Synthesis and Characterization of a Novel Microporous Titanosilicate JLU-1

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A novel microporous titanosilicate JLU-1 (*J*i*L*in *U*niversity number-*1*) has been successfully synthesized in a $SiO_2-TiO_2-Na_2O-H_2O-(TMA)_2O$ system. It is found that the JLU-1 sample requires a relatively low alkalinity and appropriate titanium content. The products are indexed as triclinic, $a = 13.043(6)$ Å, $b = 12.538(3)$ Å, $c = 17.022(6)$ Å, $\alpha = 79.05°$, $\beta = 115.00°$, $\gamma = 84.81°$. The samples have been characterized by powder X-ray diffraction (XRD), ^{29}Si magic-angle spinning (MAS) NMR, scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HREM), infrared spectroscopy (IR), differential thermal−thermogravimetric analysis (DT-TGA), and adsorption measurements. Factors such as the initial TiO_2/SiO_2, Na_2O/SiO_2, and $TMABr/SiO_2$ molar ratios, crystallization temperature, and cations which dominate the hydrothermal synthesis of the product are discussed.

Introduction

The incorporation of titanium into molecular sieve frameworks has opened up an important research area. For example, TS-1 and TS-2 with the MFI and MEL structures, respectively, show remarkable catalytic properties in various reactions involving partial oxidation of organic compounds in the presence of dilute solutions of H_2O_2.[1−4] After the early studies on TS-1 and TS-2, other titanium silicates such as Ti-beta,[5,6] TS-48,[7] TS-NU-1,[8] Ti-MCM-41,[9] and Ti-HMS[10] were reported. In these materials, the Ti^{4+} has tetrahedral coordination. Later, two novel titanosilicates ETS-10 and ETS-4 were discovered.[11,12] ETS-10 is a crystalline, wide-pore microporous framework material containing tetrahedrally coordinated silicon and octahedrally coordinated titanium.[13,14] Another synthetic titanosilicate, ETS-4, has a framework structure similar to that of the mineral zorite.[15] It contains 12- and 8-membered ring channels and TiO_6 octahedral chains. Recently, some new microporous titanosilicates and synthetic analogues of minerals have been reported in the literature. Among these are pharmacosiderite,[16,17] GTS-1,[17] UND-1,[18] zorite,[17,19] umbite,[20] penkvilksite,[20,21] and nenadkevichite.[22]

In recent years, we have devoted effort toward hydrothermal synthesis in titanium−silicate systems to find novel titanosilicates.[19,23−25] We have prepared a novel titanosilicate JDF-L1 and two synthetic analogues of minerals zorite and penkvilksite-1M[19,23−25] JDF-L1 is a new layered titanosilicate which has potential application in catalysis, intercalation, and ion exchange. In its structure, Ti atoms are five-coordinate and each is linked to SiO_4 tetrahedra-forming continuous sheets. Titanosilicate AM-1, which possesses the same structure as JDF-L1, was first reported by Anderson et al.[14] In this paper, we report the synthesis of a novel microporous titanosilicate, named as JLU-1.

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Experimental Section

Synthesis of Titanium Silicate JLU-1. JLU-1 was synthesized hydrothermally using tetrabutyltitanate (TBOT, 98%, Beijing chemical reagent factory), fumed silica (99.9%, Shenyang chemical plant), tetramethylammomium hydroxide (TMAOH, 10%, Beijing chemical plant), tetramethylammomium bromide (TMABr, 99%, Shanghai chemical reagent factory), and sodium hydroxide (96%, Tianjin chemical reagent factory) as reagents. The chemical composition of the initial gel was $4.0SiO_2{:}xTiO_2{:}yNa_2O{:}130H_2O{:}0.32(TMA)_2O$, where $x = 0.68-1.2$ and $y = 0.16-0.35$. In a typical run, the procedure was as followed: 1.80 g of TBOT was slowly into sodium hydroxide solution (0.25 g of NaOH dissolved in 12 mL of H_2O) with stirring at room temperature, followed by 3 mL of TMAOH and 1.25 g of fumed silica. The mixture was stirred until it became homogeneous, then transferred into a Teflon-lined stainless steel autoclave, and heated at 473 K for ~8−10 days. The products were recovered by filtration, washed with water, and dried at 353 K.

Characterization. Powder X-ray diffraction (XRD) data were obtained using a Rigaku D/MAX-IIIA diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). ^{29}Si MAS NMR was recorded at 79.5 MHz on a Bruker MSL-400 spectrometer with a magnetic field strength of 9.7 T. A magic-angle spinning speed of 4 kHz was used for ^{29}Si. The acquisition parameters were 4 μs pulse width and 4 s recycle delay. The chemical shifts were relative to external standards of tetramethylsilane. A Hitachi X-650B scanning electron microscope was used for SEM experiments. High-resolution electron microscopy (HREM) images were obtained with a JEOL-3010 (300 kV, $C_s = 0.6$ mm) transmission electron microscope. The electron diffraction (ED) pattern was a Fourier transition pattern of the HREM. Thermogravimetry (TG) and differential thermal analysis (DTA) were performed on a Perkin-Elmer TGA 7 thermogravimetric analyzer and a DTA-1700 differential thermal analyzer, respectively, under a flow of atmosphere at a heating rate of 10 K min^{-1}. The IR spectra were recorded on a Nicolet Impact 410 FTIR spectrometer using KBr pellets. The UV−visible diffuse reflectance spectra were performed on a Perkin-Elmer UV/vis spectrometer. The JLU-1 products were calcined at 450 °C for 4 h to remove the TMAOH template before adsorption test. Nitrogen adsorption measurement was conducted on an ASAP 2010M porosimeter at 77 K. The surface areas were determined by the BET method. The pore volumes and the pore size distributions were obtained from single-point and Horvath−Kawazoe methods, respectively. Water and hexane adsorptions were measured isothermally on a Cahn-2000 electronic recording balance. The element analyses were performed on a Perkin-Elmer 2400 element analyzer and the inductively coupled plasma (ICP) analysis on a Perkin-Elmer Optima 3300 DV ICP instrument.

Catalytic Activity in Phenol Hydroxylation by H_2O_2. The phenol hydroxylation experiment was run in a 50-mL glass reactor and stirred with a magnetic stirrer. In a standard run, 1.6 g of phenol, 0.08 g of catalyst, and 20 mL of water were mixed, followed by addition of 0.67 mL of H_2O_2 (30% aqueous). The reaction temperature was 80 °C. After reaction for 4 h, the products were taken out and analyzed by a Shimadzu GC-9A gas chromatograph.

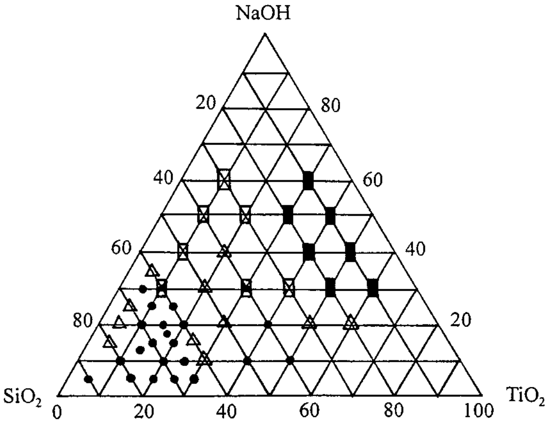

Figure 1. Crystallization field diagram of $SiO_2-NaOH-TiO_2$ system at 453 K (△, ●, □, and ■ correspond to penkvilksite-1M, JLU-1, zorite, and an unknown phase, respectively.)

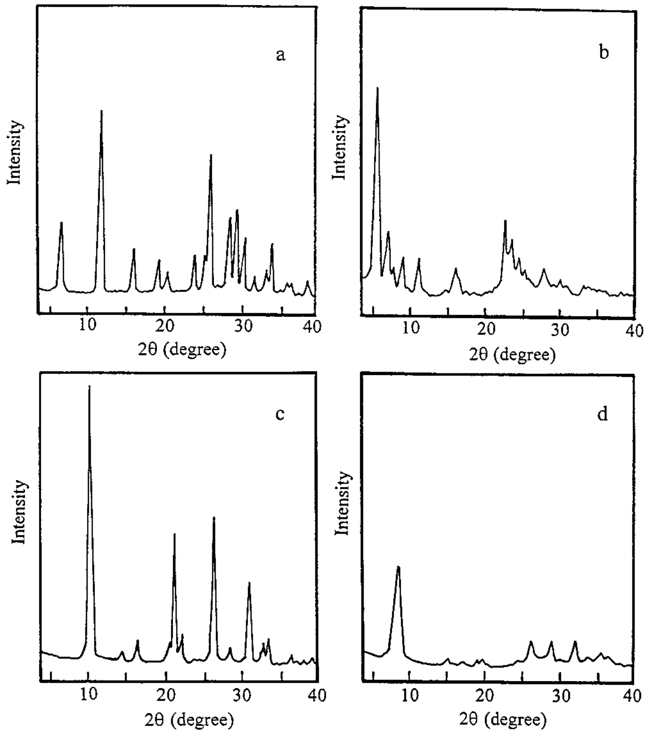

Figure 2. XRD patterns of zorite (a), JLU-1 (b), penkvilksite-1M (c), and unknown phase (d).

Results and Discussion

1. Synthesis of JLU-1. Figure 1 shows the diagram of $SiO_2-NaOH-TiO_2$ under conditions of crystallization temperature at 180 °C, crystallization time for 15 days, and H_2O and TMAOH at 40 and 0.5 mol, respectively. It is clearly shown that four phases are formed. They are zorite, penkvilksite-1M, JLU-1, and an unknown phase. Zorite and penkvilksite-1M phases have been reported in earlier works,[19,21,25] and the XRD patterns of these phases are shown in Figure 2. It can be observed from Figure 1 that the microporous titanosilicate JLU-1 is synthesized only in a very narrow region. The effects of various conditions on the synthesis are described below.

Table 1. Influence of TiO_2/SiO_2 Ratio on the Crystallization of JLU-1

TiO_2/SiO_2 in the gel	TiO_2/SiO_2 in the product	product
0.29^a	0.041	JLU-1
0.25^a	0.037	JLU-1
0.21^a	0.033	JLU-1
0.17^a		JDF-L1 + quartz
0.17^b	0.025	JLU-1
$0.12^{a,b}$		JDF-L1 + zorite
$0.07^{a,b}$		JDF-L1 + quartz
$0.04^{a,b}$		JDF-L1 + quartz

[a] $4.0SiO_2:0.65Na_2O:130H_2O:0.3TMAOH$; $T = 473$ K; $t = 12$ days. [b] $5.8SiO_2:0.65Na_2O:130H_2O:0.3TMAOH$; $T = 473$K; $t = 11$ days.

Table 2. Influence of the Na_2O/SiO_2 Ratio on the Crystallization of JLU-1[a]

Na_2O/SiO_2	t (d)	product
0.08	12	JLU-1
0.16	10	JLU-1
0.24	8	JLU-1 + zorite
0.33	8	JLU-1 + zorite
0.49	8	zorite

[a] $4.0SiO_2:1.0TiO_2:130H_2O:0.3TMAOH$; $T = 473$ K.

Table 3. Powder XRD Pattern of the As-Synthesized JLU-1

h	k	l	d_{obs}(Å)	d_{calc}(Å)	I/I_o	h	k	l	d_{obs}(Å)	d_{calc}(Å)	I/I_o
0	0	1	14.9277	14.9272	100	3	1	2	3.0320	3.0286	7
0	1	0	12.0818	12.0818	18	3	3	1	2.9441	2.9418	11
1	0	0	11.6062	11.6016	27	4	0	0	2.8993	2.9004	3
0	1	1	10.8239	10.8239	8	−3	3	3	2.8685	2.8681	4
1	1	0	9.3071	9.3081	14	−2	4	3	2.7030	2.7036	5
1	0	1	7.6389	7.6442	15	4	0	1	2.6335	2.6340	5
			6.9564		4	−4	2	5	2.5936	2.5955	4
2	0	0	5.8034	5.8008	5	−4	0	6	2.5353	2.5337	5
−1	−2	1	5.4024	5.4024	16	−1	−1	6	2.5065	2.5095	3
1	0	2	5.2871	5.2871	13	−5	0	1	2.4705	2.4674	2
−3	0	2	4.3174	4.3174	3	−4	3	5	2.3579	2.3594	3
0	3	0	4.0271	4.0271	7	−1	5	4	2.3102	2.3102	2
−3	1	3	3.8579	3.8589	39	−1	5	0	2.2820	2.2790	3
−2	−1	4	3.7118	3.7123	28	−3	3	7	2.2091	2.2080	2
0	3	3	3.6080	3.6080	21	−6	0	3	2.1595	2.1600	3
−3	1	0	3.4937	3.4937	11	1	6	2	2.0754	2.0746	3
2	−1	2	3.4018	3.4023	4	−6	0	6	2.0328	2.0327	2
−1	1	5	3.3465	3.3477	3	1	0	7	1.9468	1.9472	2
3	2	1	3.2931	3.2913	2	0	6	5	1.9075	1.9079	2
−2	−2	4	3.1780	3.1804	17	6	2	1	1.8506	1.8504	4
−3	1	5	3.1256	3.1282	9	1	−6	1	1.8345	1.8349	2

Effect of the TiO_2/SiO_2 Ratio. The effect of TiO_2/SiO_2 on the synthesis of JLU-1 products is shown in Table 1. We find that the TiO_2/SiO_2 ratio is an important factor for the synthesis. When the TiO_2/SiO_2 ratio is in the range 0.17−0.29, the pure JLU-1 product can be formed. Lower titanium content ($TiO_2/SiO_2 < 0.17$) in the gel usually results in the formation of JDF-L1 and quartz phases. At higher titanium content in the reaction mixture, the rate of crystallization decreases, leading to the formation of amorphous or quartz phases.

Effect of the Na_2O/SiO_2 Ratio. The Na_2O/SiO_2 ratio in the original reaction mixture also plays an important role in the formation of JLU-1. Table 2 shows the influence of the Na_2O/SiO_2 molar ratio on the crystallization of JLU-1. As shown in Table 2, we can obtain pure JLU-1 samples at lower Na_2O/SiO_2 ratio. The suitable Na_2O/SiO_2 molar ratios for JLU-1 are in the range from 0.08 to 0.16. As the concentration of sodium hydroxide increases, the crystallinity of JLU-1 becomes poor, and an impurity phase of zorite is crystallized with the JLU-1. On increasing the Na_2O/SiO_2 ratio to greater than 0.5, the gel forms a pure zorite. Thus, low-sodium hydroxide concentration favors the formation of JLU-1, and high-sodium hydroxide concentration forms the JDF-L1 and zorite phases.

Effect of the H_2O/SiO_2 Ratio. The H_2O/SiO_2 ratio in the JLU-1 synthesis was also studied. It is found that the water content has little influence on the JLU-1 phase, but strongly influences the rate of crystallization. When the water content is low ($H_2O/SiO_2 = 20$), the crystallization time is 8 days. When the H_2O/SiO_2 ratio is increased from 20 to 65, the crystallization time increases from 8 to 12 days. On increasing the H_2O/SiO_2 ratio to 80, the crystallization period increases to 15 days. When the H_2O/SiO_2 ratio is higher than 100, no crystallization occurs within 18 days.

Effect of the Template Concentration. To investigate the effect of template content, mixtures of NaOH and TMABr were used to keep the alkalinity unchanged, with a Na_2O/SiO_2 molar ratio of 0.03. When the TMABr/SiO_2 ratio was lower than 0.65, the crystallized products often contained zorite impurity. On increasing TMABr/SiO_2 ratio from 0.65 to 0.95, the pure JLU-1 product was obtained. The appropriate TMABr/SiO_2 ratio is at the range of 0.95−1.25.

Effect of Crystallization Temperature. The JLU-1 product was crystallized in the temperature range 170−210 °C. High-temperature accelerates the crystallization; however, at higher temperature (>240 °C), the JLU-1 product was not obtained.

Effect of the Alkali Metal Cations. It is interesting to observe the effect of cations on JLU-1 synthesis. In a $SiO_2-TiO_2-H_2O-$TMAOH system, JLU-1 was not crystallized. Thus, sodium hydroxide is an important mineralizer in the formation of JLU-1. When other inorganic salts containing Na^+ are added into the reaction system, such as NaCl, NaF, Na_2CO_3, or Na_2SO_4 (The $Na^+/SiO_2 = 0.75$), the crystallized product contains the zorite phase. In addition, when K^+ is added into the gel in the form of KCl, KF, or K_2CO_3, ETS-10 is readily obtained.

2. Characterization. *XRD Analysis.* The X-ray diffraction pattern of the as-synthesized JLU-1 was performed on a Rigaku, D/max-rA, 12 kW diffractometer with a rotating target and Ni-filtered Cu Kα radiation at room temperature. The index of powder patterns was carried out with the program TEROR 90.[26] The indexed unit-cell parameters for JLU-1 are $a = 13.043(6)$ Å, $b = 12.538(3)$ Å, $c = 17.022(6)$ Å, $\alpha = 79.05°$, $\beta = 115.00°$, $\gamma = 84.81°$; triclinic system (Table 3). These results clearly show that the JLU-1 is a pure and novel titanosilicate phase.

SEM and HREM. Scanning electron microscopy of JLU-1 (Figure 3) show that the crystals appear as spherical particles with diameters of ~1.5 μm. The spherical aggregates are made up of a variety of thin stacked crystals in rosette form.

HREM and ED pattern of JLU-1 is shown in Figure 4. The HREM suggests that the white dots are the channels. It is of interest to note that channel pores are clearly observed, and the distance of channel to channel

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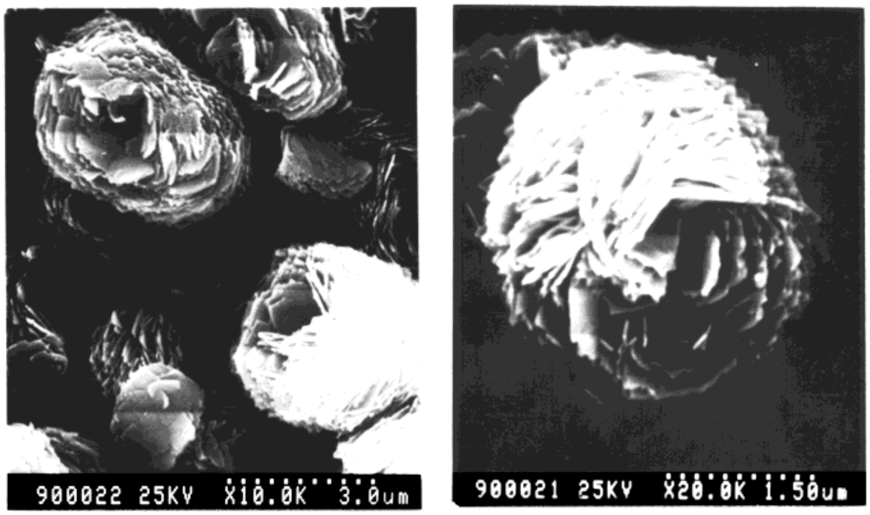

Figure 3. Scanning electron micrograph of JLU-1.

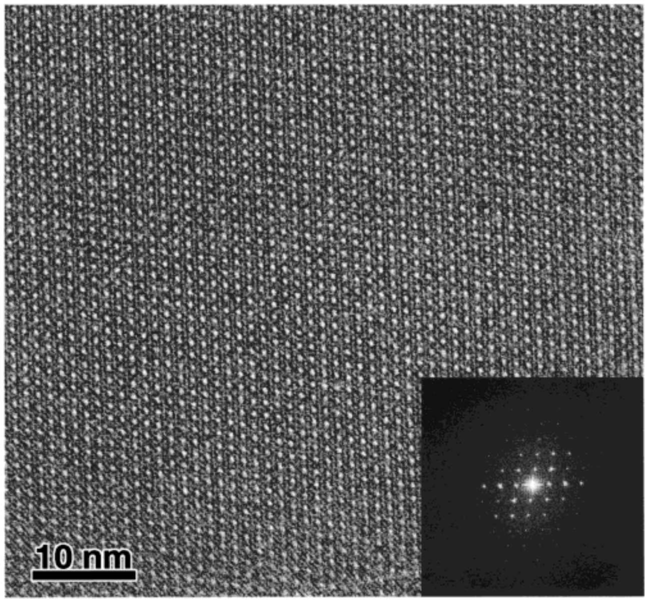

Figure 4. High-resolution electron micrography of JLU-1 with an electron diffraction pattern inset (at bottom right).

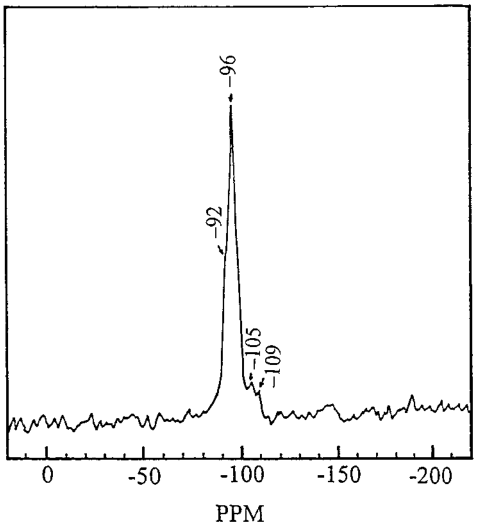

Figure 5. ^{29}Si MAS NMR spectra of JLU-1.

is ~6 Å, which is in good agreement with the pore size of 6.2 Å, determined by N_2 adsorption.

NMR Results. The ^{29}Si MAS NMR spectra of JLU-1 is shown in Figure 5. The product gives one sharp band at $\delta = -96$ ppm and a shoulder at $\delta = -92$ ppm, and two weak bands at approximately $\delta = -105$ ppm and $\delta = -109$ ppm, respectively. Table 4 presents the ^{29}Si MAS NMR spectra data of reported titanosilicates.[13−15,19,20,25,27−29] Balmer et al. studied the correlation between crystal structure information and experimental ^{29}Si NMR data and showed that a systematic downfield chemical shift occurs with an increasing number of titanium polyhedra coordinating a given silicon tetrahedron.[27] The ^{29}Si NMR spectra of TS-1 exhibits a intense peak at −112 ppm and a broad peak at −116 ppm. Thangaraj et al. ascribed the peak at −116 ppm to Si in distorted tetrahedra containing Si−O−Ti bonds.[28, 29]

The ^{29}Si MAS NMR resonances of six-coordinated titanium silicates are typically in the range from −90 to −110 ppm, those of five-coordinated AM-1 (JDF-L1) displays a single peak at −107.4 ppm,[20] and those of four-coordinated TS-1 are in the range from −110 to −116 ppm.[28,29] The ^{29}Si resonances for JLU-1 are in the range from −92 to −110 ppm. Therefore, we suggest that the Ti^{4+} atoms in JLU-1 are reasonably assigned to six-coordination.

It is suggested that the peaks at −92 ppm be assigned to the Si(3Si,1Ti), and the peaks at −96, −105, and −109 ppm be assigned to Si(4Si,0Ti) species, respectively.

UV−Visible Diffuse Reflectance Spectra. The diffuse reflectance spectrum in the UV−vis region of synthesized JLU-1 is given in Figure 6. The synthesized JLU-1 sample gives one strong peak at ~240 nm, which may be isolated six-coordinate Ti^{4+} atoms.[6] A shoulder at ~270 nm is also observed in the spectrum, which is assigned to six-coordinate Ti species in JLU-1. The absence of a band at ~330 nm suggests that anatase is not present in the JLU-1 samples.

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Table 4. ^{29}Si MAS NMR Spectra Data of Some Titanosilicates

titanosilicate	silicon chemical environment (ppm) Si(2Si,2Ti)	Si(3Si,1Ti)	Si(4Si,0Ti)	coordination of titanium	ref(s)
ETS-10		−94.1, −95.8, −96.5	−103.3	6	13, 14
ETS-4	−90	−95		6	15
zorite	−90.7	−95.8		6	19
penkvilksite-2O	−95.7	−100		6	20
penkvilksite-1M	−95.7	−101.1		6	25
benitoite	−94.3			6	27
AM-1(JDF-L1)	−107.4			5	20
TS-1		−116	−112	4	28, 29
JLU-1		−92	−96, −105, −109	6	this work

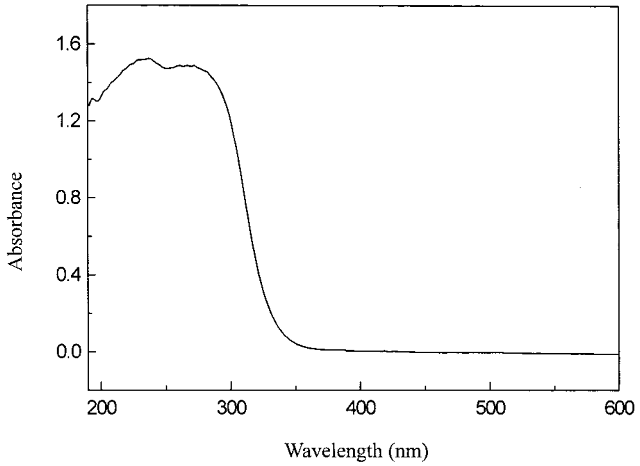

Figure 6. UV-vis diffuse reflectance spectra of JLU-1.

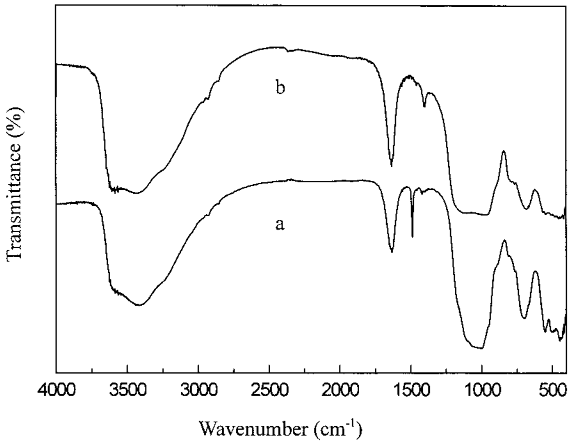

Figure 7. Infrared spectra of JLU-1: (a) as-synthesized and (b) calcined.

Infrared Spectroscopy. Figure 7 shows the IR spectrum of the JLU-1 in the region 4000−400 cm^{-1}. The absorption bands appear at 3430, 1637, 1489, 1040, 1011, 950, 798, 695, 554, 496, and 448 cm^{-1}. Mihailova et al. studied the Raman and IR absorption spectra of ETS-4 and ETS-10, and identified the peaks in the spectra through model calculations of the internal modes of vibration for representative clusters.[30] According to their results and the framework vibration models of Flanigen et al.,[31] the IR absorption spectrum of JLU-1 can be assigned as follows: 1040 and 1011 cm^{-1} bands are attributed to Si−O bond stretching; 950, 798, and 695 cm^{-1} bands are attributable to the Ti−O bond stretching; and 554, 496, and 448 cm^{-1} bands may be due to the vibrations of the Ti−O and Si−O bending modes. The bands due to OH stretching and bending of the water molecules are seen as broad peaks at around 3430 and 1637 cm^{-1}, respectively.

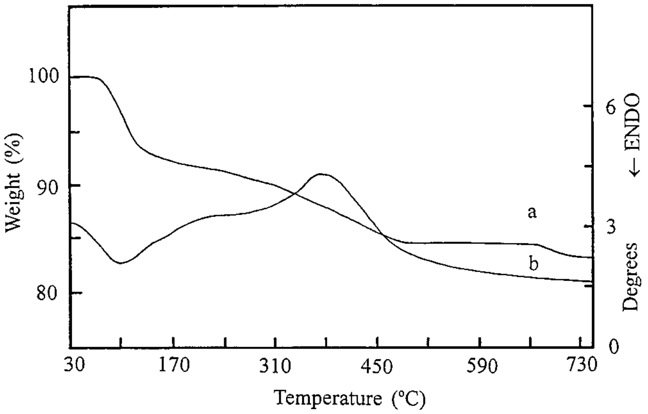

Figure 8. TG (a) and DTA (b) curves for JLU-1.

Thermal Properties. The representative thermoanalytical curves of JLU-1 are illustrated in Figure 8. The DTA curve has one endothermic and one exothermic effect in the ranges 300−423 K and 550−773 K, respectively. The TG curve can be divided into two corresponding stages ranging from 333 to 443 K and from 443 to 723 K. The former is associated with the removal of water located on the external surface and in the pores, and the latter is due to the oxidative decomposition of occluded TMAOH template during the synthesis of JLU-1. The total mass loss is ~16%. In addition, there is a small weight loss between 933 and 973 K, which may be due to the loss of terminal Si−OH group. The ICP analysis gives rise to a SiO_2/TiO_2 ratio of 30 and SiO_2/Na_2O ratio of 3.4. The elemental analysis shows that the C, H, and N contents are 3.64, 1.96, and 1.08 wt % respectively, corresponding to an empirical molar ratio of C:H:N = 4.0:25.5:1.0. These analysis results also indicate that the organic amine TMA^+ and Na^+ cations exist in the channel for charge balance of the anionic framework of JLU-1.

The thermal stability of the products treated at different temperatures shows that below 773 K the structure of JLU-1 remains unchanged. However, it collapses at 873 K and converts into a dense phase at 973 K.

Isothermal Adsorption of Nitrogen. The isothermal adsorption result shows that the microporous volume of JLU-1 is 0.14 cm^3 g^{-1}, and the BET surface area is 363 m^2 g^{-1}. The pore diameter calculated by using the Horvath−Kawazoe method is 6.2 Å, suggesting that JLU-1 is a medium-pore material.

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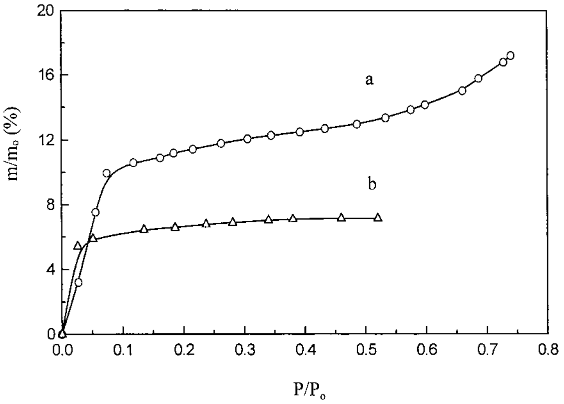

Figure 9. Water (a) and hexane (b) adsorption isotherms for JLU-1 at 293 K.

Isotherms of Water and Hexane. The water and hexane adsorption isotherms at 293 K for JLU-1 are shown in Figure 9. Prior to the measurement the sample was dehydrated at 473 K at 10^{-3} Torr for 2 h, and then cooled to room temperature under vacuum. Results show that both hexane and water adsorption follow Langmuir-type adsorption. The adsorption capacity of water and hexane are 11 and 7 wt % at $P/P_0 = 0.2$, respectively. These results also suggest that JLU-1 is microporous.

3. Catalytic Phenol Hydroxylation. A JLU-1 sample calcined at 450 °C exhibits very low catalytic activity in phenol hydroxylation, with the conversion of 0.61%. In contrast, the TS-1 sample with four-coordinated titanium shows the conversion at 26.4% at the same conditions.[32] These results suggest that the Ti^{4+} species in this sample is six-coordinated, in good agreement with the NMR and UV–vis results.

Conclusions

In summary, a novel microporous titanosilicate JLU-1 has been synthesized hydrothermally from the system $SiO_2-TiO_2-Na_2O-H_2O-(TMA)_2O$, and its crystallization conditions are discussed. The TiO_2/SiO_2 and Na_2O/SiO_2 ratios play important roles in the formation of JLU-1. HREM, XRD, N_2, H_2O, and hexane adsorption studies indicate that JLU-1 is a novel median porous titanosilicate. The investigation of thermal properties shows that JLU-1 is thermally stable up to 500 °C.

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