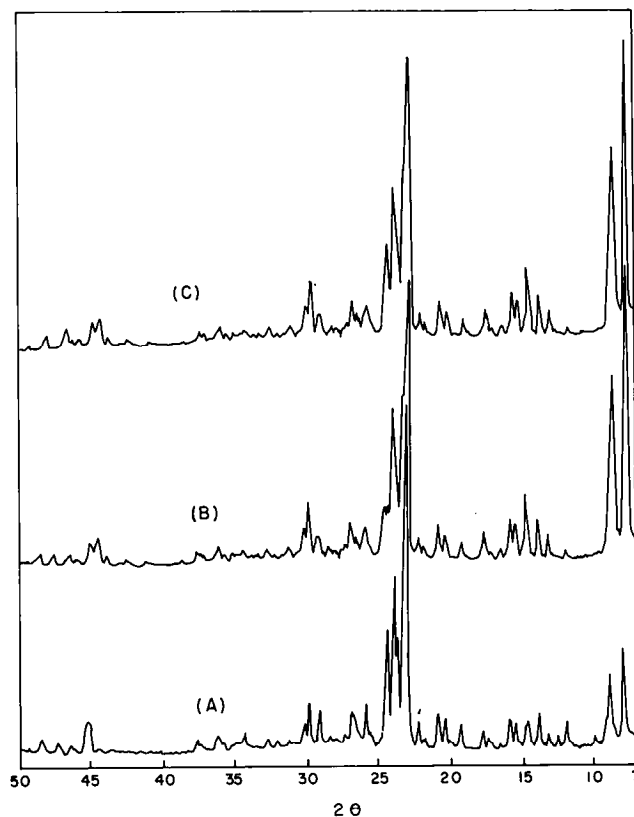


Figure 2 XRD pattern of [Zr]-ZSM-5 (Si/Zr = 24) in the as-synthesized form (A), after calcination in air at 773 K (B), and after calcination, first in N₂ at 673 K and then in air at 673 K (C)

The electron micrograph confirms the absence of amorphous matter *outside* the crystals of zirconium silica. The average size of the crystals is around 0.2 μm. The 'd' values calculated from both XRD and electron diffraction for the sample III, calcined first in N₂ and then in air, are compared in *Table 1*. The orthorhombic unit cell parameters for the three samples of [Zr]-ZSM-5 and pure [Si]-ZSM-5 (Si/Al > 2000), all in the calcined form, calculated from the XRD data, are given in *Table 2*. The increase in unit cell volume (on going from the silicon to the zirconium analog) is probably due to the introduction of the larger ion Zr⁴⁺ (0.73 Å) in the MFI lattice.⁵

Adsorption studies

The nitrogen BET surface area of sample III was 483 m²/g. At 293 K and $P/P_0 = 0.5$, it adsorbed 6.1, 13.7, and 8.95 wt% H₂O, *n*-hexane, and cyclohexane, respectively. Values for the adsorption of *n*-hexane and cyclohexane are very similar to those observed in the case of [Si]-ZSM-5 and indicate the absence of occluded matter (like ZrO₂) within the pore system.

Infrared spectroscopy

The framework i.r. spectra of crystalline [Zr]-ZSM-5 (Si/Zr = 24) recorded in the range 200–1200 cm⁻¹ (*Figure 4*) shows an absorption band at 963 cm⁻¹ in addition to other bands characteristic of the MFI

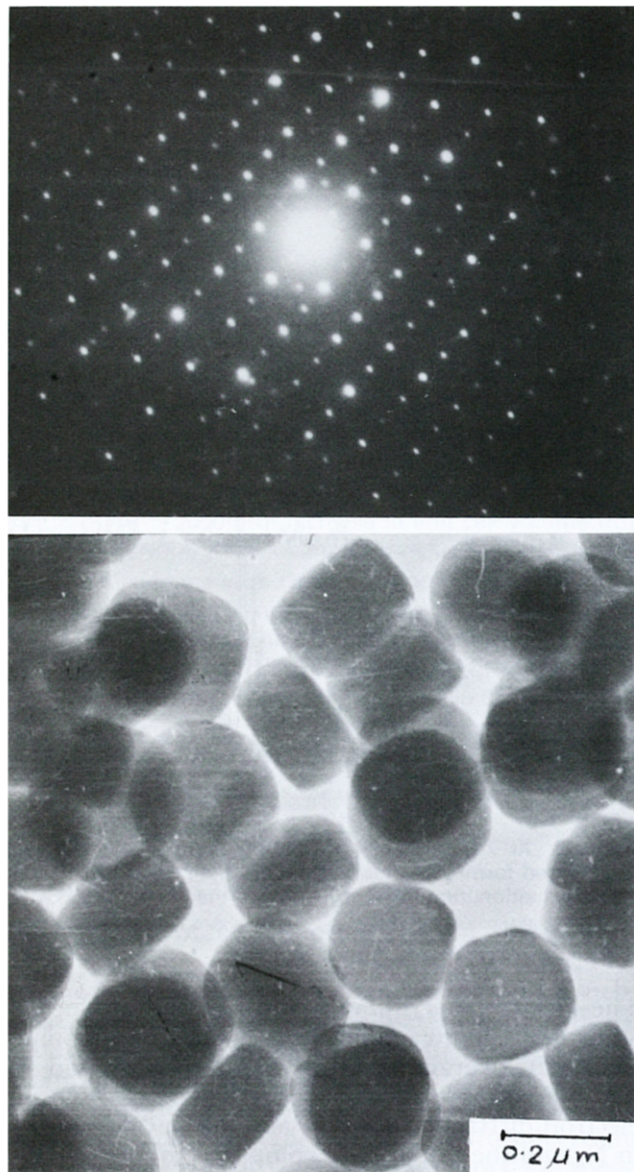


Figure 3 Selected area electron diffraction (A) and brightfield electron micrograph (B) of [Zr]-ZSM-5 (Si/Zr = 24)

structure. This band probably arises from (SiO₄) tetrahedra perturbed by the presence of adjacent zirconium ions. A similar band is observed in the case of [Ti]-ZSM-5, wherein it has been attributed⁶⁻⁷ to the presence of titanium in the lattice framework.

Table 3 Hydroxylation of benzene with hydrogen peroxide over [Zr]-ZSM-5 (Si/Zr = 100)

Catalyst	H ₂ O ₂ selectivity (wt%) to hydroxy benzenes	Product wt%			
		Phenol	Catechol	HQ	BQ
Zirconium silica	16	81.85	7.86	6.30	3.99
Silicalite-1	No reaction				
ZrO ₂	No reaction				
No catalyst	No reaction				

Reaction conditions: Temp. = 333 K; benzene to hydrogen peroxide, mole ratio = 8; reaction time = 4 h; catalyst wt = 3.5 g; HQ = hydroquinone; BQ = *para*-benzoquinone

Table 1 d' values of [Zr]-ZSM-5 (Si/Zr = 24) calcined first in N₂ and then in air

<i>hkl</i>	$d(\text{Å})$ XRD	I/I_0 (%)	$d(\text{Å})$ electron diffraction
101	11.182	100	11.181
200	10.045	84	
020	9.90	35	9.89
111	9.774	25	
002	6.701	14	6.69
102	6.365	19	
112	6.013	27	
131	5.712	16	
400	5.012	18	
410	4.89	14	4.87
131	4.604	12	
132	4.058	8	
501	3.854	100	3.852
051	3.824	60	
303	3.717	54	
133	3.648	27	
432	3.434	13	
104	3.306	18	
503	2.985	21	
044	2.78	10	2.78
0101	1.987	15	1.97
583	1.915	6	

The XRD pattern of this sample is given in Figure 2 (curve C) and its electron diffraction is given in Figure 3A.

Table 2 Unit cell parameters of [Zr]-ZSM-5 from XRD

Sample	Unit cell parameters (Å)			Unit cell volume V [(Å) ³]
	<i>a</i>	<i>b</i>	<i>c</i>	
I	20.03	19.927	13.43	5376
II	20.07	19.927	13.474	5388
III	20.08	10.96	13.48	5402
[Si]-ZSM-5	19.98	19.88	13.33	5294

Catalytic studies

[Zr]-ZSM-5 is found to be active in the hydroxylation of benzene to phenol and phenol to dihydroxy benzenes. Table 3 compares the catalytic activity of [Zr]-ZSM-5, silicalite-1, and pure ZrO₂ in the conversion of benzene to phenol, catechol, hydroquinone, and benzoquinone. Phenol is the major product of the hydroxylation reaction. Although the conversion of H₂O₂ was complete, the selectivity to hydroxy benzenes was only 16%. The hydroxylation of aromatic compounds with H₂O₂ using [Ti]-ZSM-5 is already known.^{6,8} Our results indicate that [Zr]-ZSM-5 also

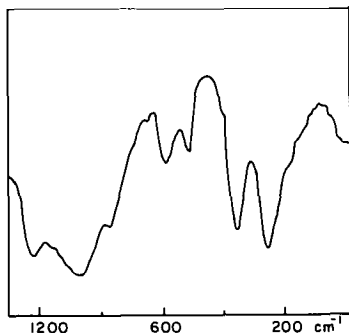


Figure 4 Framework i.r. spectrum of [Zr]-ZSM-5 (Si/Zr = 24)

possesses catalytic activity in this reaction. However, the activity and selectivity of the zirconium analog was lower than that of the titanium analogs. The nature of the active sites responsible for this reaction over [Zr]-ZSM-5 is, as in the case of titanium analogs, not established.

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