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Influence of the acid–base/redox properties of TiO_x-sepiolite supported vanadium oxide catalysts in the gas-phase selective oxidation of toluene

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Abstract

Catalytic behaviour in the selective oxidation of toluene of a series of vanadium systems supported on TiO_x-coated sepiolite (6, 12 and 25 wt.% TiO_2) with a vanadia loading around the theoretical monolayer (10 wt.%) has been investigated. The surface acid–base/redox properties of the solids were also evaluated by using 2-propanol conversion and pyridine chemisorption. The reducibility of surface vanadia species was studied by H_2-TPR. Surface properties of vanadia species and, consequently, their catalytic behaviour were influenced by titania loading on sepiolite. Thus, the vanadium systems with the highest titania loading were the most active and selective in toluene oxidation. Furthermore, this behaviour seems to be mainly related to the density of the active sites capable of being reduced and producing propanone in the vanadium systems.

Keywords: TiO_x-sepiolite supported vanadium oxide; TiO_x-sepiolite; Acid–base/redox properties; 2-Propanol conversion; Pyridine chemisorption; H_2-TPR; Toluene selective oxidation

1. Introduction

At present, supported vanadium oxide catalysts are still being intensively studied because of their wide range of applicability in the chemical industry [1]. Thus, vanadia supported on titania (anatase) is known to be an efficient catalyst in the partial oxidation of hydrocarbons [2,3]. However, during the last 15 years, TiO_2-based composites have been developed as supports of vanadia, in particular TiO_2–SiO_2, mainly in order to improve the mechanical strength, thermal stability and surface area of TiO_2 [4–9]. In this respect, our research is concerned with the use of a natural sepiolite (Sep), instead of silica, as the starting material for the preparation of TiO_x-Sep supports of vanadium oxide. This very cheap fibrous hydrated magnesium silicate belonging to the clay mineral family possesses a relatively high surface area and surface –OH groups that could interact with titanium salt. Many papers have been published concerning the use of Sep and modified Sep as catalysts, or metal supports [10–12], though we have no proof of the use of TiO_x-coated sepiolite as a support for vanadium oxide.

The partial oxidation of toluene in gas-phase to benzaldehyde (BA) and benzoic acid (BAc) is a reaction of increasing industrial interest. The reaction follows the Mars–van Krevelen mechanism so an effective catalyst could involve redox potential and acid–base properties [13]. In this context, the present work is aimed at the study of vanadium systems with the same vanadium loading supported on TiO_x-Sep with appropriate amounts of titanium to provide a range of surface coverage of sepiolite support. We, specifically, have researched the effect that the dispersion of titania on Sep might have on the structure and surface properties of vanadia species and, consequently, on their catalytic behaviour in the selective oxidation of toluene. Furthermore, the influence that the previous thermal treatment of the Sep had on the titania dispersion was also evaluated. Conversion of 2-propanol was selected for characterization of acid (responsible for dehydration to propene) and basic/redox (responsible for propanone formation) sites of solids [14]. Surface acidity was also evaluated through pyridine chemisorption. The reducibility of vanadia species was studied by H_2-TPR. Structural and textural characterization of the vanadium systems and of the supports by XRD, DR UV–vis, Raman, ^{29}Si MAS NMR and nitrogen adsorption has been previously reported [15].

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2. Experimental

The TiO_x-Sep supports were obtained by wet impregnation of the natural Sep ($S_{BET} = 143\ m^2/g$) as previously reported [15]. These supports will be denoted 6Ti-Sep, 12Ti-Sep and 25Ti-Sep where the numbers indicate the theoretical percentage of TiO_2 which represent approximately 0.6, 1.1 and 2.4 monolayers of titania on Sep, respectively, calculated as 0.088 wt.% TiO_2/m^2 [6]. The 6Ti-Sepc support was prepared using the Sep previously calcined at 923 K. The solids were calcined in air at 923 K for 3 h. The vanadium systems, 10V/%Ti-Sep and 10V/6Ti-Sepc, were prepared by wet impregnation of the supports with vanadyl oxalate in methanol solution ($NH_4VO_3/C_2O_2H_2$ molar ratio = 1/2), followed by calcination in air at 723 K for 3 h [15]. The theoretical vanadium loading, 10 wt.% V_2O_5, approached the amount required to cover the surface of the supports calculated as 0.1 wt.% V_2O_5/m^2 of support [1,3]. Two binary 10V/TiO_2 (Aldrich Chemie anatase) and 10V/Sepc (Sep calcined at 923 K) systems were also obtained in the same way. In Table 1, the values of the surface atomic V and Ti concentrations obtained from chemical analysis by energy dispersion of X-rays (EDAX) are shown. The Ti concentrations in the supports as well as the atomic V/Ti ratio at the surface of the 10V/25Ti-Sep system were closer to the theoretical composition, whereas the V/Ti ratio in all other systems varied slightly.

Pyridine (Py) chemisorption was measured using a pulse-chromatographic technique [14] in the range $T = 373–573$ K. TPR experiments were performed in a Micromeritics TPD/TPR 2900 analyser with TCD detector. Samples of 50 mg were first treated in Ar (373 K, 1 h) and then 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 was $\leq 2\%$. The 2-propanol conversion was studied using a microcatalytic pulse reactor [14] under the following conditions: 2-propanol pulse size 2 μl; $T = 443–523$ K; $w = 0.1$ g; $F_{N_2} = 10\,cm^3/min$.

Toluene oxidation was carried out in a continuous-flow fixed-bed reactor [16]. An analysis of reagent and product composition was carried out on-line using a multicolumn GC equipped with FID and TCD detectors in parallel. Catalyst (ca. 200 mg, <0.149 mm) was pretreated at the reaction temperature (633 and 653 K) for 1 h in a $F_{N_2} = 30\,cm^3/min$. Toluene was fed at 3 ml/h and the molar ratio toluene/O_2/He was 1/7/10. Previously, products were identified by GC–MS. Conversion (X) 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 toluene oxidation rate, r_{tol}, were obtained from X values, according to the equation, $r_{tol} = (XF)/W \times 100$, where, W is catalyst weight, and F is the feed rate of toluene (mol/h).

3. Results and discussion

3.1. Surface acid properties

The results obtained in Py chemisorption experiments are shown in Table 1 as well as the surface area values, S_{BET}. According to these results, both the surface acidity (Bronsted- and Lewis-acid sites) and the strength of those acid sites on the supports decreased with the Ti content and with the thermal treatment of the Sep. In relation to the Sepc, the supports exhibited a higher density of acid sites of weak–medium strength and a similar or lower density of strong acid sites, mainly 12 and 25Ti-Sep. The vanadium systems showed, in general, higher values than their supports. Furthermore, there was not a clear tendency with the titanium loading obtaining the sequence: 10V/6Ti-Sepc < 10V/25Ti-Sep ≤ 10V/6Ti-Sep < 10V/12Ti-Sep for medium–strong acid sites density (Py values at 473 and 573 K). 10V/Sepc, exhibited both acid site density and strength values similar to the 10V/6Ti-Sep, and 10V/TiO_2 was not able to retain Py.

3.2. TPR

TPR profiles of vanadium systems are presented by the H_2 consumption as a function of the temperature in Fig. 1 (TiO_x-Sep, TiO_2 and Sepc supports were not reduced in the temperature range studied). The maximum reduction rate peak

Table 1

EDAX V and Ti concentrations; surface area and porous diameter; chemisorption pyridine values at 373–573 K; maximum temperature, T_M; H_2 consumption and average oxidation state (AOS) of vanadium from TPR experiments

Catalyst	V (at.%)	Ti (at.%)	S_{BET} (m^2/g)	d_p (Å)	Py (μmol/m^2)			T_M (K)	H_2 (μmol/m^2)	AOS[a] of V
					373 K	473 K	573 K			
10V/6Ti-Sepc	3.8	1.9	45	255	0.71	0.22	0.09	856	10.0	4.20
10V/6Ti-Sep	5.2	3.5	47	215	1.36	0.49	0.30	806	8.8	4.24
10V/12Ti-Sep	4.3	4.2	34	239	2.15	1.09	0.77	846	12.8	4.16
10V/25Ti-Sep	4.2	10.6	35	188	1.71	0.40	0.20	816	12.6	4.18
10V/Sepc	2.6	–	58	196	1.36	0.55	0.41	836	7.4	4.22
10V/TiO_2	2.4	32.6	5	–	–	–	–	803, 905	54.2, 35.6	4.24
6Ti-Sepc	–	1.5	69	202	0.55	0.12	–	–	–	–
6Ti-Sep	–	1.8	79	164	0.75	0.57	0.15	–	–	–
12Ti-Sep	–	3.7	82	139	1.01	0.29	0.11	–	–	–
25Ti-Sep	–	7.2	71	134	0.31	0.30	0.10	–	–	–
Sepc	–	–	80	185	0.34	0.26	0.15	–	–	–

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

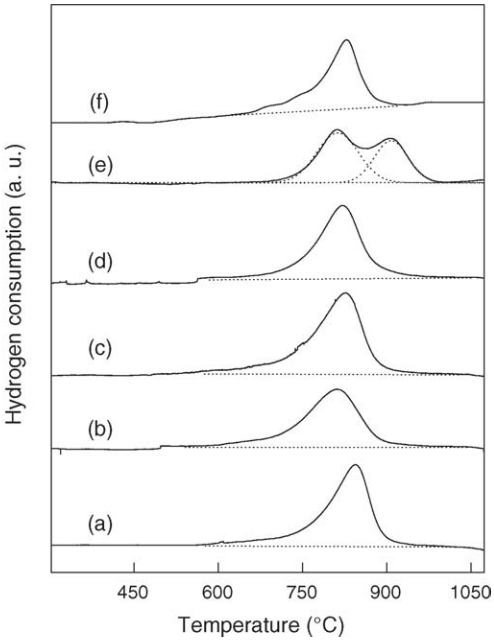

Fig. 1. TPR profiles for (a) 10V/6Ti-Sepc; (b) 10V/6Ti-Sep; (c) 10V/12Ti-Sep; (d) 10V/25Ti-Sep; (e) 10V/TiO_2; (f) 10V/Sepc.

temperature (T_M), the consumption of H_2 and the average oxidation state (AOS) of vanadium after reduction are presented in Table 1. As can be seen, with the exception of the 10V/TiO_2 TPR profile, the rest of the profiles were very similar, exhibiting only one defined peak in the 806–856 K temperature range, Table 1. Both the T_M and the H_2 consumption values for 10V/%Ti-Sep systems increased with Ti loading, 10V/12Ti-Sep showing the highest value of T_M. Thus, in spite of the fact that the density of sites capable of being reduced was very similar in the two systems with the highest Ti loading, the vanadium species on the 12Ti-Sep were more difficult to reduce (higher T_M value). In addition, in both systems the vanadium species were more strongly reduced (lower AOS values) than in other systems. As far as the 10V/6Ti-Sepc is concerned, it exhibited a higher density of sites than 10V/6Ti-Sep but they were reduced with greater difficulty. The 10V/TiO_2 TPR profile showed two peaks, after deconvolution. The first one, 60% of total area, at $T_M = 803$ K and the second one at a higher temperature $T_M = 905$ K. The H_2 consumption total value for this reference system was very similar to the rest of systems, 449 μmol/g, though the value shown in Table 1 was the highest due to the small surface area that it possesses compared to the other systems (ca. 8 times smaller). The assignment of the two peaks in the 10V/TiO_2 TPR profile will be done taking into account the Raman spectrum, not shown, obtained for this system that displayed a very intense band at 996 cm^{-1} and another one at 970 cm^{-1} which can be assigned to crystalline vanadia and polymeric species of vanadium with octahedral coordination, respectively, according to Baiker and co-workers [4]. So, the peaks at $T_M = 905$ and 803 K can be due to the reduction of crystalline vanadia and polymeric species, respectively. Accordingly, the peak observed in the rest of the systems, with similar T_M values, would be ascribed to such vanadia polymeric species since these species, along with isolated monovanadate species, would be present in the 10V/%Ti-Sep and 10V/Sepc systems according to the results previously obtained from Raman and XRD [15]. These results revealed preferential interaction between V and Ti species as well as a high dispersion of vanadium mainly in the supports with the highest Ti loading (no presence of vanadia phase). Consequently, the small shoulders in 10V/Sepc and 10V/%Ti-Sep profiles in a 600–750 K temperature range could be assigned to the aforementioned monomeric species. This order for the reducibility of the different vanadium species is in accordance with that reported by several authors [2,3,17]. However, Wachs and Weckhuysen [18] and Bulushev and co-workers [19] reported that monomeric and polymeric species would be reduced by H_2 at the same temperature.

3.3. 2-Propanol decomposition

In all the solids studied, 2-propanol decomposition produced propene and propanone, as shown in Table 2, where the only values collected are those obtained by selectivity at 503 and 523 K for supports and at 443 and 463 K for vanadium systems. Diisopropyl ether was also sometimes observed. Furthermore, the total conversion of 2-propanol along with the propene selectivity values increased notably, while the propanone selectivity values decreased with the increasing reaction temperature. Taking this into account, the evaluation of the surface acidity and of the basic/redox sites has been on the basis of the selectivity values to propene and propanone, respectively, obtained for the solids at isoconversion (≅3 mol%) due to the deep dependence of the propene selectivity values with the temperature (or with the conversion). In Table 2 the apparent rate constants (kK) are also collected for 2-propanol conversion obtained by analysis of the conversion data through the Basset–Habgood equation [14]. Thus, the supports were more active than Sepc and activity increased with the Ti loading, the 25/Ti-Sep support being the only one that presented activity in all the temperatures tested. Furthermore, Sepc and 6Ti-Sepc showed activity only in the dehydration reaction while the other supports not only exhibited dehydration ability, but also a dehydrogenation ability which decreased and increased with the Ti content, respectively. Furthermore, with the exception of 25Ti-Sep, all the supports presented an acid site density slightly higher than Sepc. These results along with the Py ones seem to indicate the formation of new weak–medium strength acid sites in the supports with the TiO_2 percentage under 25% and basic/redox sites, especially in the 25Ti-Sep. Parallelly, the results previously obtained from XRD, UV–vis and Raman [15] indicated a high dispersion of TiO_x on the Sep surface with the formation of a anatase phase in 12Ti-Sep and mainly in 25Ti-Sep, which is logical given that both have a theoretical composition above the monolayer. However, the previous calcination of Sep negatively affected titanium

Table 2
Apparent rate constants (kK) and selectivity to propene ($S_{C=C}$) and propanone ($S_{C=O}$) for 2-propanol decomposition, and activity (r_{tol}) and selectivity to benzaldehyde and benzoic acid (S_{BA+BAc}) and carbon dioxide (S_{CO_2}) in selective oxidation of toluene on all catalysts studied

Catalyst	2-Propanol decomposition				Toluene selective oxidation			
	T (K)	kK ($\times 10^8$ mol/atm s m^2)	$S_{C=C}$ (mol%)	$S_{C=O}$ (mol%)	T (K)	r_{tol} ($\times 10^5$ mol/h m^2)	S_{BA+BAc} (mol%)	S_{CO_2} (mol%)
10V/6Ti-Sepc	443	4.25	*49*[a]	*51*	633	3.33	*26 + 0*	–
	463	9.06	77	21	653	8.47	18 + 0	9
10V/6Ti-Sep	443	1.63	4	96	633	0.53	100 + 0	–
	463	6.55	*70*	*28*	653	3.60	*36 + 4*	*42*
10V/12Ti-Sep	443	6.74	*9*	*85*	633	2.41	64 + 0	–
	463	28.60	85	12	653	7.59	*41 + 0*	*31*
10V/25Ti-Sep	443	2.88	2	98	633	4.63	*48 + 4*	*34*
	463	5.10	*4*	*96*	653	15.60	26 + 3	71
10V/TiO_2	443	74.20	*18*	*82*	593	213.60[b]	8 + 54	–
	473	138.40	47	52				
10V/Sepc	443	1.67	7	93	633	0.84	49 + 0	–
	463	4.84	*69*	*28*	653	3.31	*33 + 0*	*29*
6Ti-Sepc	503	0.26	68	–	–	–	–	–
	523	1.49	*83*	–	–	–	–	–
6Ti-Sep	503	0.48	57	16	–	–	–	–
	523	1.71	*75*	*5*	–	–	–	–
12Ti-Sep	503	0.44	48	32	–	–	–	–
	523	1.97	*77*	*7*	–	–	–	–
25Ti-Sep	503	1.0	*53*	*23*	–	–	–	–
	523	4.39	82	4	–	–	–	–
Sepc	523	1.18	*96*	–	–	–	–	–

[a] Selectivity values at isoconversion are marked in italics.
[b] S_{BET} = 5 m^2/g.

dispersion. On the other hand, the vanadium systems displayed higher activity than their corresponding supports in both processes of dehydration to propene and dehydrogenation. In addition, the 10V/6Ti-Sep catalyst presented the highest value of surface acidity and the 10V/25Ti-Sep the highest of dehydrogenation ability along with 10V/TiO_2, according to the values of selectivity at isoconversion in Table 2. So, the 2-propanol conversion and Py chemisorption results obtained seem to indicate that the vanadia species formed on the supports contribute in a decisive way to the surface acidity exhibited by the vanadium systems. In this way, the vanadia species on the supports with a titania loading of 6 and 12 wt.% exhibited higher acidity (medium–strong acid sites) than the vanadia species formed on the support with a titania loading of 25 wt.% which in turn exhibited the highest number of basic/redox sites. In general, our results agree with the acid nature of V_2O_5 and with the existence of both acid sites and sites with dehydrogenation ability in the surface species of V_2O_5/TiO_2 systems as a function of the vanadia loading [2,3,6,18]. Furthermore, a relationship between the density of sites capable of being reduced and the density of those responsible for propanone formation on the vanadium systems seems to exist according to Fig. 2, that would corroborate criteria widely reported in the sense that the 2-propanol dehydrogenation process takes place on active sites with basic and redox properties.

3.4. Selective oxidation of toluene

Also compiled in Table 2 are the selectivity values to partial (S_{BA+BAc}) and total oxidation (S_{CO_2}) product obtained for all the catalysts at the two temperatures studied and at time on

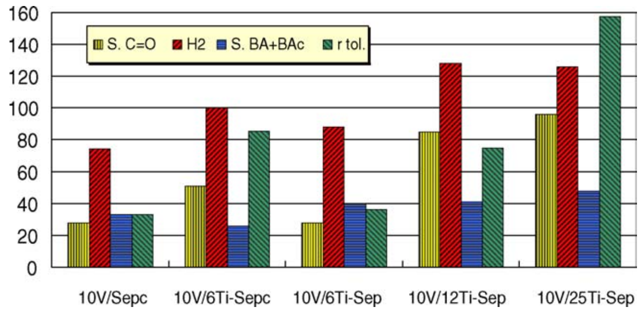

Fig. 2. Activity ($r_{tol} \times 10^6$ mol/h m^2) at 653 K and selectivity to BA and BAc (S_{BA+BAc}, mol%) at isoconversion in oxidation of toluene; selectivity to propanone at isoconversion in 2-propanol decomposition ($S_{C=O}$, mol%) and H_2 consumption in TPR experiments (H_2 10 μmol/m^2), as a function of titanium loading for vanadium systems.

stream of 1 h. Several coupling products belonging to Andersson's route 2 [20] were also obtained. The formation of the reaction products was influenced by the reaction temperature. Thus, the values of S_{BA} deeply decreased, coupling products slightly changed and CO_2 increased as the reaction temperature did, Table 2. On the other hand, the coverage of the Sep (with or without thermal treatment) with titania positively affected the activity values of the 10V/%Ti-Sep systems, which were more active than the 10V/Sepc one and the activity of the systems increased with titania content, Table 2. 10V/6Ti-Sepc was also more active than 10V/6Ti-Sep. As far as the selectivity values are concerned, the coverage of the Sep with titania again affected positively showing the 10V/%Ti-Sep systems higher values of S_{BA} than 10V/Sepc, these values increasing with the titania loading according to values at isoconversion (≅3 mol%) in Table 2. Furthermore, the 10V/6Ti-Sepc was the most selective to coupling products while 10V/TiO_2 was to BAc (although it was the most active). So, as the coverage of the Sep with titania increased, the systems obtained were more active and selective to partial oxidation products and less selective to total oxidation products. In addition, these systems exhibited the highest density of sites capable of being reduced and producing propanone, Fig. 2, and in general, the lowest density of medium–strong acid sites. The present results are in agreement with those reported by different authors studying oxidation reactions [2,3,7,19]. Currently, studies in development of vanadium systems with different vanadia loading will allow us to obtain more information about the structures of the vanadia species.

4. Conclusions

Catalytic activity data on the selective oxidation of toluene indicate the importance of supports in the catalytic performance of vanadium species. Specifically, the presence and loading of titania on a natural Sep were very important to provide adequate supports. Thus, the vanadium systems supported on TiO_x-Sep were more active than the supported on Sepc. Furthermore, the 10V/%Ti-Sep with the highest titania contents exhibited the best catalytic performances (activity in toluene conversion and selectivity to BA). This behaviour seems to be mainly related to the density of the active sites capable of being reduced by H_2 treatment as well as of producing propanone, which depend on the titania loading. Previous thermal treatment of Sep promotes an increase in activity though selectivity decreased.

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