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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.