Selective oxidation of *o*-xylene to phthalic anhydride on V_2O_5 supported on TiO_2-coated SiO_2

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A ternary V–Ti–Si catalyst was prepared by depositing the vanadium oxide precursor on a SiO_2 previously coated by TiO_2. The ternary V–Ti–Si catalyst and the corresponding binary V–Ti and V–Si counterparts were tested for the selective oxidation of *o*-xylene to phthalic anhydride. Silica-supported vanadium oxide shows lowest activity and selectivity, meanwhile selectivity to phthalic anhydride is higher on titania-containing catalysts. The best yield to phthalic anhydride (82.5%) is obtained at 573 K on the ternary V–Ti–Si catalyst which is comparable to that claimed for the best conventional V–Ti catalysts described in literature.

Keywords: vanadia–titania–silica ternary catalysts, *o*-xylene oxidation, phthalic anhydride production, catalyst characterization

1. Introduction

The selective oxidation of *o*-xylene to phthalic anhydride (PA) is a very interesting industrial process due to the use of PA in many applications of the organic industry such as in the production of polyester resins, pesticides and mostly in the production of plasticizers in PVC manufacture [1]. The reaction is usually conducted on a vanadia-based catalyst [2–5] and the best yields claimed in the literature are ca. 75% [6]. For this reaction, it is well known that V_2O_5 supported on TiO_2(anatase) is a catalyst superior to bulk V_2O_5, and that surface dispersed vanadia is more active and selective than crystalline V_2O_5 [2,7,8]. At high temperatures, the presence of supported vanadia induces conversion of the TiO_2 support from the anatase to the rutile phase [9,10]. This structural transformation unfavourably affects the activity and selectivity towards selective oxidation products [11]; the higher performances of anatase-supported catalysts can be explained in terms of the remarkable fit of the crystallographic structures in contact at the interface between V_2O_5 and TiO_2(anatase) [9].

The moderate surface area and poor mechanical strength of V_2O_5/TiO_2(anatase) catalysts are serious drawbacks to be overcome. The use of mixed TiO_2–SiO_2 oxides, instead of TiO_2 alone, as support for the vanadia phase is a very promising option because silica-supported titania yields a new material characterized by its better mechanical properties, higher surface area and higher thermal stability [12]. It has been shown that vanadium oxide species deposit almost exclusively on the titania support in the simultaneous presence of titania and silica [13]. Moreover, as the exposed titania support appears to be associated with non-selective oxidation into CO_2 [3,8,14], vanadium oxide loadings must be in the region of monolayer coverage and above. The performance in selective oxidation of *o*-xylene to phthalic anhydride of vanadia supported on TiO_2 previously deposited on SiO_2 is reported here and compared to binary conventional titania- and silica-supported vanadia catalysts. The V–Ti–Si catalysts were prepared in such a way as to overcome the exposure of SiO_2 to gas phase that would happen in the conventional coprecipitation of TiO_2 and SiO_2 but without losing the advantages of high surface area and good mechanical properties.

2. Experimental

2.1. Preparation of titania–silica support and catalysts

Titania–silica supports were prepared by the homogeneous precipitation method of Ti^{3+} on a non-porous high surface area silica (Aerosil Degussa 200), as previously reported [15,16]. Titania loading on silica was calculated to be of two theoretical monolayers of titania on silica. The support will be denoted 2TiSi. Supported vanadium oxide catalysts were prepared by adding an aqueous solution of ammonium metavanadate solubilized with H_2O_2 to the supports (Aerosil Degussa 200 silica, Degussa P-25 titania and SiO_2 coated by TiO_2). Water was removed by heating at 353 K under vacuum. The solid was dried in air at 373 K for 16 h and calcined at 773 K during 2 h. Vanadium oxide loading corresponds to a complete "theoretical" monolayer that will cover the surface area of the support. The ternary system was referred to hereafter as V2TiSi. The catalysts are labelled VSi, VTi and V2TiSi. Vanadium oxide loading determined by AAS was 24.2, 24.8% and 11.0 wt%, respectively.

2.2. Characterization techniques

BET surface areas were calculated from nitrogen adsorption isotherms at 77 K measured with a Micromeritics ASAP 2000 surface analyzer. X-ray diffraction patterns were recorded on a Seifert 2000 diffractometer using Ni-filtered Cu-Kα radiation. Bragg angles between 5° and 70° theta were scanned at 2 deg/min. Temperature-programmed reduction (TPR) was carried out in a Micromeritics 2900 TPR equipment by passing a 10% H_2/Ar flow (50 cm^3/min) through the sample. Temperature was increased from 323 to 773 K at a rate of 10 K/min and the amount of hydrogen consumed was determined with a TCD.

Photoelectron spectra were acquired with a Fisons Escalab 200R spectrometer equipped with a hemispherical electron analyzer and an Mg-Kα X-ray exciting source (1253.6 eV). The C 1s, O 1s, Si 2p, Ti 2p and V 2p peaks were recorded. The intensities were estimated by calculating the integral of each peak after background subtraction and fitting the experimental curve to a mix of Lorentzian and Gaussian lines.

2.3. Catalytic experiments

Catalysts were tested in a conventional flow apparatus at atmospheric pressure. The feed mixtures were obtained by injecting the *o*-xylene into the air flow using a Gilson (Model 302) piston pump. The reactor in Pyrex (12 mm inner diameter) was packed with 0.5 g of catalyst diluted with silicon carbide (mean particle size of 0.5 mm), the catalyst/diluent ratio was 1/3 by volume. Catalysts were tested in the 533–673 K range, using a 0.6 mol% *o*-xylene/air mixture and a total flow rate of 90 $cm^3\ min^{-1}$. All the lines were heated to prevent condensation of reactant and products, analyses of the reactor effluent and feed were performed by gas chromatography with TCD and FID detectors. Total oxidation products were analysed by the TCD detector, whereas the organic reactant and selective oxidation products were sensed by the FID detector. A 1% V_2O_5/TiO_2 catalyst (Eurocat) [17] was also tested for comparative purposes.

3. Results

3.1. Textural and structural characteristics of catalysts

BET areas and composition of fresh and used catalysts are compiled in table 1. The specific surface areas of the VTi, VSi and V2TiSi catalysts are much lower than for the respective TiO_2, SiO_2 and 2TiSi carriers. This decrease is 50% for VTi and VSi catalyst whereas it reaches 64% for the ternary V2TiSi catalyst. This is probably due to narrowing or even blocking of the pores following impregnation of vanadia.

Table 1
Characterization of the fresh and used catalysts

	XPS V/Ti	TPR		S_{BET} (m^2/g)	TiO_2 phase
		T_{max} (K)	O/V		
fresh					
VSi	–	889 826	0.62	101	–
V2TiSi	3.371	881	1.06	61	anatase
VTi	0.311	724 854	1.00	24	anatase + rutile
used					
VSi	0.027[a]	894 821	–	–	–
V2TiSi	1.184	876	–	–	anatase + rutile
VTi	0.249	785	–	–	anatase + rutile

[a] V/Si atomic ratio.

XRD patterns differ markedly from catalyst to catalyst. Fresh and used VTi catalyst display both TiO_2(anatase) and TiO_2(rutile) phases, and very weak V_2O_5 diffraction lines, suggesting a high dispersion degree of the vanadia. For the fresh and used VSi catalyst, the characteristic diffraction lines of V_2O_5 were observed which indicates the presence of bigger crystals, consistent with the weaker interaction of V_2O_5 with silica than with titania [13]. For the used V2TiSi ternary catalyst, both TiO_2(anatase) and TiO_2(rutile) and V_2O_5 diffraction lines were observed. Comparison with the fresh V2TiSi apparently shows sintering of TiO_2 and a very small transformation of anatase into rutile, which seems to be induced by the reaction conditions.

In table 1 the O/V ratio represents the number of O atoms removed per vanadium atom upon H_2 reduction for the different fresh samples. The O/V ratio is higher on fresh titanium-containing catalysts than on fresh VSi catalyst. Values close to 1 on titanium-containing catalysts support the assumption that most of the vanadium oxide is covering the titania and that it is fully reduced to V_2O_3 in the TPR experiment. The reduction seems to be stopped at V^{IV} in the case of the VSi sample. TPR profiles of the three fresh catalysts are summarized in fig. 1. The VSi catalyst shows a maximum TPR peak (T_{max}) at 894 K with a shoulder at 721 K. The TPR of the fresh VTi catalyst, with better vanadia dispersion (as deduced from the XRD pattern), is somewhat different: two peaks of similar intensity are observed at 724 and 854 K. Fresh V2TiSi catalyst exhibits only one peak at 883 K and a tail is observed towards lower temperatures.

The relative abundances of vanadia on the three carriers were determined by XPS. The V/Ti and V/Si XPS ratios have been measured for both calcined and used catalysts in order to see if vanadia exposure changes

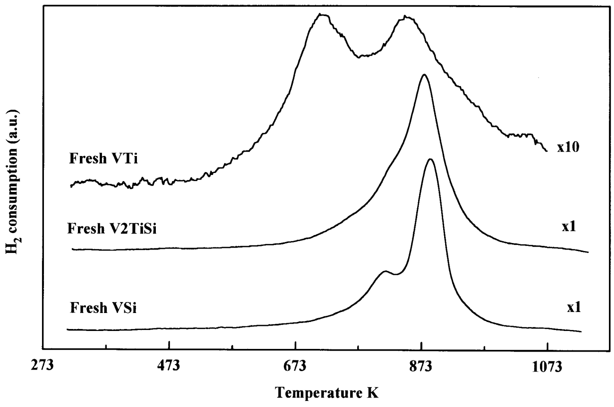


Fig. 1. Temperature-programmed reduction profiles of calcined catalysts.

while on-stream. Fresh V2TiSi presents a much higher V/Ti XPS ratio than VTi. For both VTi and V2TiSi catalysts, and particularly for the latter, there is a strong decrease in the V XPS signal after catalytic experiments, while for the VSi counterpart the V/Si ratio increases slightly. It is evident that vanadia exposure on the catalyst surface in the VTi sample, and more clearly in the V2TiSi sample, decreases after use in the oxidation of *o*-xylene.

3.2. *Catalytic behaviour in o-xylene oxidation*

o-xylene conversion after 2 h on-stream is shown in fig. 2. *o*-xylene is converted to phthalic anhydride (PA), *o*-tolualdehyde (T), phthalide (P), maleic anhydride (MA) and CO_2. No carbon monoxide was detected. Trace amounts of *o*-toluic acid are also observed on VSi catalyst. The presence of different supports renders very different catalytic performances. VSi is the least active catalyst, the VTi catalyst has higher activity while *o*-xylene conversion on the ternary V2TiSi catalyst is maximum. The activity profile of VTi is similar to that of 1% V_2O_5/TiO_2 (Eurocat) [17], in particular with respect to phthalic anhydride yield. However, as reaction temperature increases, phthalic anhydride yield decreases and CO_2 increases up to ca. 90%. This inversion in selectivity trends is not observed on the 1% V_2O_5/TiO_2 catalyst (Eurocat).

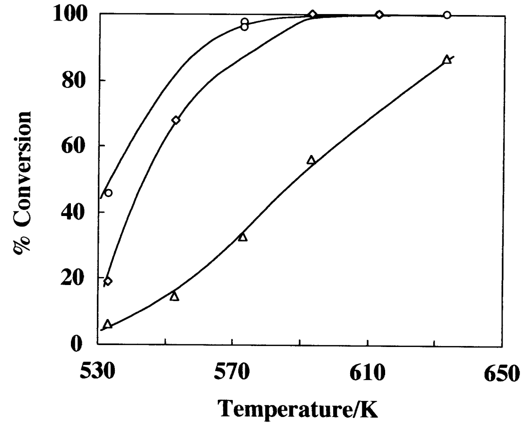


Fig. 2. *o*-xylene conversion on V2TiSi (○), VTi (◇), and VSi (△). Reaction conditions: 0.6 mol% *o*-xylene/air, 90 cm^3/min. Reaction temperature: 533–673 K.

Yields of the different products are presented in fig. 3. Phthalic anhydride is the main oxidation product at low and medium reaction temperature on titania containing catalysts. As reaction temperature increases, yields of CO_2 increase at the expense of phthalic anhydride. This trend is much more intense on VTi than on V2TiSi catalysts. Phthalide is observed at low reaction temperatures in VTi and its yields decrease as reaction temperature increases. Phthalide is an intermediate in the oxidation of *o*-xylene to phthalic anhydride (scheme 1). The increase of phthalic anhydride and CO_2 at the expense of phthalide is an expected trend. However, yield trends for phthalide on V2TiSi are rather different: it rises with reaction temperature. VSi catalyst does not present any preferential oxidation product. Phthalic anhydride and phthalide are produced in equivalent amounts but as reaction temperature

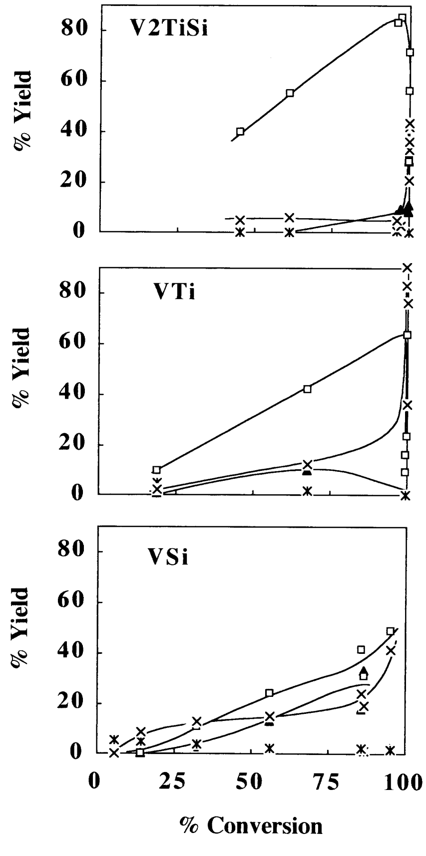
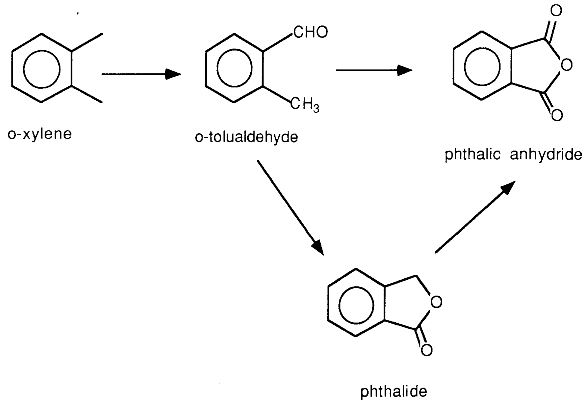


Fig. 3. Yield to phthalic anhydride (□), phthalide (▲), CO_2 (×), and maleic anhydride (∗) on the different catalysts. Reaction conditions like in fig. 2.



Scheme 1.

increases phthalic anhydride becomes slightly predominant. Yields of CO_2 increase more slowly with reaction temperature on VSi than on the VTi catalyst.

4. Discussion

The PA yield on V2TiSi at temperatures as low as 600 K is close to 85%, which is considerably higher than the other systems studied in this work and somewhat higher than on other conventional VTi catalysts [1]. The VSi system displays a very low dispersion for the active phase and V_2O_5 crystallites are present. Bulk V_2O_5 presents worse selectivity to PA than surface dispersed V_2O_5 species. VTi displays its higher PA production at low temperatures but never as high as V2TiSi. PA yield is even worse on VTi than on VSi catalyst because of the high CO_2 formation at higher temperatures. VTi activity profile is similar to that of 1% V_2O_5/TiO_2 (Eurocat) at low reaction temperatures, however, it does not show an increase in CO_2 production at high reaction temperature [17]. The Eurocat catalyst does not improve the PA yield of the V2TiSi system at low temperatures.

In order to explain the different behavior of VTi catalyst when compared with the parent Eurocat it should be reminded that Eurocat is supported on TiO_2(anatase) phase meanwhile TiO_2 support used here has ca. 25% rutile phase and the rest is anatase phase. The interaction between vanadia TiO_2 (anatase) [9] tends to form a well dispersed surface vanadium oxide species. The XRD diagram showed that vanadium phase in fresh VTi sample is well dispersed as very weak V_2O_5 diffraction lines were observed. The V/Ti XPS ratio is low which indicates that Ti cations are not covered by the vanadium phase. The ability of TiO_2(rutile) for integrating V^{4+} cations into its lattice as substitutional defects [4,18,19] may account for the low V/Ti XPS ratio. V_2O_5 is probably selectively deposited onto TiO_2(anatase) rather than onto TiO_2(rutile) which has a lower affinity for dispersing surface vanadium oxide. Probably some V^{IV} diffusion into TiO_2(rutile) structure occurs as indicated by the decrease of the V/Ti XPS ratio in the used VTi sample. In fact this diffusion has been already described in V_2O_5/TiO_2(rutile) catalyst during *o*-xylene conversion at ca. 600 K [5]. Exposed titania sites appear to be associated with non-selective oxidation [4,5,8,20]. Consequently, the remarkable increase in CO_2 production in the VTi system must be associated with the presence of the rutile phase on titania support.

The 2TiSi support is characterized by titania possessing essentially anatase phase on fresh V2TiSi catalyst. Supported vanadium oxide will preferentially deposit on titania rather than on silica [19]. V_2O_5 loading of this sample (24.8%) corresponds to a complete theoretical monolayer for the total area of the 2TiSi support. Part of the surface area originates from silica and its lower ability for dispersing supported oxides will promote aggregation of vanadia crystals since not all vanadia can deposit on the surface of titania. Therefore, V_2O_5 crystallites should be accumulated on top of dispersed surface vanadia and no Ti cations responsible for non-selective oxidation are expected to be exposed. The very high V/Ti ratio measured by the XPS supports this assumption. Due to the preparation method a higher area of active phase is exposed and that explains the higher conversion and consequently yield.

The V^{IV}/V^{V} equilibrium during the selective conversion of *o*-xylene to phthalic anhydride has been claimed to determine the selectivity [17]. The values for maximum reduction temperature (T_{max}) recorded in TPR experiments could be related to the amount of V^{IV} present under reaction conditions and its feasibility to be reoxidized to V^{V} during the conversion of *o*-xylene. Consequently, the sequence T_{max}: VTi < V2TiSi < VSi may account for the different selectivity trends observed. Total oxidation dominates at high reaction temperature for the VTi catalyst. VSi is the least reducible catalyst and the V^{IV} oxidation state has low stability, thus conversion is low. Only at high reaction temperature a significant activity is recorded and presents no defined selectivity trend since several partial oxidation products are produced to a similar extent along with CO_2. However, the intermediate T_{max} value for V2TiSi could be associated to an optimum V^{IV}/V^{V} equilibrium. This would allow the formation of the desired partial oxidation product, phthalic anhydride. However, at very high vanadium loading some vanadium may also deposit on silica support and its presence could account for the production of phthalide on V2TiSi at high reaction temperature.

5. Conclusions

Catalytic activity data on the selective oxidation of *o*-xylene reveal the importance of supports on catalytic performance of active metal oxides. The use of TiO_2-covered SiO_2 provides a support characterized by its high surface area and different redox properties. The presence of titania is required in the oxidation of *o*-xylene to phthalic anhydride. The high surface area and different redox properties of ternary $V_2O_5/TiO_2/SiO_2$ catalyst determines the high activity and selectivity in the oxidation of *o*-xylene into phthalic anhydride.

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