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Oxidative dehydrogenation of *n*-pentane on magnesium vanadate catalysts

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Abstract

Two pure magnesium vanadate phases, $Mg_2V_2O_7$ and $Mg_3V_2O_8$, were prepared and tested in the dehydrogenation of *n*-pentane in the presence of oxygen. Both magnesium vanadates are effective catalysts, with $Mg_3V_2O_8$ exhibiting higher selectivity to dehydrogenation products. Testing of mechanical mixtures, consisting of each one of the magnesium vanadates and antimony oxide, indicated that the latter had a positive effect especially on the selectivity to dehydrogenation with the $Mg_3V_2O_8$ containing samples. The main products of the reaction were pentenes, pentadienes and carbon oxides. Characterisation of the samples prior to and after catalytic tests revealed that all catalysts remained practically unchanged during the reaction. The mixtures consisted of separate magnesium vanadate and antimony oxide phases and no formation of new phases was detected.

1. Introduction

Oxidative dehydrogenation of alkanes constitutes a challenging way of upgrading them to alkenes and alkadienes. Research done up to now on pentane is limited, with recent publications focusing on selective oxidation and formation of oxygenated products, such as maleic and phthalic anhydrides [1,2].

Vanadium-magnesium oxides, either supported or unsupported, are well known catalysts for the oxidative dehydrogenation of hydrocarbons, as in the transformation of propane to propene [3–6], butane to butene and butadiene [7], and ethylbenzene to styrene [8]. Conclusions drawn on activity and selectivity of various magnesium vanadate phases are still controversial [9]. Several parameters influence catalyst performance, one of them being the nature of the hydrocarbon which is activated, a fact that prevents generalisation of the results obtained with one particular molecule.

During studies on oxidation reactions, it has been observed that some oxides, such as Sb_2O_4, although not directly active, can improve catalyst behaviour by regenerating active sites through the action of a surface mobile oxygen species. The phenomenon is known as the remote control mechanism, and the oxides providing oxygen are characterised as donors [10,11].

In the present work, single phase magnesium pyrovanadate, $Mg_2V_2O_7$, and magnesium orthovanadate, $Mg_3V_2O_8$, have been prepared and tested as catalysts for the oxidative dehydrogenation of *n*-pentane. The effect of the addi-

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tion of Sb_2O_4 on the performance of these catalysts is reported.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared by the citrate method, with $Mg(NO_3)_2.6H_2O$ (Fluka purum p.a., > 99%), NH_4VO_3 (Merck GR, > 99%) and $C_6H_8O_7 \cdot H_2O$ (Merck GR, > 99.5%) as starting materials. Briefly, a homogeneous solution containing the necessary cations in suitable proportions and 10% excess anions, was prepared, evaporated at 30°C under reduced pressure to form a syrup-like liquid, and dried in a vacuum oven at 80°C for 24 h. The solid precursor thus formed, was decomposed at 300°C for 16 h and calcined at 550°C for 20 h, forming the final catalysts.

Mechanical mixtures with Sb_2O_4 were prepared by mixing the catalysts with the oxide in fine-powder form, dispersing the mixtures in *n*-pentane under vigorous agitation, and then evaporating the solvent by overnight drying at 80°C. Sb_2O_4 was prepared by calcination of Sb_2O_3 at 550°C for 20 h. The composition of each mixture was 50% catalyst and 50% Sb_2O_4, on a weight basis.

2.2. Catalyst characterisation

Phases present in the samples were identified by X-ray diffraction (XRD) analysis carried out on a Siemens D5000 diffractometer using Ni-filtered CuKα radiation. Specific surface areas were measured by Kr adsorption at −196°C on a Micromeritics ASAP 2000 volumetric apparatus using the BET method. The bulk cation content of the catalysts was determined by atomic absorption using a Philips PC 8210 spectrometer. Surface composition was evaluated by X-ray photoelectron spectroscopy (XPS) on an SSX-100 Model 206 SSI spectrometer with monochromatised AlKα radiation (1486.6 eV). The peaks recorded in XPS were C 1*s* (284.8 eV), O 1*s* (530 eV), Mg 2*s* (89 eV), V $2p_{3/2}$ (517.5 eV) and Sb $3d_{3/2}$ (540 eV). Calculations were based on the relative intensities of the peaks, taking into account the sensitivity factors supplied by the manufacturer.

2.3. Catalytic tests

Catalytic tests were performed in the temperature range 300–500°C, at near atmospheric pressure, with a gas feed consisting of 3.5 vol.% n-C_5H_{12}, 3.5 vol.% O_2 and the balance He, at a total gas flow of 25 cm^3/min (ambient conditions). For each test, 0.5 g of sample, $-800+500$ μm, was placed between two layers of glass beads on the frit of a small U-shaped Pyrex upflow reactor. Reaction temperature was monitored by a thermocouple placed in a thermowell entering the catalyst bed. On line analysis of the product stream was performed with an HP 5890 II gas chromatograph, equipped with two column systems, one Hayesep Q – Molecular Sieve 5A connected to a TCD and one Al_2O_3/KCl fused silica PLOT connected to an FID.

3. Results

3.1. Catalyst preparation and characterisation

The XRD patterns of the fresh catalysts are shown in Fig. 1. Each pattern reveals the pres-

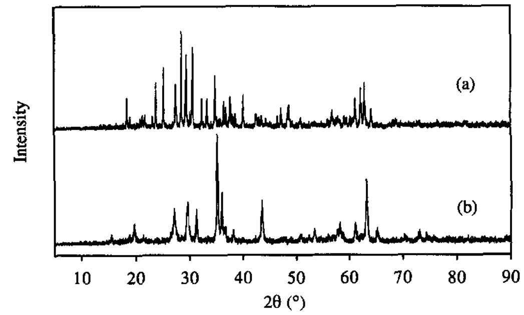

Fig. 1. X-ray diffraction patterns of fresh catalysts: (a) $Mg_2V_2O_7$; (b) $Mg_3V_2O_8$.

ence of one single phase that corresponds to the Mg to V ratio used in the preparation. Even the magnesium orthovanadate phase, which usually coexists with amounts of the pyro phase [4,7], was of high purity in our case. Phase impurities, if present, were in very low quantities, their XRD peaks not being detectable against the background noise. The structure of Sb_2O_4 prepared and used for the mechanical mixtures corresponded to the α phase, containing only minor, unidentified impurities. As expected, the XRD patterns of the mechanical mixtures included only lines attributable to the particular magnesium vanadate phase used and to α-Sb_2O_4.

The BET specific surface areas of the fresh catalysts, were 6 m^2/g for the pyrovanadate and 16 m^2/g for the orthovanadate. These values are high compared to those reported in the literature for similar materials [4,7,8]. The reason is that the calcination temperature used with our preparation method (550°C) was much lower than the ones required by other methods (650–800°C). The specific surface areas of the fresh mechanical mixtures of the pyro and the ortho phase were equal to 3 and 9 m^2/g, respectively, whereas the surface area of pure Sb_2O_4 was 0.5 m^2/g.

Vanadium on the surface of the freshly prepared catalysts was present mainly as V^{5+}, as it can be seen in the corresponding XP spectra (Fig. 2). A small proportion of vanadium was present in a different oxidation state, probably a lower one, since the V $2p$ peaks were slightly broader on their lower binding energy sides. The exact identification of this different oxidation state is difficult due to the lack of suitable standards. The reason is that the oxides of vanadium in an oxidation state less than +5 exhibit overoxidised surfaces [12]. Therefore, the determination of the exact binding energy of V different from V^{5+} in our catalysts was not possible. Rough quantitative calculations have shown that the proportion of this oxidation state in the fresh samples was in every case about 10% of the total V on the catalyst surface. A similar observation made by Gao et al. [3] on materials of the same type, lead in that case to the conclusion that this lower oxidation state corresponded to V^{4+}, which could be possibly formed during the pretreatment and analysis by XPS.

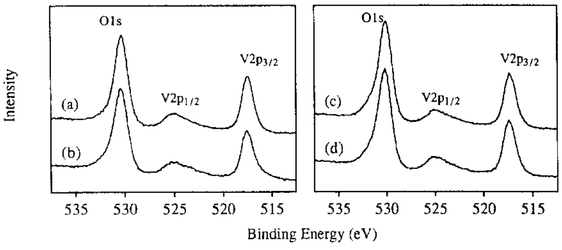

Fig. 2. XPS patterns of pure catalysts showing O $1s$ and V $2p$ peaks: (a) $Mg_2V_2O_7$ fresh; (b) $Mg_2V_2O_7$ used; (c) $Mg_3V_2O_8$ fresh; (d) $Mg_3V_2O_8$ used.

For the quantitative calculations of the surface composition of the samples, only the V $2p_{3/2}$ peak has been taken into account, since the strong influence of the neighbouring O $1s$ peak on the V $2p_{1/2}$ one complicates the decomposition of the latter peak. Mg to V surface ratios, presented in Table 1, were higher than the bulk ones, probably due to the existence of vanadium-deficient positions on the surface or to an enrichment in finely dispersed magnesium.

The freshly prepared mechanical mixtures had surface Mg/V ratios similar to the ones of the parent catalysts, while the antimony proportion on their surface was lower than the one corresponding to the bulk composition of the mixture. The Sb/(Mg + V + Sb) bulk atom ratios were almost identical to the theoretical values, which are equal to 0.30 for the pyro containing mixture and 0.28 for the ortho containing one. The apparent surface depletion in Sb reflects the fact that Sb_2O_4 has a lower surface area than the magnesium vanadates. For this reason, proportionally less photoelectrons per amount of matter can emerge from the surface and are detected during XPS analysis. The solid with the greater surface area, in this case the magnesium vanadate, gives a greater XPS signal than that expected from the bulk composition, as it has been already reported for two phase mixtures [13].

Antimony in Sb_2O_4 exists as a mixture of Sb^{3+} and Sb^{5+}. However, it was not possible to decompose with precision the Sb $3d_{3/2}$ peak corresponding to the mechanical mixtures, since the difference in binding energies of Sb^{3+} and Sb^{5+} is only 0.5 eV [13]. We therefore used the total Sb $3d_{3/2}$ peak for the quantitative calculations.

Samples used in the catalytic experiments had generally the same characteristics as the fresh ones, as judged from XRD and XPS analyses. A slight enrichment in lower oxidation state vanadium has been observed on the surface of pure catalysts after testing (Fig. 2), with a very small decrease of the magnesium to total vanadium ratio on the surface (Table 1). For the mechanical mixtures, it was observed that the proportion of antimony on the surface increased slightly after testing (Table 1). This may be the effect of a slight contamination by carbon, which occurred preferentially on the magnesium vanadates, thus shielding photoelectrons emitted by these phases and reducing the corresponding XPS signals. There is no indication of the formation of any new phase during test, since the binding energies of elemental lines in XPS and the phases identified in XRD patterns were the same for samples before and after use. In some cases with the pure catalysts, after experiments where oxygen was totally consumed, the used catalysts exhibited marked differences compared to the ones before test, having a darker colour, greater surface area and increased surface coverage in carbon. It is probable that the lack of oxygen, especially at the exit part of the catalytic bed, caused a partial reduction of the catalysts and an increase in carbon deposition, the latter contributing to the increase of the surface area.

3.2. Catalyst testing

Blank tests, performed under the same conditions as the catalytic runs, have shown that the empty reactor had practically no activity. The maximum *n*-pentane conversion, observed at 500°C, was below 1.5%. The products included pentenes, C_2 and C_3 hydrocarbons, but no carbon oxides. In our case, the low oxygen to paraffin ratio in the reactor feed made that the homogeneous reaction, which otherwise can be very important [14], did not play a significant role.

In the catalytic tests, the products of the reaction were pentenes (1-pentene, *trans*- and *cis*-2-pentene), pentadienes (*trans*- and *cis*-1,3-pentadiene), carbon dioxide, carbon monoxide and water. Oxygenated organic products have not been detected. In some cases, light hydrocarbons, especially C_2 and C_3, were also produced due to cracking reactions.

Conversions achieved at various reaction

Table 1
Catalyst composition and XPS data

Catalyst		Bulk Mg/V	B.E.		XPS	
		atom ratio [a]	O1*s* (eV)	Sb3$d_{3/2}$ (eV)	Mg/V atom ratio	Sb/(Mg + V + Sb) atom ratio
$Mg_2V_2O_7$	fresh	1.0	530.2	–	1.39	–
	used		530.3	–	1.36	–
$Mg_3V_2O_8$	fresh	1.6	530.0	–	2.06	–
	used		530.1	–	1.91	–
$Mg_2V_2O_7$-Sb_2O_4	fresh	1.0	530.3	539.7	1.23	0.20
	used		530.4	539.9	1.14	0.29
$Mg_3V_2O_8$-Sb_2O_4	fresh	1.6	530.2	539.8	2.23	0.08
	used		530.3	539.8	1.95	0.14

[a] Measured by atomic absorption spectroscopy.

Table 2
Product distribution in the oxidative dehydrogenation of *n*-pentane over magnesium vanadate catalysts

Catalyst	T (°C)	*n*-Pentane conv. (%) [a]	Product selectivity						
			CO/CO_2 [b]	HC/CO_x [c]	C_5 Product distribution (%) [d]				
					$1\text{-}C_5H_{10}$	$t\text{-}2\text{-}C_5H_{10}$	$c\text{-}2\text{-}C_5H_{10}$	$t\text{-}1,3\text{-}C_5H_8$	$c\text{-}1,3\text{-}C_5H_8$
$Mg_2V_2O_7$	350	4.9	0.43	0.91	28	42	30	0	0
	400	12.3	0.46	0.38	26	43	29	1	1
	450	18.6	0.47	0.35	22	40	26	8	4
	500	24.1	0.37	0.39	14	28	18	26	14
$Mg_3V_2O_8$	350	3.8	0.22	1.02	32	35	30	2	1
	400	13.8	0.26	0.86	32	33	29	4	2
	450	22.5	0.36	0.91	30	28	27	9	6
	500	27.9	0.25	0.70	15	26	17	27	15
$Mg_2V_2O_7\text{-}Sb_2O_4$	350	2.8	0.32	1.54	29	42	29	0	0
	400	8.2	0.41	0.34	35	37	26	1	1
	450	11.6	0.47	0.34	37	34	26	2	1
	500	15.1	0.51	0.45	39	31	25	3	2
$Mg_3V_2O_8\text{-}Sb_2O_4$	350	1.8	0.19	1.87	28	38	30	2	2
	400	7.8	0.25	1.35	29	34	30	4	3
	450	15.4	0.32	1.25	29	30	28	8	5
	500	20.7	0.34	1.02	30	26	26	11	7

[a] Calculated from *n*-pentane concentration in the inlet and the outlet of the reactor.
[b] Molar ratio.
[c] Calculated as the ratio of *n*-pentane moles transformed to C_5 hydrocarbons to *n*-pentane moles transformed to CO plus CO_2.
[d] Molar distribution: t-, *trans* isomer; c-, *cis* isomer.

temperatures are presented in Table 2, along with the selectivities to the main products. Light hydrocarbons are not included in this table; in any case, their proportion in total products did not exceed 1.0% mol. Total *n*-pentane conversion, calculated from its concentration in the inlet and outlet of the reactor, increased with increasing temperature for all samples. At each temperature in the range examined, the conversions achieved by the two pure catalysts were similar, and the same observation was made when comparing the two mechanical mixtures. Conversions achieved by the mechanical mixtures were slightly better than the ones by the parent catalysts, when the amount of the magnesium vanadate phase in the sample was taken into account. This increase in conversion in the presence of Sb_2O_4 could be an indication of cooperation effects between the magnesium vanadate and the antimony oxide, since the latter is inactive for the reaction when tested alone.

When conversion increased, the proportion of the combustion products (CO, CO_2) generally increased at the expense of the dehydrogenation products (alkenes, alkadienes). This variation in opposite directions of the conversion and the dehydrogenation selectivity is typical in alkane activation processes [9]. The orthovanadate phase was much more selective towards dehydrogenation reaction than the pyrovanadate one, in single phase as well as in mixed samples. The selectivity to dehydrogenation was favoured by the low oxygen/alkane ratio used in the feed, as it was observed for similar oxidation reactions of other hydrocarbons [8,15]. This was verified by changing the feed ratio; the results of these experiments will be reported in detail elsewhere [14].

The predominant dehydrogenation products in all cases were the 2-alkenes. With increasing conversion and temperature, selectivity to 2-alkenes generally decreased and selectivity to alkadienes increased. The variation of selectivity to 1-pentene depended on the sample considered: with increasing conversion and temperature, this selectivity decreased substantially in the case of the pure catalysts, while for the mechanical mixture containing the pyro phase it increased, and for the mechanical mixture containing the ortho phase it did not change. The *trans*- to *cis*-isomer ratio in the 2-pentene fraction was higher for the samples containing the pyro phase, this being in accordance with a higher acidity of the pyro phase relative to the ortho one. In the pentadiene fraction, the *trans*- to *cis*-ratio showed no simple trend, possibly due to complications from secondary reactions.

Considering the two carbon oxides, CO_2 was always produced in larger amounts than CO. The proportion of CO was higher for the samples containing the pyro phase, and the same observation can be made in almost all relevant studies concerning these two phases, regardless of the nature of the alkane [7,8]. For given reaction conditions, this proportion does not change markedly between the pure catalyst and its mechanical mixture, especially for reaction temperatures up to 450°C.

The dehydrogenation selectivity of the mechanical mixture containing the pyrovanadate phase was very similar to the selectivity of the parent catalyst. However, the orthovanadate-containing mixture was conspicuously better, producing more dehydrogenation products and less carbon oxides than the pure catalyst, under the same reaction conditions.

4. Discussion

Both pure magnesium vanadates prepared and tested proved to be effective catalysts for the activation of *n*-pentane. Their overall activities, as judged by the total conversion levels achieved, were similar under the same reaction conditions. Since the specific surface area of $Mg_2V_2O_7$ was significantly lower than that of $Mg_3V_2O_8$, one can assume that for the same surface area, the pyrovanadate catalyst could give higher conversions than the orthovanadate one, thus exhibiting higher specific (per unit surface area) activity. This can be considered as logical, because in the pyro phase the density of the vanadium ions considered responsible for activity, is higher than that of the ortho phase [9]. However, since the conversion levels were rather high, no quantitative specific activity values can be drawn from the present results.

Of the two magnesium vanadates examined in this work, the orthovanadate was the most selective to dehydrogenation products, i.e. pentenes and pentadienes. The nature of the products depends on the way the alkyl intermediate formed after breakage of the first C–H bond interacts with surface active sites. In the magnesium orthovanadate catalyst, the active sites consist of isolated VO_4 tetrahedra, while in the pyrovanadate one the active sites are V_2O_7, which are in fact corner-sharing VO_4 units [9]. If one adsorbed alkyl intermediate can take up more oxygen from V_2O_7 than from VO_4, this can result in the pyrovanadate phase being more selective to oxygen-containing molecules and less selective to hydrocarbons than the orthovanadate one, as in the case of *n*-pentane studied here. The enhanced selectivity that we observed for the ortho phase is in accordance with the case of *n*-butane [7] and ethylbenzene [8]. In the case of propane, magnesium orthovanadate is active, but certainly not as selective as the pyrovanadate [3,4]. Acidity measurements were not made in the present work and a direct proof of a possible correlation between acid-base properties and selectivity is lacking at present.

The addition of Sb_2O_4 had little effect on catalyst selectivity for the pyrovanadate phase, but the selectivity to dehydrogenation in the case of the orthovanadate was improved. At each temperature studied, the conversion achieved with the mechanical mixture was lower than that of the corresponding catalyst and this decrease of conversion alone could lead to an improvement of selectivity. Still, if the comparison of dehydrogenation selectivity is made for the same levels of total conversion (this being achieved at different temperatures), the mixture has again a better performance than the pure catalyst. This can be an indication of the existence of a synergy effect due to creation of spillover species. This interpretation is supported by the fact that no changes of the nature of the mixtures were found by characterising the samples prior to and after testing with XRD and XPS techniques, implying that the alternative explanations of mutual contamination or formation of a new compound must be excluded. The existence of a remote control mechanism has been observed in the oxidation reactions of other light alkanes such as propane [6] and butane [16]. However, in order to clarify the existence of similar phenomena in the case of *n*-pentane, more thorough investigation would be needed, including in particular accurate kinetic determinations. Reaction conditions could be modified, so that all side effects could be excluded, and new combinations of donors with the particular catalysts could be tested.

5. Conclusions

High-purity magnesium pyro and ortho vanadate phases, prepared by the citrate method, proved to be effective catalysts for the oxidative dehydrogenation of *n*-pentane. When compared under the same reaction conditions, the two phases exhibited similar overall pentane conversions, but the selectivity to dehydrogenation was much better in the case of the orthovanadate phase. Addition of Sb_2O_4 further improved the selectivity to dehydrogenation products in the case of the orthovanadate, having no significant effect on the selectivity of the pyro phase. Conversion per unit mass of the active phase was slightly improved by the presence of antimony oxide in all cases. There were indications that a positive cooperation takes place between magnesium vanadate phases and antimony oxide, since their mixtures consisted of separate coexisting phases and no changes of the samples have been observed by XPS and XRD studies of the samples before and after test.

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