

Novel synthesis of a vanadium–titanium aluminophosphate molecular sieve of MFI structure (VTAPO-5) and catalytic activity for the partial oxidation of methanol

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A new vanadium–titanium substituted aluminophosphate molecular sieve of MFI structure (VTAPO-5) was synthesized hydrothermally and found to be active and selective in partial oxidation of methanol; catalytic activity depends on the vanadium sites; however, the presence of titanium influences the reactivity of vanadium species during reaction.

Aluminophosphate (AIPO) molecular sieves classified as a new class of microporous crystalline inorganic solids are contemporary to the zeolites. A variety of AIPOs have been reported with a rich diversity of structures.^{1,2} They are framework oxides with Al and P in tetrahedral coordination with oxygen. In spite of different structural properties from zeolites, AIPOs also apparently obey Loewenstein's rule with an avoidance of Al–O–Al bonds and thus include framework topologies analogous to zeolites. Although titanium and vanadium substitution is well documented in various topologies,^{3–7} very little information on isomorphously substituted Ti and V AIPOs have been reported. Excluding the original patent on synthesis of some titanium containing AIPOs, only the synthesis and characterization of TAPSO-5,⁸ and more recently TAPO-5, –11, –31 and –36 have been published.^{9–11} Many important issues encountered in the synthesis and application of substituted AIPOs are still unaddressed. Very few reports are available in the literature regarding the catalytic behavior of substituted AIPOs such as TAPOs and VAPOs.

Ulagappan and Krishnasamy⁸ found that TAPO-5 and -11 were active in phenol hydroxylation. Also some activity was reported for VAPO-5 and Ti-VPI-5 in the catalytic oxidation of cyclohexane to cyclohexanol using *tert*-butyl hydroperoxide (TBHP). Recently, it has shown that TAPOs of structure types AFI, AEL, ATO and ATS (TAPO-5, -11, -31 and -36 respectively) have comparable activities to titanium silicates (TS-1) in a series of oxidation reactions using dilute H₂O₂ (30 wt%) as the oxidant.^{10,11} Vanadium–titanium catalysts, (either supported or impregnated) are widely used in industry for the partial oxidation of hydrocarbons and for the selective catalytic reduction of NO with NH₃. In the literature there are some interesting reports¹² concerning the structural characteristics of coprecipitated VTiO systems and their activity in *n*-butene oxidation for the selective production of acetaldehyde and acetic acid. In a very recent report¹³ the nature of vanadium sites in a V/ α -Ti phosphate catalyst for the oxidative dehydrogenation of ethane were investigated. Here, we report for the first time, the novel synthesis of vanadium–titanium aluminophosphate-5 (VTAPO-5), which is found to be an active and selective catalyst for the partial oxidation of methanol.

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VTAPO-5 was synthesized using a gel composition 0.30 NPr₃:0.70 TPAOH:0.02 TiO₂:0.047 V₂O₅:P₂O₅:42 H₂O. In a typical synthesis, the calculated amounts of phosphoric acid (85 wt%) and pseudoboehmite, as P and Al sources respectively, were mixed and dissolved in distilled water. Then vanadium and titanium as hydrated oxovanadium(IV) sulfate and titanium isopropoxide, respectively, were introduced dropwise to the homogenous gel under vigorous stirring. A mixture of tripropylamine (NPr₃) and TPAOH (an organic template as structure directing agent), was used to direct the MFI structure type in the VTAPO-5 molecular sieve and was slowly introduced into the gel. Finally the entire gel was further stirred for at least 1 h and transferred into a Teflon-coated stainless-steel autoclave for hydrothermal crystallization. Based on a series of systematic syntheses, pure and highly crystalline VTAPO-5 was synthesized aging the gel directly at 458 K for 200 h. After heating, the autoclave was cooled and solid product was separated by centrifugation and repeatedly washed with distilled water followed by drying at 358 K for 6 h followed by calcination in air at 813 K for 8 h. It was interesting that the systems involving only NPr₃ or TPAOH gave no VTAPO molecular sieve while pure VTAPO was obtained from the gel with a mixture of NPr₃ and TPAOH. Substituted TAPO-5 and VAPO-5 were also synthesized by essentially following a reported procedure,^{10,14} using the gel composition TPAOH : 0.04 TiO₂:P₂O₅:40 H₂O:NPr₃:0.047 V₂O₅:P₂O₅:40 H₂O respectively.

The samples were characterized by X-ray diffraction (XRD), diffuse reflectance UV-VIS spectroscopy (DRS), Raman spectroscopy and ²⁷Al and ³¹P MAS NMR. Pore volumes were measured by *n*-butane adsorption and N₂ adsorption methods (BET). Bulk chemical analysis was carried out using inductively coupled plasma atomic emission spectroscopy (ICP). Chemical and physical properties of all samples are given in Table 1.

The XRD patterns of TAPO-5 and VAPO-5 were similar to those reported earlier and confirm the purity of the crystallized product with the XRD pattern of VTAPO-5 being closer to that of pure TAPO-5. Intercalation of vanadium moieties in the framework can be discounted since no change in the basal spacing is observed. Pore plugging as well as evidence for an extraneous phase were checked by *n*-butane and nitrogen adsorption. The measured BET surface area for VTAPO-5 was 304 m² g⁻¹ and the void volume was 0.121 ml g⁻¹. The amount

Table 1 Physico-chemical properties of substituted AIPOs.

Material	Chemical analysis				N ₂ adsorption		<i>n</i> -Butane adsorption V _p /ml g ⁻¹
	Ti	V	Al	P	S _{BET} /m ² g ⁻¹	V _p /ml g ⁻¹	
VTAPO-5	0.015	0.022	0.484	0.491	304	0.121	0.114
TAPO-5	0.028	—	0.489	0.481	311	0.117	0.110
VAPO-5	—	0.024	0.492	0.483	298	0.123	0.118

Table 2 Partial oxidation of methanol over substituted AIPOs

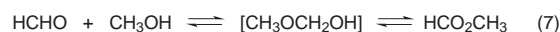
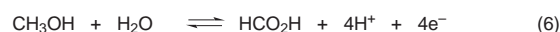
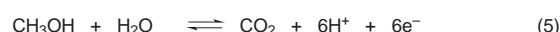
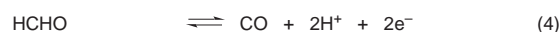
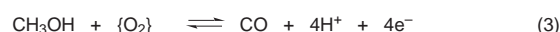
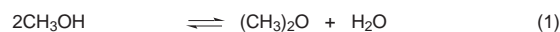
Material	Methanol Conversion (%)	Product selectivity (mol%)						
		HCHO	CO	(CH ₃) ₂ O	CO ₂	CH ₃ CHO	MF	FA
TAPO-5	0.01 ^a	nd	nd	nd	nd	nd	nd	nd
VAPO-5	5.73 ^a	79.2	12.6	5.8	3.4	nd	nd	nd
	7.28 ^b	74.8	14.4	7.2	3.6	nd	nd	nd
	10.16 ^c	69.2	16.3	9.4	5.1	nd	nd	nd
VTAPO-5	5.91 ^a	31.4	20.7	6.0	3.1	8.1	29.5	1.2
	7.87 ^b	22.9	22.2	7.3	3.3	9.3	33.4	1.6
	11.09 ^c	13.8	24.4	9.6	4.5	10.7	35.3	1.7

Reaction conditions: Feed = 20% methanol in Ar; 10% O₂ in Ar, reaction temp. = 200 °C; F/W (contact time) = ^a 21400 (0.29 s), ^b 15600 (0.40 s), ^c 9800 (0.64 s); catalyst = 0.2 g; MF = methyl formate; FA = formic acid; nd = not detected.

of *n*-butane adsorbed at STP was 0.114 ml g⁻¹. The DRS UV–VIS spectrum of VTAPO-5 shows a single peak with λ_{max} 232–238 nm and no evident shoulder around 300 nm. This suggested that VTAPO-5 is free from anatase or extraframework species such as titanium or vanadium oxide, in line with the BET and *n*-butane adsorption results. Moreover, in all samples studied, no oxide species were detected by Raman spectroscopy. ³¹P and ²⁷Al MAS NMR spectra of calcined TAPO-5, VAPO-5 and VTAPO-5 indicate that in all samples the aluminium was present in a tetrahedral environment and octahedral Al was absent as found in pseudoboehmite.¹⁵ The ²⁷Al MAS NMR spectra of TAPO-5 and VAPO-5 show a main peak at δ 32.4 while VTAPO-5 showed a slight shift to δ 34.1. Similar results were obtained from ³¹P MAS NMR spectra; a single ³¹P band assigned to framework tetrahedral phosphorus was observed at δ –29.8 for VAPO-5 and TAPO-5 samples whereas VTAPO-5 showed a shift to δ –27.2. The overall characterization results indicates that the novel VTAPO and its analogs TAPO-5 and VAPO-5 are pure and well crystallized.

Previous work indicates that the incorporated metal environment is essentially the same for all substituted AIPO analogs and is quite different from that in metal silicates. However, VTAPO-5 is found to be an active catalyst for the partial oxidation of methanol. The catalytic measurements were carried out in a conventional continuous flow differential reactor system. The typical reaction products were methyl formate, formaldehyde, acetaldehyde dimethyl ether, formic acid, CO and CO₂. Measurement of formic acid was performed by acid–base volumetric analysis while other products were analyzed by gas chromatography. The methanol oxidation reaction results (at steady state) and reaction conditions are summarized in Table 2. The catalytic tests were conducted at 200 °C and measured at different contact times (space velocities) of the feed under differential conditions. TAPO-5 was found to be totally inactive for methanol oxidation at the reaction condition studied except for very low activity observed at higher temperature (> 280 °C). VAPO-5 showed a significant activity. The major products obtained were formaldehyde and CO along with small amount of CO₂ and dimethyl ether. On VTAPO a considerable quantity of methyl formate and acetaldehyde were obtained as major products in addition to CO, formaldehyde, CO₂ and dimethyl ether. For methanol oxidation the product formation is proposed to be accompanied by several known complex equilibrium reactions (1)–(7) (Scheme 1).

With regard to the influence of contact time of the feed on the activity and selectivity, the system clearly showed that increased contact time improves methanol conversion and selectivities to methyl formate, acetaldehyde and CO with a decrease in the selectivity to formaldehyde. Thus, it can be proposed that formaldehyde is the initial product of methanol partial oxidation and is an intermediate species in the production of methyl formate, acetaldehyde and CO while the formation of dimethyl ether and CO₂ are independent of the production of the major products. According to these results, the methanol chemisorbs on vanadium species as a surface methoxy (CH₃O), and depending on the nature of Ti sites present on the surfaces of the catalyst, can react *via* various pathways to form

**Scheme 1**

acetaldehyde, methyl formate, formaldehyde, dimethyl ether and carbon oxides. While titanium itself is not an active site for the partial oxidation of methanol, VTAPO-5 selectively generates methyl formate and acetaldehyde which are more complex than products generated from pure VAPO-5. Thus titanium plays an important role in catalysis possibly due to strong V–Ti interactions. Verification of the precise reaction mechanism is linked to the measurement of the quantity and nature of the active sites. The fact that titanium modifies the active reaction sites would explain why VAPO-5 does not produce acetaldehyde or methyl formate. Further investigation of the catalytic behavior of VTAPO-5 and analogous VAPO-5 catalysts in various hydrocarbon conversion reactions such as oxidative dehydrogenation and epoxidation are in progress.

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