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Oxidative dehydrogenation of ethane on a magnesium–vanadium aluminophosphate (MgVAPO-5) catalyst

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Vanadium and/or magnesium substituted aluminophosphate with $ALPO_4$-5 structure have been prepared by hydrothermal synthesis. These catalysts have been tested for the oxidative dehydrogenation (ODH) of ethane. $ALPO_4$-5 has a low activity and low selectivity for the ODH of ethane. The presence of Mg^{2+} ions in MgAPO-5 increases the selectivity to ethene, while the presence of V^{5+} species in VAPO-5 increases both the activity and the selectivity for this reaction. The presence of Mg^{2+} and V^{5+} species in the vanadium–magnesium aluminophosphate (MgVAPO-5) results in a more selective catalysts for the ODH of ethane. The behavior of MgVAPO-5 could be attributed to the presence of acid sites (Mg^{2+}) near to the redox sites (V^{5+}) in the molecular sieve framework.

Keywords: vanadium and/or magnesium aluminophosphates (VAPO-5, MgAPO-5 and MgVAPO-5); vanadium based catalysts; oxidative dehydrogenation of ethane

1. Introduction

Vanadium containing molecular sieves are interesting alternatives to supported vanadium catalysts for redox type reactions. Thus, during the oxidative dehydrogenation (ODH) of propane on VAPO-5 [1] or V-silicalite [2,3], higher yields to propylene than with selective vanadium supported catalysts are obtained.

For the ODH of ethane, supported vanadium materials, i.e. V/SiO_2 [4] or V/Al_2O_3 [5], or mixed metal oxides [6,7] have been proposed as selective catalysts. On molecular sieve based catalysts, it has been reported that ALPO-5 [8] or MnALPO-5 [9] have a high selectivity to ethene. However, these results were obtained at low conversion of ethane and high C_2H_6/O_2 ratio. Similar conditions were also used in the study of the catalytic properties of metal substituted aluminosilicates or silicalite, and it was observed that V-ZSM-5 presents high selectivity [10].

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The synthesis of metal substituted $ALPO_4$-5 was published by Flanigen et al. [11] some years ago, but since then, little information regarding their catalytic properties for selective oxidation reactions, using molecular oxygen, has been published.

In this paper a magnesium–vanadium substituted aluminophosphate molecular sieve with AFI structure (MgVAPO-5) has been synthesized and characterized. Its catalytic properties for the oxidative dehydrogenation of ethane have been compared with those of the corresponding magnesium aluminophosphate (MgAPO-5) or vanadium aluminophosphate (VAPO-5).

2. Experimental

MgAPO-5, VAPO-5 and MgVAPO-5 were synthesized hydrothermally according to the preparation procedure indicated previously [1]. V_2O_5 and/or $MgSO_4$, in addition to phosphoric acid, pseudobohemite, triethylamine (except for MgAPO-5 in which tetraethylammonium was used) and water were incorporated in the synthesis gel. The molar compositions of the gels are listed in table 1. The gels were heated in teflon lined stainless-steel autoclaves at 200°C ($ALPO_4$-5, VAPO-5 and MgVAPO-5) or 150°C (MgAPO-5) for 16 h and then centrifugated, washed and dried at 80°C.

Pure and substituted ALPO-5 samples were calcined in an air flow at 600°C for 6 h.

Table 1
Physico-chemical characterization of metal substituted ALPO-5 samples

Sample	Metal content				Yield of solid (%)	Crystallinity (%) [c]		Vanadium species [d]
	in gel [a]		in solid [b]			as-made	calcined	
	V (x)	Mg (y)	V (%)	Mg (%)				
$ALPO_4$-5	0	0	0	0	14	100	88	–
MgAPO-5	0	0.05	0	0.88	17	91	68	–
VAPO-5	0.117	0	0.44	0	12	100	100	VT (VO)
MgVAPO-5								
cat. A	0.117	0.20	0.52	2.68	18	100	70	VT (VO)
cat. B	0.117	0.47	2.4	4.4	16	68	48	VT (VO)

[a] Vanadium and magnesium contents in gel for an $Al_2O_3/P_2O_5/V_2O_5/MgSO_4$/template/$H_2O$ molar ratio of $0.8/1/x/y/1.76/40$ ($ALPO_4$-5, VAPO-5 and MgVAPO-5) and 1/1/0/0.05/1/40 (MgAPO-5).

[b] Vanadium and magnesium content in calcined samples, given in wt% of V or Mg atoms, obtained from atomic absorption spectrometry.

[c] Crystallinity (%) is referred to as-synthesized $ALPO_4$-5.

[d] Vanadium species in calcined samples: VT = tetrahedral V^{5+} species; VO = isolated V^{5+} species with coordination higher than 4.

Characterization of the catalysts was carried out as follows. X-ray diffraction (XRD) patterns were recorded in a Phillips 1060 diffractometer using nickel-filtered Cu Kα radiation ($\lambda = 0.1542$ nm), crystallinity was determined by measuring the intensity of the peaks appearing at $2\theta \approx 19.8°, 21.1°$ and $22.4°$ and comparing with the as-synthesized $ALPO_4$-5. Diffuse reflectance (DR) spectra in the UV–visible region were obtained with a Shimadzu UV-2101 PC spectrophotometer equipped with a reflectance attachment.

Catalytic reactions were performed in an isothermal fixed bed quartz tubular reactor at atmospheric pressure. Samples of 0.7–1.7 g were mixed with SiC to keep a constant volume in the catalyst bed (3 cm^3). The reaction was studied in the temperature interval 500–600°C using an ethane/oxygen/helium molar ratio in the feed of 4/8/88. The total flow was varied from 100 to 200 ml min^{-1}. Experimental procedure as in ref. [12].

3. Results and discussion

In fig. 1 the XRD patterns of the as-synthesized and calcined MgVAPO-5 samples are shown. In both cases AFI was the only crystalline phase detected by XRD. The nature and crystallinity of the as-synthesized samples, as well as the crystallinity and composition of calcined metal substituted aluminophosphate samples are shown in table 1. It can be seen there, that the as-synthesized samples present a high crystallinity, but this decreases after calcination. In addition to this, we must notice that the incorporation of vanadium in MgVAPO-5 is higher than on the corresponding pure VAPO-5, indicating an inductive effect of the magnesium present in the synthesis gel for the incorporation of vanadium [13].

The diffuse reflectance (DR) spectra of the as-synthesized and calcined MgVAPO-5 are shown in fig. 2. The DR spectrum of the as-synthesized sample shows bands in the 530–800 nm region, indicating the presence of vanadyl VO^{2+} species. After calcination, the bands in the 530–800 nm region disappear and the DR spectrum only shows a band at 270 nm, which can be assigned to the presence of tetrahedral V^{5+} species [14]. No band at $\sim$ 500 nm corresponding to V_2O_5 is observed.

The catalytic properties of $ALPO_4$-5, MgAPO-5, VAPO-5 and MgVAPO-5 samples for the oxidative dehydrogenation of ethane, are shown in table 2. In all cases, ethene, CO and CO_2 are the reaction products. From the results of table 2 it can be concluded that activity and selectivity to ethene decrease in the trend: MgVAPO-5 > VAPO-5 > MgAPO-5 > ALPO-5.

The catalytic activity for the conversion of ethane decreases in the order: VAPO-5 = MgVAPO-5 (cat. B) > MgVAPO-5 (cat A) >> MgAPO-5 = ALPO-5. For this reason it can be concluded that, at the same vanadium content, the conversion of ethane on VAPO-5 is higher than on MgVAPO-5. However, a higher yield of ethene is obtained on MgVAPO-5 than on VAPO-5.

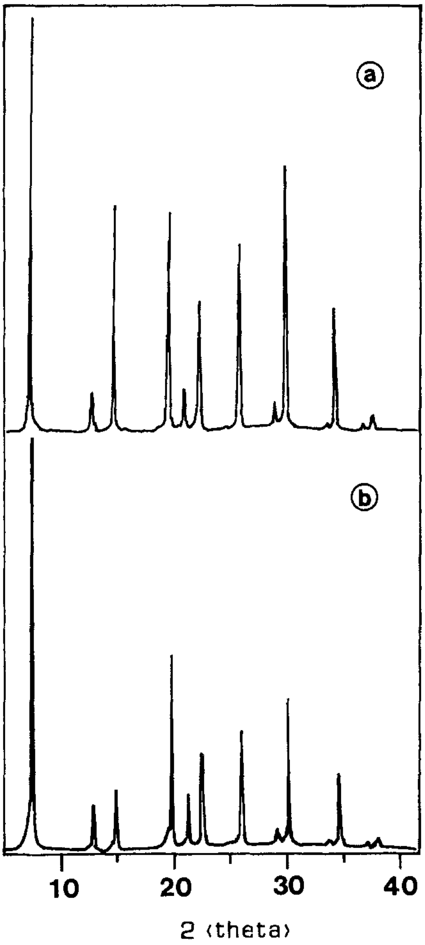

Fig. 1. XRD patterns of as-synthesized (a) and calcined (b) MgVAPO-5 (cat. B) sample.

The variation of the selectivities to the main reaction products with the conversion of ethane, obtained at 600°C on the MgVAPO-5 (cat. B) sample is shown in fig. 3. It can be seen that the selectivity to ethene decreases and the selectivities to CO and CO_2 increase when increasing the conversion level of ethane. In addition, the CO/CO_2 ratio increases when increasing the conversion of ethane. Thus, on MgVAPO-5 a selectivity to ethene higher than 70% is achieved at low conversion of ethane, while, at high conversion levels of ethane, a yield to ethene of 20–25% is obtained.

It has been reported that the selective ODH of ethane on $ALPO_4$-5 occurs at low conversion of ethane and a high ethane/oxygen ratio [8]. In this case, as well as for the ODH of propane on H-ZSM-5 [2], it has been postulated that the reaction occurs on two different sites: one originates from the zeolite surface and the other from the zeolite surface with adsorbed oxygen.

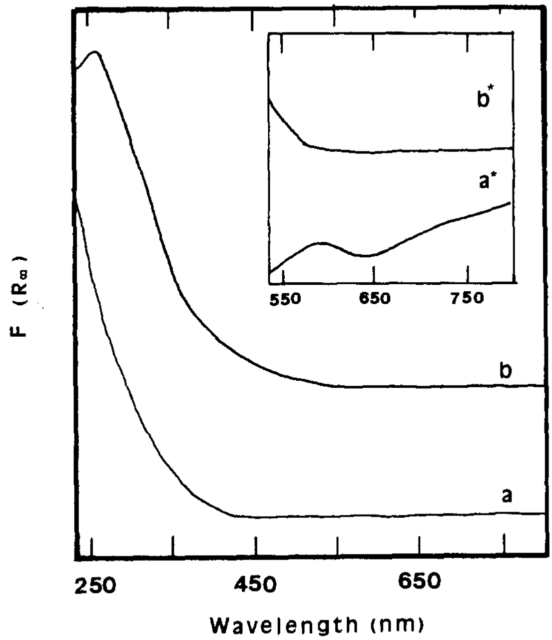

Fig. 2. DR spectra of as-synthesized (a) and calcined (b) MgVAPO-5 (cat. B), and the corresponding enlarged spectra in the 530–800 nm region (a*, b*).

In our reaction conditions, i.e., low ethane/oxygen ratios, the ODH of ethane on ALPO4-5 occurs with a low selectivity to ethene. The presence of Mg^{2+} ions in MgAPO-5, which increases the acidity of the catalyst, increases the selectivity to ethene although the activity is not influenced. On the other hand, the presence of vanadium species in VAPO-5, which increases the redox character of the catalyst, increases both the activity and selectivity for the ODH of ethane.

In addition to this, the better catalytic properties of MgVAPO-5 can be attribu-

Table 2
Oxidative dehydrogenation of ethane on metal substituted ALPO-5 catalysts [a]

Sample	W/F [b]	Conversion (%)	Selectivity (%)		
			ethene	CO	CO_2
ALPO-5	93	4.8	6.9	13.4	19.7
MgAPO-5	93	4.1	21.7	46.3	31.9
VAPO-5	93	28.1	32.1	40.9	27.0
	47	19.0	35.6	40.7	23.7
MgVAPO-5					
cat. A	93	16.3	61.0	28.0	11.0
cat. B	93	28.7	59.7	30.6	9.7
	47	12.9	60.5	28.6	10.9

[a] Reaction temperature = 600°C.

[b] Contact time, W/F, in g_{cat} h (mol $C_2H_6)^{-1}$.

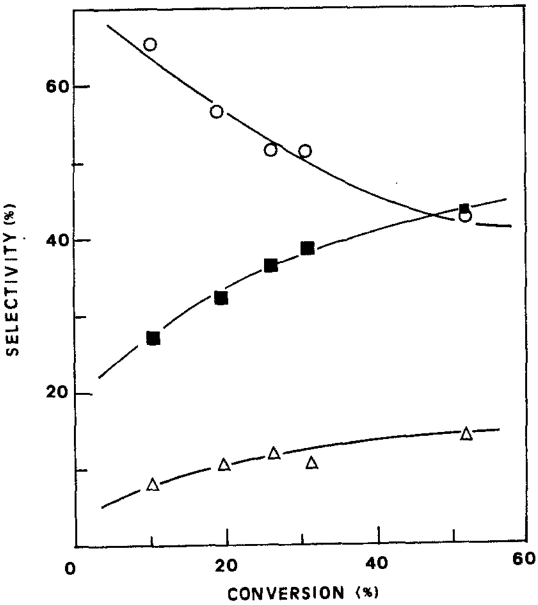

Fig. 3. Variation of the selectivities to ethene (○), CO (■) and CO_2 (△) with the conversion of ethane, at 600°C, on MgVAPO-5 (cat. B) catalyst.

ted to a high concentration of isolated VO_4 tetrahedron stabilized by the presence of Mg^{2+} in the molecular sieves and/or to the presence of V–Mg pairs which are active and selective for the ODH of ethane.

Isolated VO_4 tetrahedra have been proposed as selective sites for the ODH of ethane [4,5], propane [1–3,12], and *n*-butane [15] on vanadium based catalysts. According to our results, tetrahedral V^{5+} species are present in both MgVAPO-5 and VAPO-5, and nevertheless, differences in the selectivity to ethene are observed for these catalysts.

The presence of acid sites, related to Mg^{2+} ions in the framework of molecular sieve, has been observed for MgAPO-5 [16]. In this way the contribution of acid sites can explain the higher selectivity to ethene in the ODH of ethane on MgAPO-5. Similar acid sites as in MgAPO-5 are observed in MgVAPO-5 [13]. For this reason, the better catalytic properties of MgVAPO-5 for the ODH of ethane could be explained on the basis of the presence of acid sites near to vanadium sites.

Indeed, magnesium vanadium oxide catalysts, in which Mg–O–V pairs are present but acid sites are not observed, show low selectivity for the oxidative dehydrogenation of ethane [17].

In conclusion, it appears that the vanadium–magnesium aluminophosphate MgVAPO-5 is an attractive catalyst for the oxidative dehydrogenation of ethane. Its catalytic properties can be related to the presence in the framework of close acid and redox sites, related to the presence of Mg^{2+} and V^{5+} species, respectively.

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