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Gas-phase selective oxidation of toluene on TiO_2–sepiolite supported vanadium oxides
Influence of vanadium loading on conversion and product selectivities

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Abstract

Gas-phase selective oxidation of toluene has been carried out on vanadium oxide systems (5–20 wt.% of V_2O_5, equivalent to 0.4–1.7 theoretical monolayers) supported on TiO_2–sepiolite (with titania loading around the theoretical monolayer, 12 wt.%) and on sepiolite. A study has been made on both the influence of vanadia loading and of the support on the catalytic behaviour of the supported vanadium systems. The reducibility by H_2 TPR was also studied as well as the acid and basic/redox sites from the results of conversion of the 2-propanol test reaction of the solids. Benzaldehyde, benzoic acid and several coupling products were the main ones detected, attaining over 50% selectivity towards the benzaldehyde and benzoic acid products at a total conversion around 10%. The activity and selectivity to the selective products exhibited by vanadium systems supported on mixed support were superior to those exhibited by the systems supported on sepiolite and increased notably in both series with the increase in vanadium loading. The best catalytic behaviour exhibited by the vanadium systems supported on mixed support, which also exhibited the highest density of sites capable of being reduced (as well as their reducibility) and of those responsible for propanone formation, could be attributed not only to the different balance of the vanadia species existing in the two supports (monomeric + oligomeric/polymeric), but also to such other factors as the nature of the support and, concretely, its chemical composition.

Keywords: TiO_2–sepiolite supported vanadium oxides; Sepiolite supported vanadium oxides; Acid–base/redox properties; 2-Propanol conversion; H_2 TPR; Gas-phase selective oxidation of toluene; Benzaldehyde; Benzoic acid

1. Introduction

Gas-phase hydrocarbon partial oxidation is a very attractive and difficult challenge in heterogeneous catalysis. Specifically, the oxidation reaction of toluene to benzaldehyde (BA) and/or benzoic acid (BAc) is one of the most extensively researched reactions because of its significance for the chemical industry. Both products, BA and BAc, are versatile chemical intermediates in the manufacturing of pharmaceuticals, dyes, perfume and flavouring chemicals, alkyld resins, polyesters, plasticizers, etc. However, the direct use of this reaction for the manufacturing of BA and BAc has not yet been achieved in spite of many efforts to improve catalytic selectivity [1–12]. Supported vanadium systems, mainly on TiO_2 support, represent one of the most widely studied catalysts for this reaction [2,4,5,7,10,11] which is generally assumed to occur according to the Mars–van Krevelen mechanism [13]. This mechanism involves a reduction–oxidation cycle of the vanadia active sites through consecutive steps starting with the adsorption of the reactant molecule. Thus an effective catalyst could involve redox potential and acid–base properties [14,15]. Furthermore, the nature and the surface area of the support as well as its vanadium content are all key factors in the formation of active surface species [4,7,8,10,16–21]. In this sense, there are different opinions in the literature related to the active vanadia species implicated in hydrocarbon selective oxidation and particularly in toluene oxidation: monomeric and/or polymeric species and bridging or vanadyl oxygen atoms. Thus, Freitag et al. showed that monomeric species are the

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active ones and that lattice vanadyl oxygen is inserted into the BA product [22] in agreement with the results of Konietzni et al. [8]. Wachs and Weckhuysen on the other hand, stressed the critical role of bridging oxygen in V–O-support [19] as did Bulushev et al. [10]. Grzybowska-Swierkosz pointed out the necessary participation of both monomeric and polymeric species [18].

In our previous studies [23–25] on vanadium systems supported on TiO_2-coated sepiolite, a high dispersion of TiO_x was found on sepiolite, a very cheap fibrous hydrated magnesium silicate belonging to the clay mineral family. The surface properties of the vanadia species and, consequently, their catalytic behaviour in toluene oxidation were influenced by titania loading on sepiolite, the vanadium systems being those with the highest titania loading and therefore the most active and selective catalysts [23,24]. Furthermore, well-dispersed vanadium was achieved in the systems supported not only on the TiO_2-coated sepiolite support but also on the sepiolite depending on the vanadia species structures of support type and vanadium loading [25]. Thus, at the lowest vanadia loadings, isolated tetrahedral and polymetavanadate type species predominated. At higher loadings (15 wt.% or above), vanadium oxides were also presented as crystalline V_2O_5 nanoparticles and, especially in %V/Sepc systems, as pyro- and meta-magnesium vanadates. In our present work, we study the catalytic behaviour of the aforementioned vanadia species in toluene selective oxidation. Their reducibility by the H_2 temperature programmed reduction (TPR) technique was also studied along with the acid and basic/redox sites of the solids from the results of conversion of 2-propanol test reaction.

2. Experimental

2.1. Catalyst preparation

Vanadium oxide systems (5–20 wt.% of V_2O_5) supported on TiO_2–sepiolite (with titania loading around the theoretical monolayer, 12 wt.%) 12Ti-Sep, and on sepiolite, Sepc, were prepared by the wet impregnation method as previously reported [25]. These systems will be denoted xV/12Ti-Sep and xV/Sepc where x indicates the theoretical percentage of V_2O_5 ($x = 5$, 10, 15 and 20 wt.%) which represents approximately 0.4, 0.8, 1.2 and 1.7 two-dimensional polyvanadate theoretical monolayers, respectively, calculated as 0.15 wt.% V_2O_5/m^2 of support [16,17]. The impregnation was carried out with vanadyl oxalate in methanol solution ($NH_4VO_3/C_2O_2H_2$ molar ratio = 1/2) and the resulting solids were calcined in air at 723 K for 3 h.

The 12Ti-Sep support was obtained by wet impregnation of the natural sepiolite (Sep) ($S_{BET} = 143\ m^2/g$) with the desired volume of titanium isopropoxide in *n*-hexane solution as previously reported [23,24]. Both 12Ti-Sep and Sepc supports were calcined in air at 923 K for 3 h.

2.2. 2-Propanol decomposition

The 2-propanol conversion process was studied by using a microcatalytic pulse reactor [26] under the following conditions: 2-propanol (liquid) volume/pulse size 2 μL; reaction temperature, 443–523 K; catalyst weight, 0.1 g; flow rate of nitrogen carrier gas, 10 cm^3/min. Before the experiments, the samples were pre-treated by *in situ* heating under nitrogen (10 cm^3/min) for 30 min at 573 K. The 2-propanol pulses were injected successively until constant values of conversion and yield of products were attained (usually after 3–4 pulses). The final values reported are the mean of values obtained in 3 or 4 successive pulses after the stationary state of activity was obtained.

The reaction products, propene, propanone and diisopropyl ether, were analyzed by gas chromatography (CG) with a flame ionization detector (FID). The column was 2 m long (1/8 in., stainless-steel) packed with 5% celanese-ester on Chromosorb G AW-DMCS 80/100, at 323 K. A blank test showed the absence of thermal reaction in the absence of the catalyst.

2.3. TPR measurements

TPR experiments were performed in a Micromeritics TPD/TPR 2900 analyser with a thermal conductivity detector (TCD). Samples of 50 mg were first treated in Ar (373 K, 1 h) and then put into contact with an H_2/Ar mixture (10 mol% H_2; 50 cm^3/min) and heated (10 K/min) to a final $T = 1073$ K. The experimental error on the H_2 consumption determination was $\leq 2\%$. A cold trap (liquid nitrogen and 2-propanol) was used to prevent reaction products, mostly water, from reaching the detector.

2.4. Selective oxidation of toluene

Toluene selective oxidation was carried out in a continuous-flow fixed-bed reactor at atmospheric pressure [27]. 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 (593–653 K) was monitored by a thermocouple located in the catalyst bed. An analysis of reagent and product composition was carried out on-line using a multicolumn gas equipped with FID and TCD detectors in parallel. CO_2, CO and O_2 were separated in two columns in series, 3 m Porapak Q and Molecular Sieve 5 A (for CO and O_2 separation) and analyzed by the TCD. Toluene 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 523 K in order to avoid any condensation of the products. The catalyst (ca. 100 mg, <0.149 mm) was pre-treated at the reaction temperature for 1 h in a N_2 flow (30 cm^3/min). Toluene was fed by means of a microfeeder at 0.6 mL/h and the molar ratio toluene/O_2/He was 1/13/33. Previously, products had been identified by gas chromatography–mass spectrometry. Conversion (X_{tol}) and selectivity to products (S_i) are expressed as mol% on a C atom basis. The adequate results were those in which the carbon balance was $\leq 5\%$. The values of the toluene reaction rate, r_{tol}, were obtained from X_{tol} values, according to the equation, $r_{tol} = X_{tol}F/W \times 100$, where W is the catalyst weight and F is the feed rate of toluene

Table 1
Surface atomic ratios from EDX analysis; surface area, volume and diameter of porous; chemisorption pyridine values from Ref. [25]

Catalyst	EDX		S_{BET} (m^2/g)	V_P (mL/g)	d_p (Å)	Py (μmol/m^2)		
	V/(Ti + Si)	V/Si				373 K	473 K	573 K
12Ti-Sep	–	–	82	0.27	139	1.01	0.29	0.11
5V/12Ti-Sep	0.07	0.08	54	0.27	200	0.78	0.35	0.19
10V/12Ti-Sep	0.16	0.19	34	0.20	239	2.15	1.10	0.78
15V/12Ti-Sep	0.29	0.35	24	0.17	254	1.69	0.49	0.12
20V/12Ti-Sep	0.37	0.43	23	0.17	307	1.16	0.26	0.21
Sepc	–	–	80	0.37	185	0.34	0.26	0.15
5V/Sepc	–	0.06	70	0.33	190	0.85	0.36	0.19
10V/Sepc	–	0.09	58	0.28	196	1.36	0.55	0.41
15V/Sepc	–	0.20	38	0.26	272	0.86	0.55	0.44
20V/Sepc	–	0.32	26	0.22	244	0.81	0.19	–[a]

[a] There was no Py chemisorption.

(mol/h). Likewise, the values of the product formation rate, r_i, were obtained using the corresponding value of conversion of toluene to product i. Blank runs showed the reactor walls to be inert with respect to toluene oxidation at the temperature range studied.

3. Results and discussion

Table 1 shows the results of the surface chemical composition previously determined [25] by energy dispersion of X-rays (EDX), and of pyridine chemisorption experiments, as well as the textural properties (BET surface area, S_{BET}, pore volume, V_p, and mean pore diameter, d_p) of the solids studied.

3.1. 2-Propanol decomposition

In all the catalysts studied, dehydration to propene (mainly on acid sites) and dehydrogenation to propanone (mainly on basic/redox sites) took place, as shown in Table 2, where the conversion and selectivity values obtained at the 443–523 K temperature range are collected. Diisopropyl ether was also observed, although the selectivity values attained were never higher than 10%. On increasing reaction temperature, the total conversion of 2-propanol, as well as the propene selectivity values, increased, while the propanone selectivity values decreased, which agrees with the results reported by Wang et al. [28]. In fact, propanone was the major product at the lowest temperature, 443 K, for %V/12Ti-Sep catalysts (selectivity values > 70%).

On the other hand, both dehydration to propene and the dehydrogenation to propanone data, for all the catalysts studied, were found to fulfil the Bassett–Habgood rate equation for first-order reactions:

$$\ln\left[\frac{1}{1-X}\right] = \mathrm{kK}RT\left(\frac{W}{F}\right)$$

where X is the conversion of 2-propanol to propene or to propanone, kK the apparent rate constant for propene or propanone formation, W the catalyst weight, and F is the flow rate of carrier gas.

The kK values, in mol/atm s m^2, for propene and propanone formation at each reaction temperature studied for every catalysts, are also collected in Table 2. The vanadium systems displayed higher activity than their corresponding supports in the two processes, while Sepc showed activity only in this dehydration reaction [24]. In addition, the %V/12Ti-Sep systems were more active than the %V/Sepc ones in the dehydrogenation reaction, whereas in the dehydration reaction the opposite behaviour was observed. With respect to vanadia loading, there was not a clear tendency in either reaction. However, the comparison of the $\mathrm{kK}_{C_3H_6}$ and $\mathrm{kK}_{C_3H_6O}$ values obtained around isoconversion (from 5 to 10 mol% in %V/12Ti-Sep systems and from 6 to 15 mol% in %V/Sepc) in Table 2 indicated that the propene and propanone formation and therefore the density of acid and basic/redox sites, respectively, increased as the loading of vanadium in the systems rose. In this respect, the increase of propanone with vanadium loading up to one to two monolayer content on V_2O_5/TiO_2 (anatase) has been reported [18]. Furthermore, the nature of the support and, more specifically, the presence of titania on the sepiolite surface affected both types of properties. Thus, the vanadia species present in the mixed support exhibited, as a general tendency, a higher number of basic–redox sites and a lower number of acid sites responsible for propene formation than those on Sepc. Here, it is worth noting that there is no exact correlation between the apparent rate constant values of propene formation (in Table 2) and the density of acid sites previously obtained from pyridine chemisorption at 273, 373 and 473 K (shown in Table 1). In fact, these results from pyridine chemisorption indicated a higher density of weak acid sites and a similar value in those of medium and strong strength in the vanadia species on mixed support. The non-existing correlation between the propene formation data and pyridine or ammonia chemisoption has also been reported with vanadium systems supported on SiO_2 and on MgO [29] and other catalysts like nanocrystallite alumina [28] and TiO_2–ZrO_2 [30]. A possible explanation would be the participation of the basic sites in propene formation as well as of the acid sites. In this respect, dehydration may take place via a concerted E2 mechanism which involves both sites on solids that are not purely basic or acidic [30,31].

Table 2
Conversion, selectivity and apparent rate constants for propene ($kK_{C_3H_6}$) and propanone ($kK_{C_3H_6O}$) formation, for 2-propanol decomposition on all catalysts and temperatures studied

Catalyst	T (K)	Conversion (mol%)	Selectivity (mol%)			$kK_{C_3H_6}$ ($\times 10^8$ mol/atm s m^2)	$kK_{C_3H_6O}$ ($\times 10^8$ mol/atm s m^2)
			C_3H_6	$C_6H_{14}O$	C_3H_6O		
12Ti-Sep	523	4.1	77	16	7	1.5	0.1
5V/12Ti-Sep	443	2.5	5	–	95	0.1	2.1
	463	7.1	*70*[a]	*3*	*27*	*4.2*	*1.6*
	503	20.1	86	6	8	14.4	1.3
	523	27.1	89	6	5	20.2	1.1
10V/12Ti-Sep	443	4.9	*9*	*6*	*85*	*0.6*	*5.8*
	463	20.0	85	3	12	24.6	3.5
	503	32.3	85	7	8	39.6	3.7
	523	42.6	88	6	6	56.0	3.8
15V/12Ti-Sep	443	7.0	31	1	68	4.3	9.4
	463	8.1	*59*	*2*	*39*	*9.1*	*6.0*
	503	14.5	71	8	21	18.7	5.5
	523	25.3	82	6	12	38.9	5.7
20V/12Ti-Sep	443	2.9	4	–	96	0.2	5.6
	463	10.1	*61*	*5*	*34*	*12.4*	*6.9*
	503	30.5	77	7	16	49.4	10.3
	523	37.8	81	8	11	65.1	8.8
Sepc	523	2.4	96	2	2	1.1	0.02
5V/Sepc	443	4.5	*65*	–	*35*	*2.9*	*1.6*
	463	15.8	84	1	15	13.3	2.4
	503	26.6	87	7	6	23.2	1.6
	523	43.0	89	7	4	38.3	1.7
10V/Sepc	443	2.1	7	–	93	0.1	1.6
	463	6.2	*69*	*3*	*28*	*3.3*	*1.4*
	503	23.2	87	6	7	16.0	1.3
	523	39.6	89	6	5	30.1	1.7
15V/Sepc	443	14.5	*74*	*1*	*25*	*14.0*	*4.7*
	463	20.9	83	5	12	22.5	3.3
	503	48.2	87	8	5	61.0	3.5
	523	59.4	86	8	5	79.5	4.6
20V/Sepc	443	15.5	*74*	*2*	*24*	*22.1*	*7.2*
	463	18.1	80	7	13	27.1	4.4
	503	41.4	84	9	7	69.9	5.8
	523	62.1	85	9	6	123.4	8.7

[a] Selectivity values at isoconversion are marked in italics.

3.2. TPR

TPR profiles of the two series of vanadium systems also exhibited mainly one defined peak in the 811–869 K temperature range, as can be seen in Fig. 1. 12Ti-Sep and Sep supports were not reduced in the temperature range studied [24]. Both the maximum reduction rate peak temperature (T_M) and the total $H_{2(M)}$ consumption values, shown in Table 3, increased with vanadium loading. In addition, the %V/12Ti-Sep systems, with the exception of 10V/12Ti-Sep, were more easily reducible (lower T_M) than their corresponding %V/Sepc systems, and the H_2 consumption values were also higher in the %V/12Ti-Sep systems, mainly in those with vanadia loading below the theoretical monolayer (<15 wt.%). This indicates a higher density of sites capable of being reduced in the vanadium species on mixed support than on Sepc. Furthermore, the values of the [$H_{2(M)}$/V] molar ratio (between 0.4 and 0.5) and of the average oxidation state (AOS) of vanadium after reduction (about 4), as indicated in Table 3, would point to approximately a 50% reduction as well as a final oxidation state around V^{4+} in all the vanadium systems studied, based on the assumption that the vanadium had been V^{5+} before the reduction.

A more exhaustive analysis of the TPR profiles, after deconvolution, allows us to demonstrate the presence of two peaks in the 659–717 and 736–810 K temperature range, respectively, in addition to the main one in the range between 811 and 861 K, Table 3. The corresponding values of $H_{2(i)}$ consumption are also shown in Table 3. These three peaks would be ascribed to the reduction of monomeric, oligomeric and polymeric surface vanadia species, respectively. Such an assignment is in agreement with the H_2 TPR results previously obtained on systems with 10 wt.% V_2O_5 supported on %Ti-Sep and commercial anatase [24] as well with as the results reported in the literature [10,16–18,20,21]. Likewise, the very small

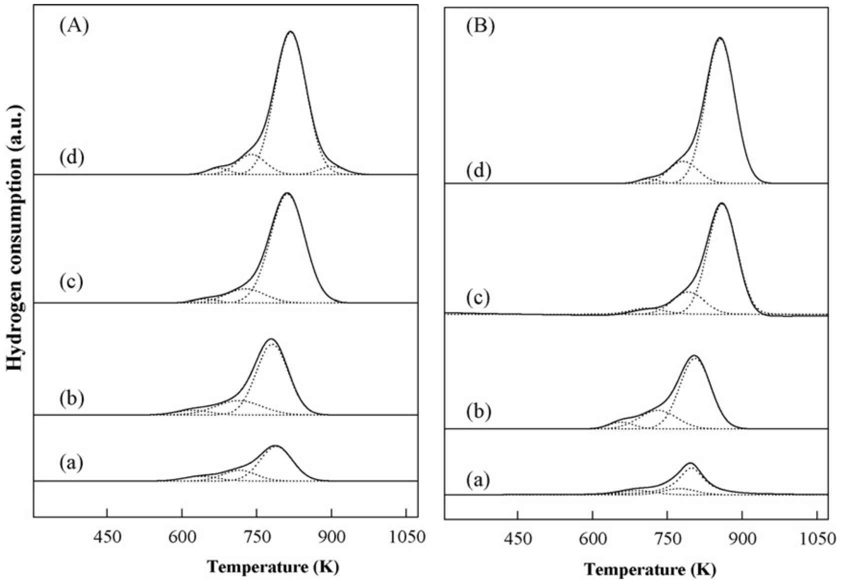

Fig. 1. (A) TPR profiles for: (a) 5V/12Ti-Sep, (b) 10V/12Ti-Sep, (c) 15V/12Ti-Sep and (d) 20V/12Ti-Sep; (B) TPR profiles for: (a) 5V/Sepc, (b) 10V/Sepc, (c) 15V/Sepc and (d) 20V/Sepc.

peak (about 4% of total area) at 916 K, Table 3, which appears only in the 20V/12Ti-Sep TPR profile, can be attributed to a reduction of V_2O_5 crystals. On the other hand, the percentage of monomeric plus oligomeric species is higher in the systems with the lowest vanadium loading whereas polymeric ones are the most important in the systems with the highest vanadium loading, as can be seen in Fig. 2, which shows the evolution of H_2 consumption for each type of vanadium species in function

Table 3

Maximum temperature, T_M; total H_2 consumption, $H_{2(M)}$; molar ratio of $H_{2(M)}$ to theoretical vanadium loading, $[H_{2(M)}/V]$; average oxidation state (AOS) of vanadium after reduction; temperature, T_i, and H_2 consumption, $H_{2(i)}$, for each peak after deconvolution from TPR experiments

Catalyst	T_M (K)	$H_{2(M)}$ (μmol/m^2)	$[H_{2(M)}/V]$[a] (mol/mol)	AOS of V[a]	T_i (K)	$H_{2(i)}$ (μmol/m^2)
5V/12Ti-Sep	811	5.9	0.58	3.84	659	0.57
					736	1.31
					811	4.02
10V/12Ti-Sep	846	12.8	0.42	4.16	681	0.64
					772	2.73
					840	9.43
15V/12Ti-Sep	850	31.0	0.46	4.08	680	0.59
					760	3.66
					845	26.75
20V/12Ti-Sep	856	42.2	0.45	4.10	704	1.06
					770	4.50
					849	35.1
					916	1.60
5V/Sepc	832	3.4	0.44	4.12	725	0.38
					810	0.52
					832	2.50
10V/Sepc	836	7.3	0.39	4.22	687	0.38
					761	1.66
					836	5.25
15V/Sepc	857	19.5	0.45	4.10	706	0.96
					789	3.31
					857	15.2
20V/Sepc	869	39.5	0.46	4.08	717	0.71
					786	5.21
					861	33.57

[a] Assuming V^{5+} before reduction.

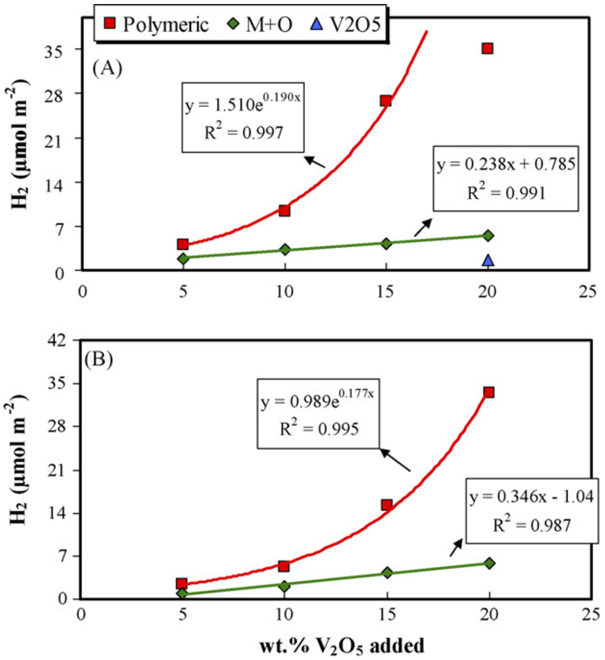

Fig. 2. Hydrogen consumption in the reduction of monomeric + olygomeric (M + O) and polymeric species as a function of vanadia loading for (A) %V/12Ti-Sep and (B) %V/Sepc systems.

of the vanadium loading of the systems. The evolution was linear in the case of monomeric + oligomeric species, whereas an exponential evolution was obtained for the polymeric species, in clear agreement with the results previously reported by Raman, UV–vis and TEM [25]. The equations obtained indicate that, regardless of the type of species, those existing on mixed support consumed more H_2 that the ones on Sepc, and consequently their AOS of vanadium in the %V/12Ti-Sep systems are lower (Table 3). Furthermore, their reducibility improved according to the lower values of reduction rate peak temperature (T_i) in Table 3.

It is noteworthy that, as in our previous study [24], here there also seems to be a relationship between the density of sites capable of being reduced and the density of those responsible for propanone formation on the vanadium systems according to Fig. 3.

3.3. Selective oxidation of toluene

The conversion and selectivity to the main products obtained for all the catalytic systems as a function of temperature are presented in Table 4. These values correspond to the average of three values (experimental error ≤4%) obtained in the steady state (1–2 h of time on stream). As can be seen, the products obtained were BA and BAc and several coupling products (CP) belonging to Andersson's route 2 [3], such as methyldiphenylmethanes and methyldiphenylmethanones (isomer distribution unknown). Phthalic (<15%) and maleic (<10%) anhydrides were also detected mainly at the highest temperatures and vanadium loadings. Likewise, CO_2 was detected only at 653 K, showing the 20V/Sep as the highest value of 36%, while CO was never obtained.

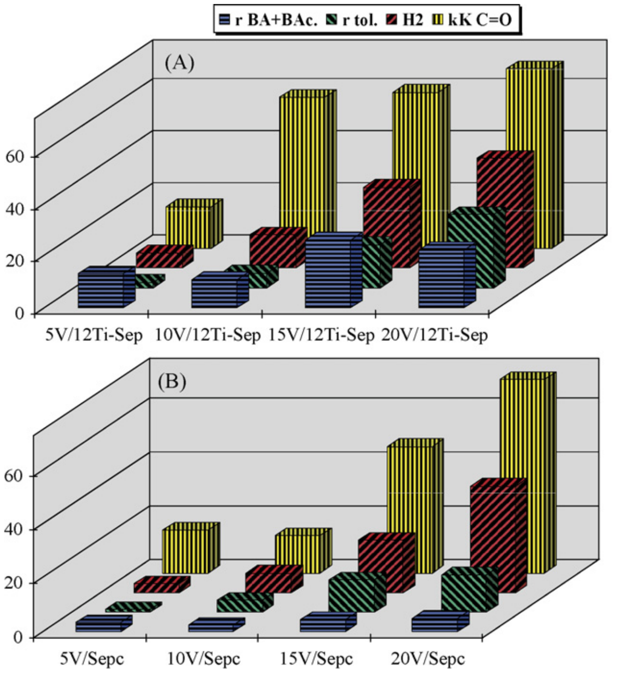

Fig. 3. Toluene reaction rate (r_{tol}, ×10^5 mol/h m^2) at 653 K and benzaldehyde and benzoic acid formation rate (r_{BA+BAc}, ×10^6 mol/h m^2) at isoconversion in selective oxidation of toluene; apparent rate constant for propanone formation (kK$_{C_3H_6O}$, ×10^9 mol/atm s m^2) at isoconversion in 2-propanol decomposition and H_2 consumption in TPR experiments (H_2 µmol/m^2), as a function of vanadia loading for (A) %V/12Ti-Sep and (B) %V/Sepc systems.

In general, the conversion increased with the reaction temperature and this increase was accompanied by a decrease in selectivity to BA (S_{BA}) and to S_{CP}, whereas the S_{BAc}, as well as the selectivity to anhydrides and CO_2, increased. Furthermore, it is interesting to note that CP became the most important products formed at the reaction temperatures below 653 K on %V/Sepc systems while in the case of %V/12Ti-Sep they were, principally, BA and BAc (selectivity values from 40 to 75% at 593 K). In fact, the yields to BA and BAc obtained with these vanadium systems supported on 12Ti-Sep are comparable to some of those reported in the literature under similar kinetically controlled experimental conditions [4,8,18]. Thus, S_{BA+BAc} = 52% and X_{tol} = 12% was obtained at 653 K on 20V/12Ti-Sep.

On the other hand, the activity, r_{tol} in mol/h m^2, of the vanadium systems supported on 12Ti-Sep was superior to that exhibited by the systems supported on Sepc, and in both series it notably increased with increases in vanadium loading (Table 4). In fact, the activity at 653 K exhibited by the systems with 20 wt.% vanadium content is over ten times that exhibited by systems with 5 wt.%. This is in accordance with the concentration of oxygen in the catalysts able to react with H_2 from TPR experiments, Fig. 2, showing that the higher the concentration of monomeric + oligomeric and, especially, of polymeric species, the higher the specific rate of the reaction. Additionally, the %V/12Ti-Sep systems were more selective to BA and BAc while %V/Sep systems were more so to CP. As a function of vanadium loading, the systems with loadings of 5 and 10 wt.% were found to be the most selective to side chain

Table 4
Conversion (X_{tol}), toluene reaction rate (r_{tol}) and selectivity values to benzaldehyde and benzoic acid (S_{BA+BAc}), coupling products (S_{CP}), carbon dioxide (S_{CO_2}), phthalic and maleic anhydrides (S_{anh}) in selective oxidation of toluene on all catalysts studied

Catalyst	T (K)	X_{tol} (mol%)	r_{tol} ($\times 10^5$mol/h m^2)	S_{BA+BAc} (mol%)	S_{CP} (mol%)	S_{CO_2} (mol%)	S_{anh} (mol%)
5V/12Ti-Sep	593	0.7	0.7	66 + 0	34	–	–
	613	0.8	0.9	65 + 0	35	–	–
	633	1.3	1.3	65 + 0	35	–	–
	653	2.1	2.2	*61 + 0*[a]	*30*	*10*	–
10V/12Ti-Sep	593	0.7	1.1	57 + 0	43	–	–
	613	1.1	1.7	56 + 0	45	–	–
	633	2.0	3.4	*44 + 15*	*34*	–	7
	653	3.4	5.7	34 + 9	28	27	
15V/12Ti-Sep	593	0.8	1.9	75 + 0	26	–	–
	613	1.7	4.0	*45 + 20*	*28*	–	*8*
	633	3.6	8.4	34 + 25	24	–	17
	653	7.1	16.6	27 + 22	15	24	13
20V/12Ti-Sep	593	2.1	5.2	*24 + 19*	*49*	–	*8*
	613	2.6	6.4	27 + 17	47	–	*9*
	633	6.2	15.2	26 + 26	32	–	17
	653	11.5	28.2	23 + 29	21	10	17
5V/Sepc	593	0.4	0.4	24 + 0	76	–	–
	613	0.5	0.4	29 + 0	71	–	–
	633	0.8	0.7	34 + 0	66	–	–
	653	1.1	0.9	*37 + 0*	*63*	–	–
10V/Sepc	593	1.0	1.0	*25 + 0*	*76*	–	–
	613	1.4	1.4	25 + 0	67	–	9
	633	3.1	3.0	21 + 14	47	–	18
	653	4.5	4.4	27 + 15	43	–	15
15V/Sepc	593	1.2	1.7	*26 + 0*	*63*	–	*11*
	613	1.7	2.5	24 + 9	56	–	11
	633	2.6	3.9	22 + 14	51	–	14
	653	8.1	12.0	15 + 18	30	17	19
20V/Sepc	593	0.6	1.3	21 + 0	80	–	–
	613	0.9	2.0	*25 + 0*	*75*	–	–
	633	1.9	4.0	23 + 11	56	–	10
	653	6.4	13.8	16 + 10	28	36	9

[a] Selectivity values at isoconversion are marked in italics.

partial oxidation products and to CP, these latter principally at the lowest reaction temperature. However, taking into account the different values of surface area exhibited by the catalysts, (Table 1), as well as the aforementioned change in the distribution of reaction products with temperature (or with conversion), the opposite tendency is obtained. Thus, as can be seen in Fig. 3 the activity for benzaldehyde and benzoic acid formation (r_{BA+BAc}, in mol/h m^2, at isoconversion) was higher in the systems with vanadium loading of 15 and 20 wt.% than in those of 5 and 10 wt.%. The same behaviour was observed in the formation of CP products. Furthermore, this tendency is also obtained using the r_{BA+BAc} values at each temperature studied, Table 4, instead of the ones corresponding to isoconversion.

On the whole, from these results and those obtained from the 2-propanol reaction and H_2 TPR, a relationship could exist between the catalytic performance in terms of specific total activity and activity for BA and BAc formation, and the density of sites capable of being reduced (as well as their reducibility) and of those responsible for propanone formation, according to Fig. 3. Such a relationship is the same as that previously obtained with vanadium systems on %Ti-Sep mixed supports [24]. An adequate density of sites responsible for propene formation also seems to be required in order to enhance the activity and selectivity of the catalysts (Tables 2 and 4). In this sense, the acidic sites favour the adsorption of the hydrocarbon molecule and increase the desorption of acidic products, thereby protecting their further total oxidation [14,15]. Moreover, the present study has also shown that the monomeric + oligomeric species were not the only ones that were active and selective in toluene selective oxidation, as other authors have reported [8,22]. The polymeric ones were also active and selective and were, at the same time, the most abundant species on the surface of vanadium systems with vanadia content over monolayer capacity (1.2 and 1.7 monolayers). This result is in agreement with those reported by other authors [10,18]. Likewise, the best catalytic performance exhibited by the vanadium systems supported on mixed support in relation to those supported on Sep could be attributed to the different balance of those vanadia species in the two supports, the ratio of monomeric + oligomeric to polymeric ones being slightly higher for vanadia supported on Sepc, as shown in Fig. 2. However, other factors should also be considered, like the nature of the support and, more specifically, its chemical composition affecting the vanadia species–support interaction. Indeed, the presence of titania on Sepc is likely to result in an interaction of the vanadia species with titania, whereas in the case of Sepc the interaction could take place with silanol groups and at high vanadia content with magnesium atoms [23,25]. The difference in the electronegativity of titanium, silicium and magnesium atoms should affect the electronic densities around vanadium and oxygen atoms and, consequently, the degree of ionicity of the V–O bond and, parallelly, the nucleophilic character (basic) of oxygen and the electrophilic (acidic) of vanadium ions as well as their redox properties [14,15]. However, the initial oxidation state of vanadium in both systems would be another factor to take into consideration given that the electronegativity of an ion varies with its oxidation state. In this sense, the initial medium oxidation state of the vanadium species present on Sepc seems to be slightly higher than that of the species on mixed support according to X-ray photoelectron spectroscopy results [32], which in turn would be in agreement with the formation of $V_3Ti_6O_{17}$ and TiV_2O_6 oxide phases on %V/12Ti-Sep as we previously reported [25].

4. Conclusions

Vanadium oxides supported on TiO_2-coated sepiolite (12Ti-Sep) and, as a reference, on sepiolite (Sepc) were found to be active and selective catalysts for the gas-phase selective oxidation of toluene. Under the kinetically controlled experimental conditions studied, benzaldehyde (BA) and benzoic acid (BAc) became the most important products formed in the whole temperature range studied (593–653 K) on %V/12Ti-Sep while in the case of %V/Sep there were several coupling products. Thus, $S_{\mathrm{BA+BAc}} = 52\%$ and $X_{\mathrm{tol}} = 12\%$ was obtained at 653 K on 20V/12Ti-Sep. CO_2 was detected only at the highest temperature, showing the 20V/Sep as the highest value of 36%. The activity of the vanadium systems supported on mixed support was superior to that exhibited by the systems supported on Sepc. In both series of catalysts the activity increased notably with vanadium loading.

A relationship between the toluene reaction rate and the BA and BAc formation rate and the density of sites capable of being reduced (as well as their reducibility) and of those responsible for propanone seems to exit, the systems with vanadium loading over theoretical monolayer capacity being the ones that showed the highest values. In these systems, mainly polymeric vanadia species exist in addition to monomeric + oligomeric ones. Thus, the best catalytic performance exhibited by the vanadium systems supported on mixed support could be attributed not only to the different balance of the vanadia species existing in the two supports (monomeric + oligomeric/polymeric species), but also to other factors like the nature of the support and, concretely its chemical composition, affecting the vanadia species–support interaction and, consequently, the active sites. The initial oxidation state of vanadium in both systems would be another factor to take into consideration.

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