

Study of catalytic behaviour and deactivation of vanadyl-aluminum binary phosphates in selective oxidation of *o*-xylene

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Abstract

This study involved the catalytic behaviour and the deactivation of aluminum–vanadium–phosphorus (Al–V–P–O) systems obtained by the sol–gel method with several P/Al/V molar ratios and calcined at 450 °C in the selective oxidation of *o*-xylene. Activity values as well as the reducibility of Al–V–P–O systems were influenced by the Al/V ratio, increasing with Al content, while selectivity to phthalic anhydride and phthalide values only changed slightly. All catalysts always showed a high degree of resistance to deactivation in function of time on-stream. Furthermore, water in the feed or coke generation treatment negatively affected catalytic activity, although the initial conversion values were recovered. This fact along with the unchanged textural properties and XRD patterns of the catalysts after such treatments suggest that reversible deactivation could be attributed to partial poisoning of active sites.

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Keywords: Vanadyl-aluminum binary phosphates; *o*-Xylene selective oxidation; Catalyst deactivation; H₂-TPR

1. Introduction

Amorphous aluminum phosphates, AlPO₄, have been intensively studied as catalysts and metal supports in a great variety of reaction processes including the oxidative dehydrogenation of ethylbenzene [1,2]. They have also been demonstrated to provide good support material for vanadium–phosphorus mixed oxides in the catalytic production of maleic anhydride [3,4]. On this basis, we decided to study some ternary systems based on aluminum–vanadium–phosphorus (Al–V–P–O), prepared by a sol–gel method like the one employed in AlPO₄ synthesis [5], in order to obtain insights on the effect that aluminum presence might have on the physical and chemical properties of binary systems and, consequently, on their catalytic behaviour, especially in some oxidation reactions. In this respect, the results obtained in previous research [6,7] on textural/structural characterization by ICP–AES, TGA, XRD, DRIFT, DR UV–vis, ³¹P and ²⁷Al MAS NMR and N₂ adsorption techniques, as well as acid–base/redox characterization by 2-propanol conversion and pyridine chemisorption of the ternary and binary systems indicated that important changes took place. Thus, the aluminum presence promoted porosity in the ternary systems, delayed

vanadyl phosphate crystallization and improved catalytic activity for 2-propanol decomposition in both dehydration processes to propene (the most important one) and dehydrogenation to propanone. Furthermore, these changes were also influenced by thermal treatment [6] and the Al/V ratio [7] of the ternary systems. In general, the porosity of the solids and their primarily amorphous character decreased (with the formation of two pure phosphates phases, β-VOPO₄ and AlPO₄ α-cristobalite) when the vanadium content and calcination temperature increased. The activity of the Al–V–P–O systems increased when the aluminum content increased, whereas the 2-propanone selectivity decreased slightly [7].

The oxidation of *o*-xylene (X) over vanadia-supported-on-titania (anatase) catalysts constitutes the current industrial reaction to produce phthalic anhydride (PA). This chemical is widely employed as a raw material in the manufacture of phthalate plasticizers, polyester and alkyl resins, paints, lacquers, insecticides, and many other products. The process is usually carried out in the 350–400 °C temperature range with a maximum PA yield of 70–80%. It is a complex reaction, including several successive and parallel steps involving intermediates, mainly *o*-methylbenzaldehyde (MBA) and phthalide (PL), and different secondary products, like carbon oxides and maleic anhydride [8–11].

The present paper reports on the catalytic behaviour of Al–V–P–O systems with several P/Al/V molar ratios and cal-

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¹ A member of the EU-funded CA “CONCORDE”.

Nomenclature

C	conversion value
DP	dimerization products
DRIFT	diffuse reflectance Fourier transform infrared spectroscopy
DR UV–vis	diffuse reflectance ultraviolet–visible spectroscopy
EDX	energy dispersion analysis of X-rays
FID	flame ionization detector
GC	gas chromatography
ICP-AES	inductively coupled plasma-atomic emission spectrometry
MAS NMR	magic angle spinning nuclear magnetic resonance spectroscopy
MBA	<i>o</i> -methylbenzaldehyde
MBAc	<i>o</i> -methylbenzoic acid
MS	mass spectrometry
PA	phthalic anhydride
PL	phthalide
S_{DL}	selectivity to dimerization products
S_i	selectivity to products
S_{MBA}	selectivity to <i>o</i> -methylbenzaldehyde
S_{MBAc}	selectivity to <i>o</i> -methylbenzoic acid
S_{PA}	selectivity to phthalic anhydride
S_{PL}	selectivity to phthalide
TCD	thermal conductivity detector
TG-DTA	thermogravimetric–differential thermal analysis
TPD	temperature programmed desorption
TPR	temperature programmed reduction
X	<i>o</i> -xylene
XRD	X-ray diffraction

cined at 450 °C in selective oxidation of *o*-xylene. Thermal treatment of the Al–V–P–O systems over 500 °C promoted an important decrease in catalytic activity not only in the 2-propanol reaction but also in oxidation reactions of aromatic hydrocarbons [6]. The studies on reducibility, by temperature programmed reduction (TPR), as well as the deactivation behaviour of those Al–V–P–O systems are also reported. The catalyst resistance to deactivation was examined not only in function of time on-stream in *o*-xylene oxidation but also after undergoing treatments of coke generation and of exposure to water in the feed. The combined action of water and coke proved to be responsible for the AlPO₄ deactivation in 1-butanol dehydration [12], whereas it was the formation of residual tar products as well as coke on the active surface that produced a reversible deactivation of the V₂O₅/TiO₂ catalyst in the oxidation of *o*-xylene [13–15] and not the over-reduction of the catalyst [15]. However, irreversible deactivation was mainly due to thermal sintering and phase transformation of anatase to rutile that could be enhanced in the hot spot zone of the catalyst bed [16]. So, the water in the feed and the coke deposition would modify the catalytic sites, mainly the acid sites (their nature and strength distribution) on the catalysts and, consequently, their catalytic behaviour. More-

over, it is also important to understand the role of water because in the catalyst regeneration process by oxidation to remove the coke, the more volatile residues are eliminated under steam.

2. Experimental

2.1. Catalyst preparation

The systems were prepared by the sol–gel method as previously reported [6,7] with appropriate amounts of NH₄VO₃ reduced with oxalic acid, AlCl₃·6H₂O and H₃PO₄ (85 wt.%). After filtration, the solids (AlVPO-I, AlVPO-II and AlVPO-III where I, II and III indicate the different Al/V molar ratios) were dried at 120 °C for 24 h and calcined in air at 450 °C for 3 h to obtain the three catalysts denoted as AlVPO-I-450, AlVPO-II-450 and AlVPO-III-450. Another system was prepared by using VOCl₃. The solid was also dried and then calcined in air at 450 and 550 °C for 3 h to obtain two catalysts denoted AlVPO-450 and AlVPO-550. As a reference, a VPO binary system (P/V molar ratio = 1/1.3) was also obtained in the same way employing NH₄VO₃. The calcined solid at 450 °C was designated VPO-450. The heating rate during the calcinations procedure of all the solids was always maintained at 10 °C/min.

A Phillips XL30 ESEM Microscope equipped with a detector which allows chemical analysis by energy dispersion analysis of X-rays (EDX) was used for the surface chemical analysis of the solids studied. Electrons were accelerated at 20 kV and the energy range was 0–20 eV.

Table 1 shows the previously obtained results [6,7] of bulk chemical composition, determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES), pyridine chemisorption experiments and 2-propanol conversion reactions as well as the surface area values, S_{BET} , of the solids studied.

2.2. TPR measurements

TPR experiments were performed in a Micromeritics TPD/TPR 2900 analyser [6]. Samples of 50 mg were first treated in Ar at 100 °C for 1 h and then put into contact with an H₂/Ar mixture (10 mol% of H₂; total flow of 50 cm³/min) and heated (5 °C/min) to a final temperature of 800 °C. The consumption of hydrogen was monitored with a thermal conductivity detector (TCD). A cold trap (liquid nitrogen and 2-propanol) was used to prevent reaction products, mostly water, from reaching the detector.

2.3. Catalytic test

o-Xylene selective oxidation was carried out in a continuous-flow fixed-bed reactor at atmospheric pressure [6]. The reactor was made of stainless-steel tubing (7 mm in internal diameter and 190 mm long) placed in a tubular electric furnace and the prescribed temperature (325–400 °C) was monitored by a thermocouple located in the catalyst bed. An analysis of reagent and product composition was carried out on-line using a multi-column GC equipped with FID and TCD detectors in parallel. CO₂, CO and O₂ were separated on two columns in series, 3 m

Table 1

Bulk atomic ratios from ICP-AES analysis, surface area, chemisorption pyridine values at 100 and 200 °C and selectivity values to propene (C₃H₆) and propanone (C₃H₆O) obtained at 2-propanol isoconversion (~3%) and isoconversion temperature (T_{iso}) from references [6,7]

Catalyst	ICP-AES		S_{BET} (m ² /g)	Py (μmol/g)		2-Propanol conversión		
	P/(V + Al)	Al/V		100 °C	200 °C	T_{iso} (°C)	$S_{C_3H_6}$ ^a	$S_{C_3H_6O}$ ^a
AIVPO-450	0.95	1.06	10.8	15.5	6.7	210	80.5	9.8
AIVPO-550	0.95	1.06	2.9	– ^b	–	230	84.1	7.6
AIVPO-I-450	0.72	2.32	17.7	9.9	5.6	170	87.2	8.0
AIVPO-II-450	0.69	0.93	4.3	2.6	–	210	76.0	14.0
AIVPO-III-450	0.51	0.32	1.9	–	–	250	82.7	10.3
VPO-450	0.78	–	1.8	–	–	– ^c	–	–

^a mol%.

^b There was no Py chemisorption.

^c Conversion obtained <3%.

Porapak Q and Molecular Sieve 5A (for CO and O₂ separation) and analysed by the TCD. *o*-Xylene and reaction products were separated in a (60 m × 0.25 mm × 0.25 μm) DB-1 capillary column and detected by FID. All lines and valves were heated up to 250 °C in order to avoid any condensation of the products, which were identified by GC–MS. The catalyst (ca. 100 mg, <0.149 mm) was pretreated at the reaction temperature for 1 h in a N₂ flow (30 cm³/min). *o*-Xylene was fed by means of a microfeeder at 0.6 and 1.2 mL/h and the flow of oxygen was 30 or 60 cm³/min to obtain the same *o*-xylene/O₂ molar ratio in each experiment. The flow of He was changed suitably in order to keep the total flow of gases (O₂ + He) of 110 cm³/min constant.

A typical run to study the deactivation of a catalyst sample consisted of evaluating the catalytic behaviour with time on stream under the so-called “standard” experimental conditions ($T=315$ °C, $W=100$ mg, $F_X=1.2$ mL/h, $F_{O_2}=60$ cm³/min), and under the same conditions but after the sample was subjected to coke generation treatment ($T=380$ °C for 24 h, $F_X=1.2$ mL/h, $F_{O_2}=60$ cm³/min) and water treatment ($F_{H_2O}=3$ mL/h for 30 min, $T=315$ °C). After each run, the catalyst sample was characterized by N₂ adsorption and X-ray diffraction techniques. The coke determination in each sample was also carried out by simultaneous thermogravimetric-differential thermal analysis, TG-DTA, using the Setaram thermobalance Setsys 12, in the presence of static air at a heating rate of 10 °C/min (temperature range, 30–1000 °C). The CO₂ signal was analysed with an on-line quadrupole mass spectrometer (Pfeiffer Vacuum Omnistar).

Conversion (C) and selectivity to products (S_i) was expressed as mol% on a carbon atom basis. The carbon balance was always within 5%. Blank runs showed the reactor walls to be inert with respect to *o*-xylene oxidation at the temperature range studied.

3. Results and discussion

3.1. Surface chemical composition

The values of the surface atomic P, V and Al concentration ratios obtained from EDX are shown in Table 2. The surface P/Al + V molar ratio was similar to the bulk one (Table 1) for the AIVPO systems, whereas it was clearly higher for the other three ternary systems. Moreover, all the ternary systems presented an impoverishment of V on their surfaces with respect to bulk although the Al hardly changed, according to the V_{EDX}/V_{Bulk} and Al_{EDX}/Al_{Bulk} atomic ratios in Table 2. On the other hand, the VPO reference system exhibited a slight excess of V on its surface.

3.2. TPR

TPR profiles of systems are presented by H₂ consumption (a.u.) as a function of the temperature in Fig. 1. The consumption of H₂, as evaluated from the total area under a TPR profile, is presented in Table 2. As can be seen, there are remarkable differences in the profiles of ternary systems and of VPO. With the exception of the AIVPO-550 profile, that exhibited two well defined peaks at 558 and 687 °C, Table 2, the rest of the profiles

Table 2

Surface atomic ratios from EDX analysis, V_{EDX}/V_{Bulk} and Al_{EDX}/Al_{Bulk} atomic ratios, and H₂-TPR results

Catalyst	EDX		V_{EDX}/V_{Bulk}	Al_{EDX}/Al_{Bulk}	TPR		V_S ^a (mmol V/g)	[H ₂ /V _S] (mol/mol)
	P/(V + Al)	Al/V			H ₂ (mmol/g)	H ₂ (mmol/m ²)		
AIVPO-450	0.93	1.18	0.96	1.06	1.6	0.15	3.16	0.50
AIVPO-550	0.92	1.29	0.91	1.11	0.9	0.31	3.27	0.27
AIVPO-I-450	0.81	2.55	0.89	0.99	1.0	0.06	2.36	0.47
AIVPO-II-450	0.79	1.01	0.91	0.98	2.0	0.47	3.83	0.53
AIVPO-III-450	0.66	0.40	0.86	1.07	3.0	1.60	5.08	0.59
VPO-450	0.63	–	1.09	–	3.2	1.81	6.76	0.48

^a $V_S = \text{mmol } V_{Bulk}/g (V_{EDX}/V_{Bulk})$.

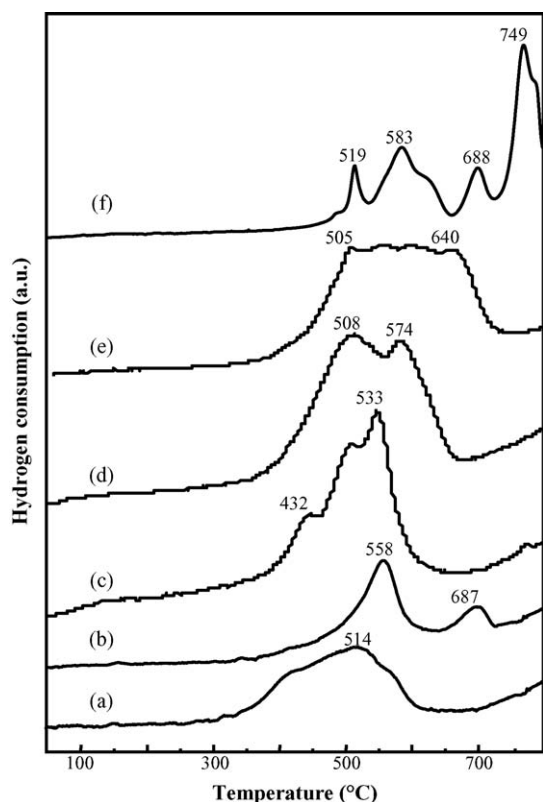


Fig. 1. TPR profiles for (a) AIVPO-450; (b) AIVPO-550; (c) AIVPO-I-450; (d) AIVPO-II-450; (e) AIVPO-III-450; (f) VPO-450.

corresponding to the ternary systems presented a wide band, with a variable number of not very well defined maximums, at different temperature ranges. These ranges shifted to higher temperatures when the V content increased in the systems. Regarding the VPO profile, it exhibited four defined peaks in a temperature range higher than the ternary systems. So, the obtained profiles, with more than one reduction peak or overlapping peaks, indicate the presence of different types of vanadium in each of the systems, which is in accordance with the existence of the other phases of vanadium phosphates (with V^{5+} and/or V^{4+}) in addition to the main one, β -VOPO₄, as was previously reported [6,7]. Furthermore, taking into account the reduction temperature values, Fig. 1, the presence of aluminum clearly promoted vanadium reducibility. A possible explanation of this fact would be the existence of an interaction of the vanadium phosphate phases with the aluminum phosphate, which would depend on the aluminum content. Thus, the systems with higher aluminum content exhibited higher reducibility: AIVPO-I-450 > AIVPO-II-450 > AIVPO-III-450; which were higher than the VPO. In this sense, a change has been reported in the reducibility of the V–P–O active phase depending on the support [17,18]. The degree of crystallinity of vanadium phosphate, which increased with the calcination temperature [6], also influenced the reducibility as can be seen by comparing the profiles of AIVPO-550 and AIVPO-450, Fig. 1 and H_2 consumption, Table 2. Thus, the AIVPO-550 showed that vanadium was not only more difficult to reduce, but also that a lower amount was affected. In fact, this system showed the lowest H_2 consumption

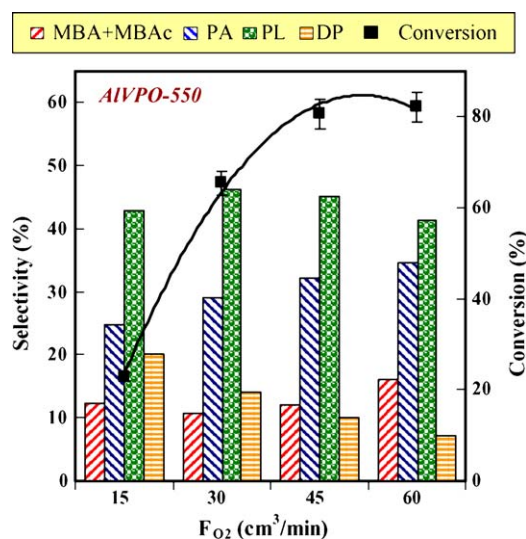


Fig. 2. Evolution of *o*-xylene conversion and selectivity values with the flow of O_2 , F_{O_2} . ($T = 350^\circ C$; $W = 0.1$ g; $F_X = 0.6$ mL/min).

value per unit of weight and per atomic vanadium surface. These results are in accordance with the lower reducibility of vanadium present in V_2O_5 crystalline form as compared to that of the amorphous form and of the vanadium species spread out on the support [9,11,19]. As expected, for the rest of the systems the H_2 consumption increased as the vanadium did although all of them exhibited a similar value of $[H_2/V]$, which oscillated between 0.47 and 0.59. Such values would indicate a 50% reduction and a final oxidation state around V^{4+} , assuming that before the reduction the vanadium had been V^{5+} . However, the existence of vanadium (IV) phosphate phases like $VOHPO_4 \cdot 0.5H_2O$, mainly in AIVPO-450 and AIVPO-I-450 [6,7], indicates that other factors related to the previous interpretation would need to be considered.

3.3. Selective oxidation of *o*-xylene

3.3.1. Influence of the reaction parameter

Figs. 2 and 3 show the conversion and product distributions in the oxidation of *o*-xylene as a function of O_2 flow (15–60 cm^3/min) and of temperature (300–420 $^\circ C$), respectively, for the AIVPO-550 system. These values plotted corresponding to the average of three values (experimental error $\leq 4\%$) obtained in the steady state (1–2 h of time on stream). The results corresponding to the rest of the systems as a function of temperature are presented in Table 3. At the experimental conditions studied, the main products obtained were methylbenzaldehyde (MBA), methylbenzoic acid (MBAc), phthalic anhydride (PA) and phthalide (PL) as well as dimerization products (DP). 2,6-Dimethyl-9,10-dihydroanthracene and 1,2-di-(2-tolyl)ethane are some of the DP identified by GC–MS. CO_2 was also detected but only in trace concentrations, whereas CO was never obtained.

The conversion increased with the flow of O_2 in the range between 15 and 45 cm^3/min and then remained unchanged, Fig. 1, whereas it increased with the reaction temperature

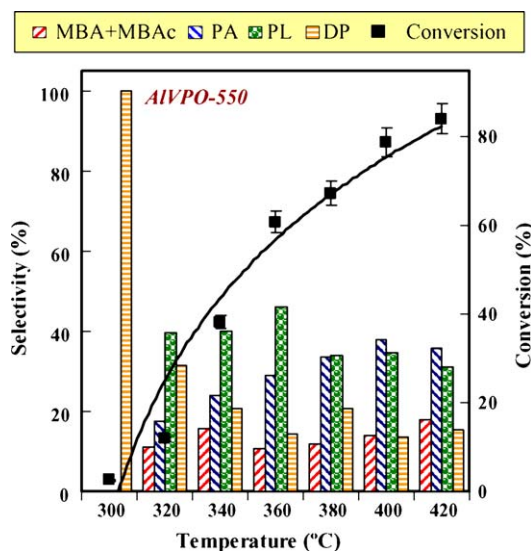


Fig. 3. Evolution of *o*-xylene conversion and selectivity values with temperature. ($W=0.1$ g; $F_X=0.6$ mL/min; $F_{O_2}=30$ cm³/min).

throughout the whole range studied, Fig. 2 and Table 3. As a general tendency, the conversion increase was accompanied by an increase in selectivity to PA (S_{PA}) and a decrease in S_{DP} , whereas the S_{PL} decreased slightly and the $S_{MBA+MBAc}$ hardly changed. However, PL was produced in higher amounts than PA, although as the reaction temperature and F_{O_2} increased, the differences between them were reduced. Likewise, DP became the only products detected at the lowest temperature studied, 300 °C. These results are in accordance with those obtained by several authors [8,10,20] that found an increase in the “residual” selectivity at lower temperatures defined as the fraction of *o*-xylene not detected as oxidised products, and that was attributed to the formation of heavy organic products, including dimerization products [14] like those detected in our experiments. Moreover, the opposite behaviour of S_{DP} and S_{PA} leads us to assume that the

same active sites must be involved in their formation, although DP would not be precursors of PA, according to Dias et al. [20].

3.3.2. Catalytic test

The values of C and S_i obtained for the rest of catalysts, Table 3, indicate that, in general, at the temperatures studied the ternary systems were more active than the VPO system and that activity increased with aluminum content. The vanadium source also influenced their catalytic behaviour. Thus, at 350 °C, AIVPO-450 and AIVPO-I-450 exhibited C values of 71% and 63%, respectively, whereas the values obtained for AIVPO-II-450 and AIVPO-III-450 were 16% and 12%, respectively, 15% being the value obtained for VPO. With respect to the selectivity values, the more active systems also exhibited the highest values of S_{PA} and the lowest of S_{PL} and S_{DP} , while the opposite trend was observed for VPO. Thermal treatment of AIVPO also influenced its catalytic behaviour, a decrease taking place in both C and S_{PA} values and an increase of S_{DP} in the solid calcined at 550 °C as compared to that calcined at 450 °C.

The higher acidity (in number of sites and strength) according to the values collected in Table 1, as well as the higher reducibility, Fig. 1, of ternary systems as compared to the VPO system, could explain their better catalytic behaviour in *o*-xylene oxidation. Moreover, the specific textural and structural characteristics of the AIVPO-450 and AIVPO-I-450 systems (the highest S_{BET} values and phases of aluminum and, especially, of poorly crystallized vanadium) as well as the number and strength of their acidic sites and the presence of sites capable of being more easily reduced would explain the best performances that both systems exhibited. In this sense, although no general correlation has been found between the redox and overall acid–base properties and the catalytic performance in *o*-xylene oxidation of vanadia supported on titania catalysts [11], an optimum V^{4+}/V^{5+} equilibrium, implicated in the oxygen insertion steps, and suitable acid–base properties, implicated in the desorption of the products, are required not only in PA formation [10] but also

Table 3

Conversion and selectivity values to methylbenzaldehyde (MBA), methylbenzoic acid (MBAc), phthalic anhydride (PA), phthalide (PL) and dimerization products (DP)

Catalyst	T (°C)	Conversion (mol%)	Selectivity (mol%)				
			MBA	MBAc	PA	PL	DP ^a
AIVPO-450	325	40.3	4.6	7.0	30.7	44.1	13.6
	350	70.7	4.4	7.1	40.8	41.5	6.1
AIVPO-I-450	300	8.4	7.1	3.7	19.7	37.1	32.5
	325	37.5	4.1	5.0	28.0	49.7	13.3
	350	63.1	3.7	7.2	32.6	44.8	11.7
AIVPO-II-450	350	15.9	5.0	10.0	25.1	44.8	15.1
	360	46.6	3.3	8.8	24.7	46.6	16.7
AIVPO-III-450	350	12.0	5.1	8.8	22.9	50.6	12.8
	360	20.9	2.1	7.3	26.4	52.1	12.1
	380	53.3	4.0	9.7	25.3	39.2	22.0
VPO-450	350	15.6	3.3	7.9	21.0	49.2	18.7
	400	36.2	2.8	5.1	22.1	39.3	30.8

$W=0.1$ g, $F_X=0.6$ mL/min, $F_{O_2}=30$ cm³/min.

^a 2,6-Dimethyl-9,10-dihydroanthracene; 1,2-di-(2-tolyl)ethane.

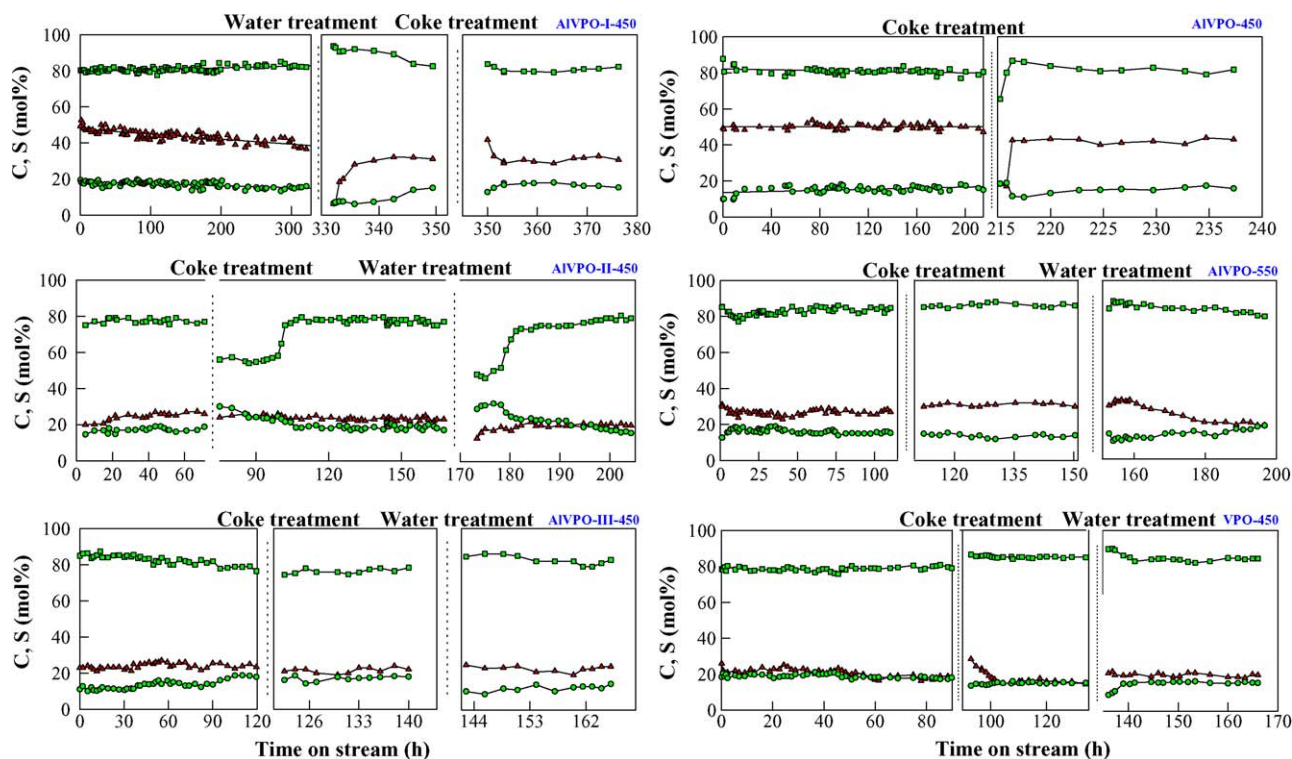


Fig. 4. Evolution of *o*-xylene conversion (▲) and selectivity to MBA+MBAc (●) and PA+PL (■) with time on stream. $T=315\text{ }^{\circ}\text{C}$, $F_X=1.2\text{ mL/h}$, $F_{O_2}=60\text{ cm}^3/\text{min}$. Coke generation treatment: $T=380\text{ }^{\circ}\text{C}$, 24 h. Water treatment: $F_{H_2O}=3\text{ mL/h}$, 30 min.

in the formation of maleic anhydride from *n*-butane on V–P–O catalysts [21]. The desorption of both products would require a high acid strength due to their acidic properties.

3.3.3. Deactivation test

The catalytic behaviour for each catalyst studied with time on stream, at standard conditions, and under the same conditions but after being subjected to coke generation treatment and water treatment, is shown in Fig. 4. As can be seen, a general characteristic was that the catalysts exhibited a very good resistance to deactivation, under the present experimental conditions. Thus, among the ternary systems, only two, AIVPO-I-450 and AIVPO-550, experimented a decrease in conversion values, which were from $\sim 50\%$ to $\sim 40\%$ after 300 h of time on stream and from $\sim 33\%$ to $\sim 27\%$ after 110 h of time on stream, respectively. Such decreases were obtained in relation to the *C* values exhibited by the systems in the steady state (around 1 h). VPO conversion also suffered an 18% loss after 80 h. With respect to selectivity values, hardly any changes took place.

On the other hand, both water and coke treatments negatively affected conversion values which, in some cases, decreased greatly although the initial values were recovered with time on stream. In fact, the one most affected by the coke treatment was one of the two systems that exhibited the best performances, AIVPO-450. This catalyst, which did not undergo changes in either *C* value (around 50%) or selectivity values ($S_{PA+PL}=80\%$; $S_{MBA+MBAc}=16\%$) after 200 h of operation, showed a 67% loss in *C* 1 h after such a treatment. However, the initial *C* value was almost recovered (43%) after 20 h of time on stream. Likewise, the S_{PA+PL} value decreased from 80% to 65%, whereas

the S_{DP} increased to the same degree. Again, the S_{PA+PL} initial value was attained after 20 h of reaction. It is important to emphasize that the colour as well as the textural properties and XRD pattern of the catalyst remained unchanged at the end of

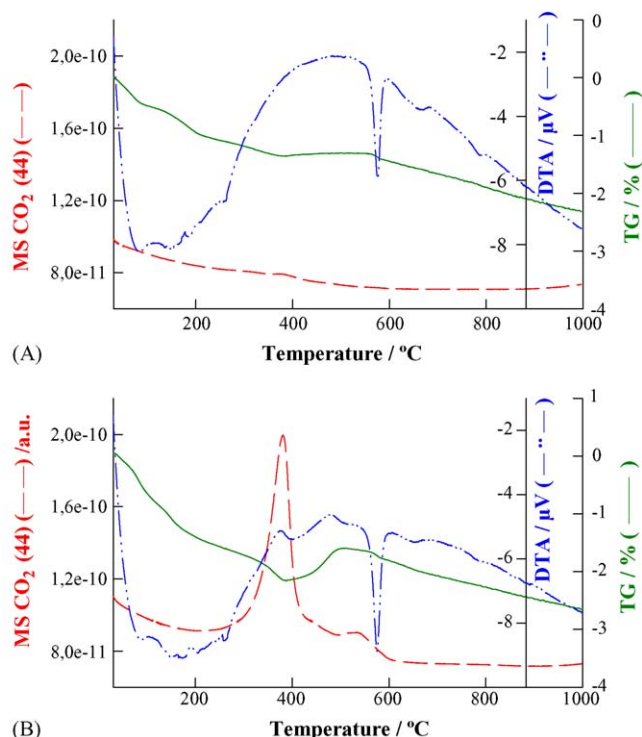


Fig. 5. TG-DTA-MS profiles of AIVPO-III-450 catalyst fresh (A) and used (B).

the deactivation run. Moreover, the TG-DTA analysis revealed a negligible weight loss <0.5% corresponding to an exothermic peak in the 280–417 °C range, similar to that shown in Fig. 5. So, reversible deactivation could be attributed to the temporary poisoning of active sites, according to several authors [13–15]. Moreover, the opposite evolution of S_{PA} and S_{DP} would corroborate the assumption above indicated in the sense that the same active sites are involved in the formation of these products.

Regarding the water treatment, the other more active system, AlVPO-I-450, was the one most affected by the steam. Thus, after 1 h of being subjected to this treatment, the C value underwent a decrease from 40% to 6%, although the initial value was, practically, recovered after 20 h of time on stream, Fig. 4. At the same time, the S_{PA+PL} increased slightly (from 83% to 93%) and the $S_{MBA+MBAC}$ decreased (from 15% to 6%). Since no change in the S_{BET} value was observed at the end of the deactivation run, changes in the equilibrium between Lewis and Brønsted acidic sites, favouring the formation of the latter, induced by the water, would explain the loss of activity observed. In fact, Lewis acid sites predominated on the $AlPO_4$ and on V–P–O [21–23].

4. Conclusions

In summary, the presence of aluminum in the precipitation medium of vanadyl phosphate resulted in systems exhibiting better catalytic behaviour than the binary system in the selective oxidation of *o*-xylene. Moreover, we found that the source of vanadium, and the composition and the thermal treatment of the ternary systems clearly influenced their performances. Thus, $VOCl_3$ as the source of vanadium, a high Al/V ratio and a thermal treatment at 450 °C are factors that improved the catalytic behaviour. Under the experimental conditions employed, total oxidation products were not detected, obtaining high values of selectivity >90% to selective products (phthalic anhydride, phthalide, methylbenzaldehyde and methylbenzoic acid) at high values of conversion (around 70%). The balance in the values of selectivity is closed with dimerization products, which predominated at the lowest temperatures. The most active systems also showed higher reducibility and higher acidity (in number of sites and strength).

In general, all the catalysts studied exhibited a very good resistance to deactivation with time on stream. Both water and coke treatments negatively affected conversion values that, in some cases, decreased greatly although the initial values were recovered with the time on stream. The most affected by the treatments were the systems that exhibited the best performances.

The recovery of the activity along with the unchanged textural properties and XRD patterns of the catalysts after being subjected to those treatments lead us to suggest that the reversible deactivation could be attributed to the partial poisoning of the active sites as well as to changes in their nature.

Acknowledgements

Subsidies granted by the Ministerio de Educación y Ciencia and FEDER funds (Project CTQ2005-04080) and (CTQ 2004-21662-E), CA Concorde (Project NMP2-CT-2004-505834) and Junta de Andalucía are gratefully acknowledged. J. Luque is indebted to the Ministerio de Educación y Ciencia for a FPU fellowship. The authors also wish to acknowledge the EDX analysis carried out by Prof. Eduardo Martínez of Dpto. Q. Inorgánica of Universitat de Valencia (Spain).

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