Short communication

Synthesis of MTW-type microporous material and its vanadium-silicate analogue using a new diquaternary ammonium cation as a template

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Abstract

A new organic template, 1,6-hexamethylene-bis(benzyldimethylammonium hydroxide), efficiently produced zeolite ZSM-12 and Al-free pure silica polymorph. The vanadium-silicate analogue, [V]-MTW, was also synthesized. These vanadium-silicate samples catalyze the oxidation of phenol, *n*-alkanes, cyclohexane, ethylbenzene, etc. using dilute H_2O_2 (30 wt.-%, aqueous)

Keywords: Hexamethylene-bis(benzyldimethylammonium hydroxide); Zeolite ZSM-12; Vanadium-silicates, [V]-MTW; Synthesis; Oxidation catalysis

1. Introduction

High-silica zeolites are of special interest in selective adsorption and catalysis. ZSM-12 (MTW topology) is a high-silica large-pore zeolite consisting of unidimentional channels with 12-membered ring pore openings [1]. MTW-type zeolites have been synthesized using various quaternary ammonium salts [2]. Here, we report a new method for the synthesis of MTW-type zeolites (alumino-silicate, pure silica polymorph and vanadium-silicate) using 1,6-hexamethylene-bis(benzyldimethylammonium hydroxide) as an organic template, which is used for the first time in zeolite synthesis.
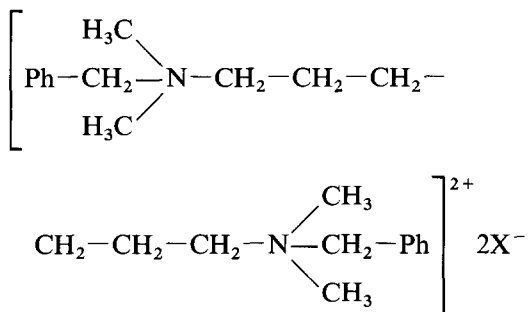
2. Experimental

The organic template was prepared by reacting 1,6-dibromohexane with benzyldimethylamine in 1:2.2 molar ratio using acetone as solvent. The mixture was refluxed for 6 h, and the white solid diquaternary salt was recovered and purified under vacuum. The material so obtained was characterized by mass spectrometry and ^1H and ^{13}C nuclear magnetic resonance (NMR). The bromide salt was converted into the corresponding hydroxide solution (15 wt.-%, aqueous) electrochemically using a two-compartment cell separated with an anion-exchange membrane. The electrochemical reaction was carried out at 298 K by taking a 30 wt.-% aqueous solution of the bromide salt as catholite and a 10 wt.-% aqueous solution of ammonium hydroxide as anolite and by passing a

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direct current (DC) till the complete conversion of bromide to hydroxide. The structural formula of the organic template is given below:

$$\left[\begin{array}{l} H_3C \\ Ph-CH_2-N-CH_2-CH_2-CH_2- \\ H_3C \end{array} \right.$$

$$\left. CH_2-CH_2-CH_2-N-CH_2-Ph \begin{array}{c} CH_3 \\ \\ CH_3 \end{array} \right]^{2+} 2X^-$$

(X = Br or OH; Ph = phenyl)

In a typical hydrothermal synthesis, 6 g of highly reactive fumed silica (Sigma S 5130) were slurried in 25.8 g of a 15 wt.-% aqueous solution of 1,6-hexamethylene-bis(benzyldimethylammonium hydroxide) under stirring (1 h) before adding to it a solution of 0.39 g of $Al_2(SO_4)_3 \cdot 16H_2O$ in 10 g of water for alumino-silicate (sample E) or the required amount of $V(O)SO_4 \cdot 3H_2O$ (for samples A–C) in 10 g of water for vanadium-silicates. For the silica analogue (sample F) no heterometal was added. Finally, an alkaline solution containing 0.4 g of NaOH in 10 g of water was added. The resultant mixture was stirred for about 1 h after adding to it the remaining 14 g of water. The crystallization was carried out in a stainless-steel autoclave at 433 ± 1 K under static conditions. After crystallization, the solid product was separated, thoroughly washed with hot deionized water, dried at 393 ± 2 K and calcined in flowing air at 843 K (heating rate $2°$ min^{-1}) for 16 h.

The as-synthesized and calcined samples were characterized through well known techniques, viz. X-ray diffraction (XRD), scanning electron microscopy, infrared, ultraviolet–visible (UV–VIS) and electron spin resonance (ESR). Liquid phase catalytic test reactions were carried out in a stirred batch reactor in the case of phenol and in a Parr reactor in the cases of n-hexane, cyclohexane and ethylbenzene. The products were analyzed through a capillary gas chromatograph (HP, 5880) using a flame ionization detector.

3. Results and discussion

The XRD pattern of the samples synthesized using the new diquaternary template was typical of the MTW [1] topology (Fig. 1a). The vanadium-silicate analogues ([V]-MTW) also exhibited the characteristic XRD pattern (Fig. 1b). Although the uptake of Al from the gel to the product was quantitative, the utilization of V was far from complete (nearly 40–50% of the input) in the case of [V]-MTW samples (Table 1). Almost similar results were obtained in the case of different vanadium-silicate molecular sieves [3–8] including recently reported VS-12, a vanadium-silicate analogue of ZSM-12 zeolite [7]. The scanning electron micrographs of [V]-MTW (sample A) exhibited a typical MTW morphology [9], composed of needle-shaped crystals (Fig. 2).

Table 1
Physico-chemical properties of ZSM-12 and [V]-MTW

Sample	Crystallization time (days)	Si/M gel[a]	Si/M product[a]	Unit cell volume (Å)	BET surface area (m^2 g^{-1})
(A) [V]-MTW	8	75	178	1455	267
(B) [V]-MTW	7	100	250	1451	259
(C) [V]-MTW	6	160	357	1444	260
(D) [V]-MTW[b]	–	–	–	1427	244
(E) Al-ZSM-12	6	80	98	1452	256
(F) Si-ZSM-12	4	–	–	1423	240

[a] M = V (for samples A–D) and Al (for sample E). Sample F is Al- or V-free pure silica analogue.
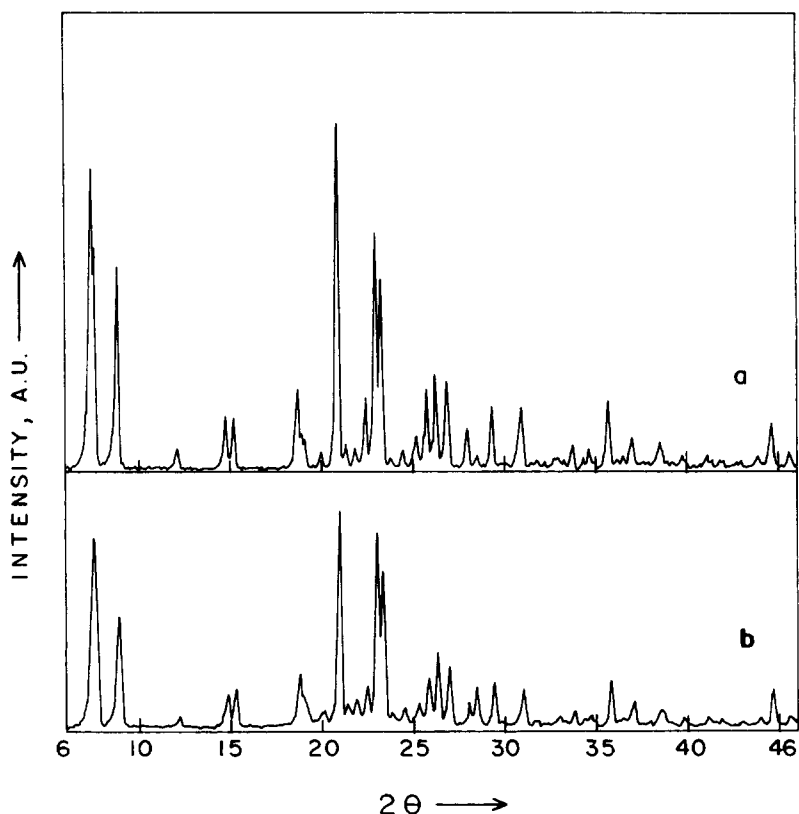[b] Sample A after steaming at 773 K for 4 h.

Fig. 1. X-Ray diffraction (powder) pattern of (a) ZSM-12 (sample E) and (b) [V]-MTW (sample A).

Fig. 2. Scanning electron micrograph of [V]-MTW (sample A).

Fig. 3 depicts the ESR spectrum of as-synthesized [V]-MTW (sample A) exhibiting eight equally spaced hyperfine splittings, indicating the presence of paramagnetic, atomically dispersed and immobile V^{4+} ions [8]. The g and A parameters calculated from the ESR spectra were $g_{\parallel} = 1.924$, $g_{\perp} = 1.960$, $A_{\parallel} = 195$ G and $A_{\perp} = 69$ G, indicating that the V^{4+} ions are most probably incorporated in the framework. On calcination in air, the ESR signals disappear, indicating the oxidation of V^{4+} to V^{5+} species. The reduction of the calcined sample in hydrogen restored the original spectrum with eight equally spaced hyperfine splittings, indicating that the $V^{4+} \rightleftharpoons V^{5+}$ transition is reversible. When calcined [V]-MTW samples were treated with 1 N ammonium acetate solution for 24 h at 298 K, almost no vanadium was detected (by atomic absorption spectrometry) in the filtrate obtained after the treatment, further suggesting that the unexchangeable vanadium species are strongly bound to the zeolite lattice.

The [V]-MTW samples exhibited the characteristic charge-transfer band at about 205 nm in addition to a very weak absorption at around 320 nm
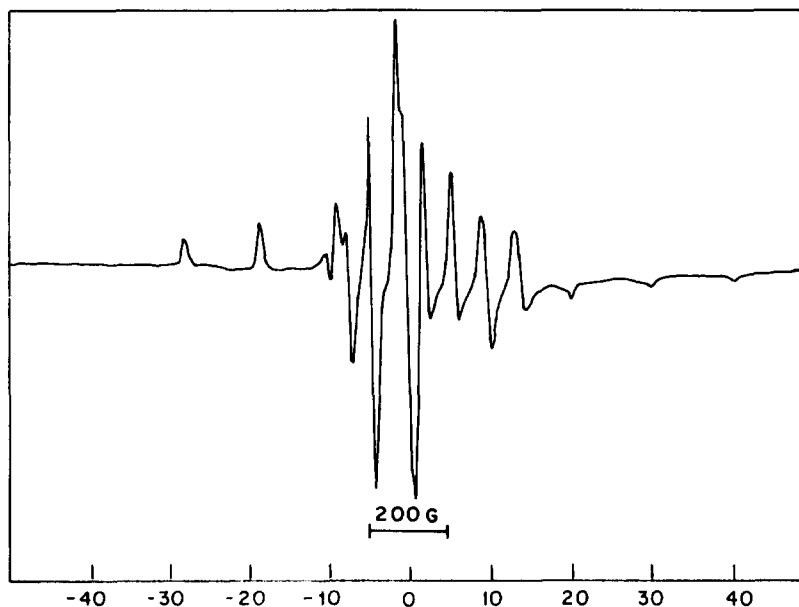
Fig. 3. ESR spectrum of the as-synthesized sample [V]-MTW (sample A) at 298 K.

(Fig. 4) suggesting that most of the vanadium ions are incorporated in the silicate network. Similar UV-VIS spectra have been reported for various microporous vanadiumsilicates [3-8].

The catalytic activity and selectivity of H-ZSM-12 (Si/Al=74) in m-xylene isomerization was found to be comparable with the activity exhibited by H-ZSM-12 synthesized through known literature procedures [9,10]. The product
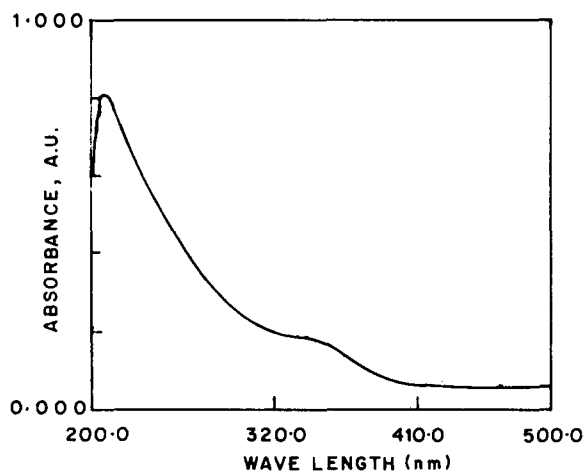

Fig. 4. UV-VIS spectrum of [V]-MTW (sample A).

selectivity [p/o-xylene ratio=1.1; log (isomerization/disproportionation ratio)=1.45; 1,3,5/1,2,4-trimethylbenzene ratio=0.05 at about 5% m-xylene conversion] exhibited by the ZSM-12 sample was characteristic of 12-membered ring zeolites [10,11].

In Table 2, the results of oxidation of various organic compounds like phenol, n-hexane, cyclohexane and ethylbenzene over [V]-MTW (Si/V= 178) are reported. [V]-MTW samples were quite active in various oxidation–oxyfunctionalization reactions (Table 2). Under similar conditions neither V_2O_5-impregnated Si-ZSM-12 nor pure Si-ZSM-12 exhibited any catalytic activity in these oxidation reactions, in accordance with earlier reports [12].

In phenol hydroxylation, the catechol/hydroquinone ratio was about 60:40, the phenol conversion being 19% (theoretical maximum ~33% at a phenol/H_2O_2 molar ratio of 3). In order to check whether any vanadium is leached out during the reaction, the following control experiment was carried out. The catalyst was filtered off, the products were analyzed by gas chromatography, then an additional amount of H_2O_2 [1:1 (mol/mol) with respect to remaining phenol] was added to

Table 2
Oxidation reactions over [V]-MTW (sample A)[a]

Substrate	Conversion (%)	H_2O_2 sel.[b] (%)	Products[c] (%)					
			2-OH	4-OH	-al	-ol	-one	others
n-Hexane	14.5	81.8	–	–	3.7	11.8	84.2	0.3
Cyclohexane	14.9	73.0	–	–	–	20.8	76.7	2.5
Phenol	19.4	59.0	58.9	39.5	–	–	–	1.6
Ethylbenzene	12.0	56.6	2.9	9.1	15.5	30.9	41.6	–

[a] $Si/V = 178$; reaction conditions: substrate (5 g)–$H_2O_2 = 3:1$ mol; solvent (25 g), acetonitrile and water (for phenol); catalyst, 1.0 g; temperature, 353 K; reaction time, 12 h; stirred parr or batch (for phenol) reactor.
[b] Utilization of H_2O_2 for hydroxy/oxy products, referred below (see footnote c).
[c] 2-OH = catechol or 2-hydroxyethylbenzene and 4-OH = hydroquinone or 4-hydroxyethylbenzene; -al; = aldehyde; -ol = alcohol; -one = ketone; others = some unidentified higher boiling compounds.

the reaction mixture (filtrate) and the reaction was further carried out under the same conditions for 12 h, exhibiting about a 1% increase in phenol conversion (20% compared to 19%). Further, the used catalyst was calcined and reused in the same way giving a comparable phenol conversion (19.5% vis-a-vis 19% in the first cycle) suggesting that the catalytic activity of the [V]-MTW (sample A) is retained after use.

Like other vanadium-silicate molecular sieves [12,13], [V]-MTW samples were found to be active in n-hexane oxidation, oxyfunctionalizing primary carbon atoms in addition to secondary carbon atoms in 2- and 3-positions. The regioselectivity with respect to the carbon position in n-hexane was: 1- (6.1%)≪2- (42.7%)<3- (51.2%). In medium-pore vanadium-silicate zeolites, e.g. VS-2, the regio-isomer distribution in n-hexane oxidation has been observed as: 1- (13.0)<2- (45.0)>3- (42.0) [12]. In medium-pore VS-1/VS-2 zeolites the diffusion of hex-3-ol/one (vis-a-vis hex-2-ol/one) may be hindered. Such diffusional constraints are not expected in the large-pore [V]-MTW resulting in higher selectivity for hex-3-ol/one. However, the secondary reaction (i.e. the formation of ketone from secondary alcohol and aldehyde from primary alcohol) was predominant over the primary reaction (i.e. the formation of alcohols). Similar observations have also been reported for other vanadium-silicate microporous materials [12].

In cyclohexane oxidation over [V]-MTW, the cyclohexanone to cyclohexanol molar ratio was 3.2.

Both ring hydroxylation and side-chain oxyfunctionalization were observed when ethylbenzene was reacted over [V]-MTW (Table 2). Among hydroxyethylbenzenes, only p- and o-monohydroxy derivatives were obtained with a p/o ratio of 3.1. Among side-chain oxidation products, secondary carbon moiety (61.1% selectivity) was favored over primary carbon (26.6% selectivity), as expected. However, the selectivity towards secondary products, namely acetophenone and phenylacetaldehyde, was significantly higher than that for primary products, i.e. alcohols (Table 2).

In conclusion, we have synthesized the MTW-type alumino-silicate, pure-silica polymorph and vanadium-silicate analogues using a new organic template (1,6-hexamethylene-bis(benzyldimethyl-ammonium bromide/hydroxide)). The isolated V^{4+}/V^{5+} ions are firmly incorporated in the silicate network. [V]-MTW is quite active in the oxidation of a variety of substrates including the bulkier ethylbenzene.

Acknowledgements

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