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Direct oxidation of isobutane to methacrolein over V-MCM-41 catalysts

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Abstract

High vanadium content mesoporous vanado-silicates with MCM-41-like structure, obtained by the atrane route, catalyse the direct oxidation of isobutane to methacrolein with 30% selectivity, and a total dehydrogenation (olefin plus methacrolein) selectivity up to 74%.

Keywords: Oxidative dehydrogenation; Isobutane; Methacrolein from isobutane; V-MCM-41 catalysts

1. Introduction

Selective oxidation of alkanes to valuable oxygenated products is an important process in the petrochemical industry, but constitutes still an unresolved issue, with the only exception of maleic anhydride production from butane. This is due to the low selectivities resulting from the high reactivity of the oxygenated products compared to the inertness of starting alkanes under the reaction conditions. Vanadium oxide constitutes the basis of most of the catalysts used for the oxidative activation of light alkanes [1,2], its catalytic behaviour being extremely dependent on the nature of V species (oxidation state, coordination sphere, dispersion, and stability). Isolated or polymeric tetrahedral V^{5+} species, obtained by spreading the oxide onto a support [3–5] are the most selective for the oxidative dehydrogenation (ODH) to alkenes [1,3,6]. It has been recently reported that isolated tetrahedral vanadium species show the highest intrinsic activity for ODH [7,8], but there are still some discrepancies about the vanadium active species for the selective oxidation of alkanes [1,2].

However, two problems are commonly faced with V-containing catalysts (both in the case of micro-, mesoporous or bulk materials): to avoid the deleterious effect of the formation of V_2O_5 microcrystals on the catalytic performance, and the very low V content (<1 wt.%) may be reached to keep a good vanadium dispersion, which in turn implies the use of high catalyst amounts to achieve reasonable yields.

Vanadium containing mesoporous silicates V-MCM-41 are able to selectively oxidise paraffins, olefins using H_2O_2 or organic peroxides as oxidants [9,10]. Recently, the ODH of propane with oxygen over V-MCM-41 prepared by various methods has been reported [11,12]. Some authors have found that the amount of vanadium atoms that can be incorporated into the MCM material structure by direct synthesis is limited [13], leading to the segregation of excess vanadium as vanadia. This phase should be responsible of the observed formation of the oxidative degradation products over these catalysts.

We report here that methacrolein can be obtained from isobutane in a single step with relatively high selectivity and moderate yields, by using as the catalysts vanadium containing MCM-41-like mesoporous silicas with high vanadium contents, prepared by synthesis via the so-called atrane route [14]. To our knowledge, these catalysts yield the highest methacrolein yields reported to date for this target reaction.

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2. Experimental

2.1. Catalysts preparation

V-doped MCM-41 catalysts were prepared by using of Si and V atrane complexes (complexes with tri-ethanol amine, TEAH3) as molecular precursors, and CTABr as “supramolecular template” for the synthesis of the MCM-41 mesostructured material [13]. In a typical synthesis to obtain Si/V = 49, 0.49 g NaOH, 1.49 and 44.71 mmol of the atrane complexes of V and Si, respectively, are dissolved at 60 °C in TEAH3, and then 4.23 g CTABr and water (4:1 v/v to TEAH3) are added under stirring. The resulting suspension is aged at room temperature for 24 h, and then the precipitate filtered and dried in air. To obtain the final catalysts, the obtained mesostructured material is calcined at 550 °C for 7 h in static air. Catalysts samples are denoted as V-MCM-41(*x*), where *x* is the final Si/V atomic ratio.

2.2. Catalyst characterisation

Elemental composition was determined by EPMA in an electronic microscope Philips SEM-515. Reported Si/V are calculated averaging the data from some 50 different particles. X-ray diffractograms were registered in 0.02° steps (measuring time 25 s/step) in the angular range $2\theta = 1\text{–}10°$, with a Seifert 3000TT diffractometer, using Cu Kα radiation. Transmission micrographs were obtained with a electronic microscope Philips CM-10, operated at 120 kV. UV-Vis diffuse reflectance spectra were registered with a Shimadzu UV-250 1 PC instrument. Adsorption–desorption isotherms of nitrogen were carried out in a Micromeritics ASAP 2010 instrument.

2.3. Catalytic tests

Catalyst samples (0.2 g) were tested for the ODH de isobutane in a tubular, fixed-bed continuous reactor at 425–525 °C using an $i\text{C}_4\text{H}_{10}\text{–O}_2\text{–He}$ feed (molar ratio 27:13.5:59.5), with on-line GC analysis of reactants and products. Void volume of the reactor was filled with SiC bits. Preliminary tests showed the absence of homogeneous reactions in the absence of catalysts [15]. Conversion, selectivity and yields were calculated on a C-atom basis, and expressed as mol%. In all tests mass and carbon balances were within 100 ± 5%.

3. Results and discussion

3.1. Catalysts characterisation

EPMA measurements revealed that all the samples have a high elemental composition homogeneity, with a good dispersion of V along the pore walls. XRD patterns of both, mesostructured materials before removing the surfactant template (not shown) and mesoporous solids after calcinations (Fig. 1) show in all cases up to four of the characteristic peaks in the low range of 2θ (<10°), corresponding to the (1 0 0), (1 1 0), (2 0 0) and (2 1 0) reflections of a hexagonal cell analogous to the MCM-41-type mesoporous silicas.

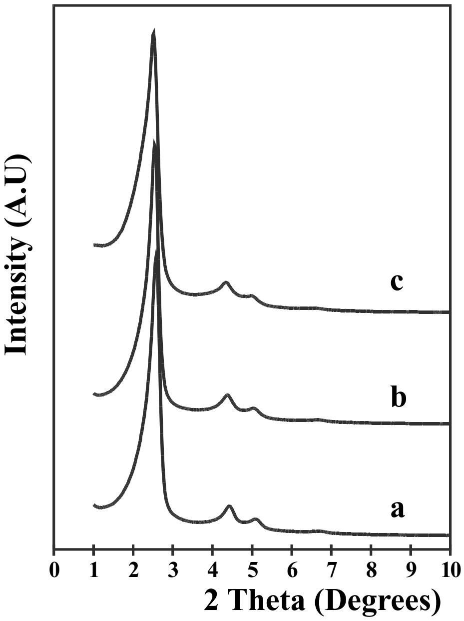

Fig. 1. XRD patterns of the mesoporous V-MCM-41 catalysts with Si/V ratios: 70 (a), 59 (b) and 49 (c).

Cell parameters, a_0, calculated from the value of the spacing of the most intense peak (1 0 0) and other textural and structural parameters are shown in Table 1. As it may be seen, the variation of V contents did not practically modify these parameters, and in this V-content range a high hexagonal order is kept upon introducing V in the pore wall. This is confirmed by TEM (Fig. 2) which shows that the final catalyst materials show a highly regular pore topology with hexagonal symmetry in the plane (1 1 0). The absence of reflections at $2\theta > 10°$, along with the chemical homogeneity of every sample (from EPMA), indicates that no segregation of V_2O_5 crystallites occurs. Hence, these catalysts can be considered as monophasic solids having a high chemical and structural homogeneity.

Nitrogen adsorption–desorption isotherms (not shown) present a well-defined adsorption at intermediate partial pressures ($p/p_0 = 0.25\text{–}0.35$), corresponding to the filling of the mesopores by capillarity, and no hysteresis phenomenon; both data confirm the high regularity of the pores. BET surface areas, all higher than 1000 m^2/g, pore volume and sizes (BHJ), and wall thickness, calculated from XRD and adsorption data are summarised in Table 1. All these data allow to observe that the original characteristics of the materials prepared by the atrane route are kept after the catalytic tests.

Table 1
Textural and structural properties of V-MCM-41(*x*) catalysts

Si/V atom. ratio (*x*)	S_{BET} (m^2/g)	Pore volume (cm^3/g)	BHJ pore diameter (nm)	a_0 (nm)	Pore wall thickness (nm)
As prepared					
70	1152	0.96	2.54	3.92	1.38
59	1154	0.97	2.57	3.99	1.42
49	1128	0.96	2.60	3.99	1.40
After catalytic testing					
70	1077	0.85	2.54	3.95	1.41
59	1101	0.91	2.50	4.01	1.51
49	1061	0.88	2.56	4.04	1.48

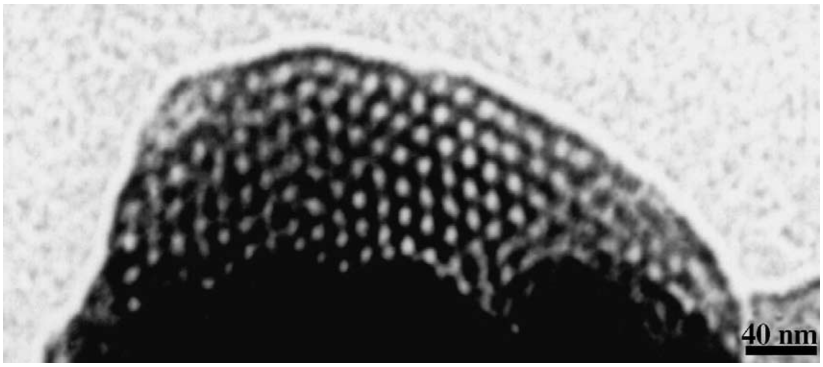

Fig. 2. TEM micrograph of V-MCM-41 samples.

3.2. Nature of the vanadium centres

UV-Vis diffuse reflectance spectra of the samples (Fig. 3) recorded at ambient atmosphere (and therefore hydrated) shows an intense charge transfer band centred at 264 nm, that can be assigned to V(V) species in tetrahedral environment, and a less intense one at 387 nm, assigned to V(V) in penta- or hexa-coordinated environment. The latter disappears upon sample dehydration (at 350 °C for 2 h): spectra of the dehydrated samples show two intense bands at 246 and 211 nm, that can only be attributed to V(V) in pseudo-tetrahedral environment. However, this effect is reversible: the spectra of the rehydrated samples are identical to that of the starting samples. Nevertheless, to obtain a reasonable fit, the deconvolution of each spectrum needs to consider an additional band at 274 nm (Fig. 3b, inset), which width and relative intensity are practically equal for every fit. These results suggest the presence of, at least, two different species of isolated V: tetrahedral centres (274 nm) embedded in the inorganic wall and inaccessible to water, and accessible V centres (246 and 211 nm) which may modify its co-ordination with the degree of humidity. Besides, the tailing above 300 nm in the spectrum of the dehydrated sample may be interpreted as due to the presence of dimers or one-dimensional low oligomeric tetrahedral species, as reported for V–Mg–O catalysts [7]. It is noteworthy that the absence of bands corresponding to octahedral coordination agrees well with the absence of segregated V_2O_5.

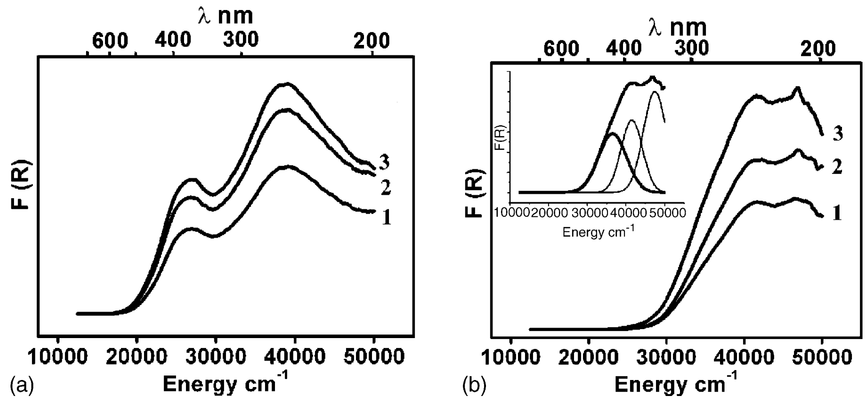

Fig. 3. Diffuse reflectance spectra of hydrated (a) and anhydrous (b) samples: (1) Si/V = 70; (2) Si/V = 59; (3) Si/V = 49. The inset shows a representative deconvolution of the spectrum (sample 2, Si/V = 59).

Table 2
Selective oxidation of isobutane over V-MCM-41 catalysts[a]

Catalyst Si/V ratio	Reaction temperature (°C)	Conversion (%)		Selectivity (%)								Yield (%)	
		iC_4H_{10}	O_2	iC_4H_8	MAL[b]	ACT[c]	C_3H_6	HCHO	CO	CO_2	Others[d]	iC_4H_8	MAL
49	425	2.7	7.6	48.1	26.3	8.8	2.5	1.9	5.7	4.8	1.9	1.3	0.7
	450	5.6	21.1	40.5	28.5	8.6	3.5	3.0	7.1	5.5	2.3	2.3	1.6
	475	10.6	41.6	35.1	28.7	8.0	4.4	4.4	8.9	6.7	3.8	3.7	3.0
	500	17.1	41.6	30.6	26.8	7.3	5.4	5.5	11.9	7.9	4.6	5.2	4.6
	525	25.2	99.5	30.7	22.9	6.6	5.7	5.0	14.0	8.0	7.1	7.7	5.8
59	500	12.4	45.6	34.8	21.0	6.3	7.8	7.4	11.8	6.9	4.0	4.3	2.6
70	500	11.5	38.6	38.7	16.9	5.6	7.9	7.8	11.6	7.8	3.7	4.4	1.9

[a] Reaction conditions: iC_4:O_2:He = 27.0:13.5:59.5 (mol%), W/F = 12 g_{cat} h/(mol_{C4}).
[b] Methacrolein.
[c] Acetone.
[d] Acrolein, acetaldehyde, ethylene, etc.

3.3. Catalytic results

In the reaction conditions used, isobutene, methacrolein (MAL), acetone (ACT) and carbon oxides (CO_x) were the main products, accounting for near 90 mol% of the total. Oxidative degradation and cracking products were also detected, especially at the higher temperatures. In all cases, start-up activity initially decreased down to a steady-state value, which was reached after 1 h on stream. Neither coke formation nor change of BET surface area were detectable after the catalytic tests (cf. Table 1). Some representative steady-state catalytic data are shown in Table 2. Similar trends were observed with the three samples. The catalysts were very selective to ODH: taking into account that methacrolein is the product of the selective oxidation of isobutene, the overall dehydrogenation selectivity varies between 71 and 50% within the conversion range obtained. Besides, selectivity to CO_x is very low and there is a moderate portion of oxygenated products, mainly methacrolein.

The most remarkable result is the relatively high selectivity to MAL, which allows to obtain yields per pass up to 5.8%, to our knowledge the highest ever reported for the direct oxidation of isobutane. It should be underlined that, at similar isobutane conversions, the higher the V content in the V-MCM-41 material, the higher the conversion and MAL selectivity and the lower the isobutene selectivity (Table 2).

The formation of oxygenated products during the ODH of propane with oxygen over V-MCM-41 prepared by other methods has been reported [11–13]. However, in these cases no meaningful amounts of the olefin selective oxidation product, acrolein, are found and the oxygenates came mostly from the oxidative degradation, as previously observed on SiO_2-supported vanadia catalysts, its formation has being attributed to the V species segregated from the mesoporous material network. Only Zhang et al. [13] report the formation of acrolein with 10–15% selectivity on V-MCM-41 prepared by the direct hydrothermal method. However, selectivity to methacrolein in the ODH of isobutane on the same catalysts is much lower, hardly reaching 10%, excepting for low conversions (20% at 6% conversion) on catalyst with low V content (Si/V = 87).

The formation of methacrolein besides isobutene, the expected ODH product for this catalyst, probably means that at least two types of active vanadium species for this reaction exist: one responsible for abstracting hydrogen and the other for inserting oxygen, respectively. Isolated tetrahedral vanadium species has been proposed to be the active and selective sites for ODH of alkanes over some supported vanadium catalysts, e.g. V-silicalite [16] and VAPO-55, and dimers or oligomers of tetrahedral species for the formation of partially oxygenated compounds from alkanes (e.g. on VPO [4]), while highly polymeric cluster or crystalline-like V_2O_5 are believed to be responsible of the total oxidation. Therefore, here we can assume that the isolated tetrahedral V^{5+} species is responsible to the ODH of isobutane to isobutene, and the low oligomeric V^{5+} species may be active for the formation of methacrolein. This is consistent with the experimental results, as selectivity to MAL at isoconversion increased with the increase of vanadium content in the three V-MCM-41 catalysts, in parallel to the increasing concentration of low oligomeric V^{5+} species that could be expected with the increase of vanadium loading in the studied range [17,18].

4. Conclusions

The atrane route allows preparing highly homogeneous V-MCM-41 catalysts with high V content, where vanadium is incorporated into various types of tetrahedral environments: embedded in the pore walls, and two types of accessible centres in the pore inner surface. They are active and stable catalysts for isobutane ODH and direct formation of methacrolein. The good selectivity to isobutene and methacrolein could be attributed to the better dispersion of isolated and low oligometric V^{5+} species on the high specific surface mesoporous MCM-41 material, and the simultaneous presence of two types of accessible centres.

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