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Preparation by atomic layer deposition and characterization of active sites in nanodispersed vanadia/titania/silica catalysts

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Abstract

The dispersion, acidity, reducibility and adsorption capacities of nanostructured, atomic layer deposited (ALD) $V_2O_5/TiO_2/SiO_2$ catalysts were examined by BET, XRD, FTIR and Raman spectroscopy, XPS, H_2-TPR and microcalorimetry. TiO_2-supported and standard liquid-phase impregnated catalysts were characterized for comparison, and the influence of the catalyst properties on their performance was probed in a test reaction of *o*-xylene selective oxidation. Gas-phase deposited, isolated vanadia species were highly dispersed independently of the support nature, whereas crystalline vanadia was detected in the impregnated catalysts with submonolayer coverage of titania. Likewise, the reducibility of the ALD catalysts was enhanced in relation to the corresponding impregnated catalysts. The activity of the ALD and impregnated catalyst increased with the decrease in number of strong surface Lewis acid and *o*-xylene adsorption sites. *o*-Xylene conversion was greater on the highly dispersed ALD catalysts on TiO_2, and on TiO_2/SiO_2 supports with high titania content, than on their impregnated counterparts.

Keywords: Atomic layer deposition; Titania-/silica-supported vanadia catalysts; Acidity; Reducibility; *o*-Xylene, phthalic anhydride

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1. Introduction

Synergistic interactions of highly dispersed vanadia and titania species on silica have been shown to control, e.g. the acidity [1], reducibility [2,3], and thus the overall activity of the $V_2O_5/TiO_2/SiO_2$ catalysts in selective oxidation reactions of toluene [4], *o*-xylene [5] and ethanol [6]. Nanosized, novel vanadia–titania–silica-based surface structures were prepared in the present contribution by atomic layer deposition (ALD). This layer-by-layer processing method relies on surface-saturating reactions of separately fed gaseous precursors with well-defined support adsorption sites. The ALD method permits adsorption, i.e. surface-controlled and highly reproducible growth of active species, and is thus less dependent on the operating parameters, e.g. the reaction temperature, vapor pressure and concentration of the precursors [7]. It represents thus significant advantages over other gas-phase deposition techniques, such as chemical vapor deposition (CVD) [7–9], where the less controlled growth is often based on simply thermal decomposition of the precursors and governed by several deposition parameters. Compared to the liquid-phase preparation techniques, even greater benefits, e.g. in terms of species dispersion and uniformity are gained by the use of the ALD technique. The usefulness of the technique for nanotechnology applications [9], and the merits of the method for the manufacturing of future generation catalysts [7,10,11] have been recently discussed. A sensible test reaction of selective oxidation of *o*-xylene into phthalic anhydride (PA) was used to evaluate the influence of surface characteristics of highly dispersed ALD prepared $V_2O_5/TiO_2/SiO_2$ catalysts, and for comparison, of traditional liquid-phase impregnated catalysts. Pyridine adsorption infrared spectroscopy technique provided information on the acidity, and H_2-TPR measurements on the reducibility of the catalysts. Adsorption microcalorimetry of *o*-xylene probed the interaction of the reagent with the surface.

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2. Experimental

The ALD preparations were carried out in a stationary-bed reactor [7] (F-120, ASM Microchemistry Ltd.), following a general procedure [11]. The supports used were: (i) submonolayer or above monolayer titania/silicas prepared by ALD starting from titanium isopropoxide by applying three or seven precursor binding–oxidation cycles [12] and (ii) bare titania (Degussa, P25). To control the support adsorption sites, the carriers were pretreated beforehand in air at 773 K for 11–16 h and in N_2 at 373 K for 2.5 h while keeping the reactor pressure at 1–3 kPa. Controlled chemisorption of volatilized vanadyl triisopropoxide on the supports was carried out at 363 K during 8 h, followed by a N_2 treatment at 363 K for 2 h and a calcination under O_2 flow at 773 K for 11 h. This ALD cycle was repeated once in order to increase the amount of vanadia on the carriers. The impregnated reference catalysts were prepared with ammonium metavanadate aqueous solutions. After drying at 383 K, the solids were calcined in O_2 at 773 K for 11 h.

The experimental procedures used for N_2-adsorption, XRD, Raman spectroscopy, XPS and NH_3 adsorption microcalorimetry can be found in Ref. [11], where the first information on the structure, dispersion and acidity of the catalysts has been reported.

The infrared spectra of pyridine adsorption were collected with a FTIR spectrophotometer (Bruker Vector 22) in the range of 1000–4000 cm^{-1}, with a resolution and acquisition of 2.0 cm^{-1} and 100 scans, respectively. The sample disks were activated in O_2 at 673 K, then evacuated, and finally exposed to pyridine at 298 K. The spectra were recorded at 298 K after desorption at 353 K.

H_2-TPR measurements were carried out in a microreactor by exposing the samples, pretreated in O_2 at 673 K, to a 5 vol.% H_2/Ar (1.2 L/h) and raising the temperature at 5 K/min up to 1113 K.

The catalytic tests were carried out under atmospheric pressure at temperatures of 573, 598 and 623 K in a fixed-bed tubular microreactor. The powder catalysts (0.11–0.30 mm, W/F 4.5×10^{-2} g h/L) were diluted nine times in mass with sand. Liquid *o*-xylene (0.083 mL/h) was fed by means of a perfusion pump and vaporized by mixing with pre-heated air (0.5 mol% *o*-xylene/air) before being introduced into the reactor. The unreacted *o*-xylene and the reaction products were condensed in an ice-bath trap kept at ca. 258 K. The weighted products were analyzed in a FID gas chromatograph (HP 5890 II), using a Supelco-SPB5 column (length 30 m, i.d. 0.32 mm) and He as carrier gas. The *o*-xylene conversion and selectivity to the most important reaction products, i.e. phthalic anhydride (*o*-tolualdehyde and phthalide) were calculated in wt.%. Other products, e.g. maleic anhydride, were ignored because they were present in very small quantities.

The microcalorimetry of *o*-xylene adsorption was performed in a heat flow calorimeter (Setaram HT) coupled to a volumetric apparatus [13]. After activating the samples at 673 K in air and then under vacuum, consecutive *o*-xylene gas pulses were introduced onto the catalyst kept at 313 K until equilibrium was reached. A readsorption carried out at the same conditions allowed the determination of irreversibly adsorbed uptakes (V_{irr}).

3. Results and discussion

3.1. Dispersion, structure and crystallinity

The surface-controlled gas-phase deposition of titania and vanadia on silica progressed at a growth rate of $1\ \mathrm{atoms/nm^2_{support}}$ per ALD cycle, affecting only slightly the surface area of the support (Table 1). Highly dispersed, amorphous and isolated, monomeric vanadyl species were developed at the interspace of support Ti–O–Si interactions, as shown by XRD, XPS and Raman spectroscopy [11]. Attached from the gas phase, vanadium was directly stabilized both onto titania and silica surface sites, creating nanostructures based on both V–O–Ti and V–O–Si bonding [2,11]. The method of vanadia deposition influenced greatly the catalyst properties, especially at submonolayer titania contents. For example, the impregnated vanadia in I-2V3TiSi catalyst had a tendency to migrate during calcination onto titania components of the support and its partly crystalline form decreased the surface area (Table 1). Also when compared to literature results [2], the A-2V3TiSi catalyst had preserved ~25% higher surface area than a corresponding liquid-phase impregnated catalyst.

No crystalline V_2O_5 was detected in the above monolayer of titania containing catalysts A-2V7TiSi and I-2V7TiSi. HoweverHoweverHhhh, a slight difference was noticed in the S_{BET} values (Table 1) and in the relative vanadium and titanium dispersion on silica in favor of the gas-phase prepared catalyst. On the other hand, on pure titania, vanadia was less dependent of the preparative method and present mainly in the form of highly dispersed, tetra-coordinated VO_x species.

3.2. Acidity

The acidic properties of the catalysts, obtained by NH_3 adsorption microcalorimetry and pyridine adsorption FTIR spectroscopy, are summarized in Table 1 and presented in Fig. 1, respectively. The titania/silica supports and corresponding impregnated and ALD catalysts showed mainly strong Lewis, but also some strong Brønsted acid sites (Fig. 1). The general trend for surface acidity with identical, low metal surface densities have been shown to be: vanadia/silica < titania/silica < vanadia/titania [10]. In the A-2V3TiSi catalyst, where the highly dispersed vanadia was associated with both the titania and silica surface species, a rather strong acidic nature of the 3TiSi support was conserved (Table 1

Table 1
Physico-chemical properties, acidity and reducibility data of the catalysts

Catalyst[a]	Vanadium analysis		S_{BET} (m^2/g)	Microcalorimetry of NH_3 adsorption at 353 K, number of strong acid sites ($\mu mol\ NH_3/g_{catalyst}$)[b]	H_2-TPR			
	wt.%	atoms/$nm^2_{support}$			T_{onset} (K)[c]	T_M (K)[d]	FWHM[e] (K)	AOS of V after reduction[f]
3TiSi	6.7[g]	3.2[g]	297	148	–[h]	–	–	–
A-2V3TiSi	4.4	1.9	276	150	697	828	65	3.7
I-2V3TiSi	4.3	1.8	269	124	708	838	70	3.6
7TiSi	13.2[g]	7.1[g]	274	158	–	–	–	–
A-2V7TiSi	4.3	2.0	262	180	644	799	85	3.7
I-2V7TiSi	4.3	2.0	252	209	655	809	90	3.8
TiO_2	–	–	55	172	–	–	–	–
A-2VTi	1.4	2.9	41	96	617	710	75	3.5
I-2VTi	1.4	2.9	50	128	623	712	70	3.5

[a] A: ALD, I: impregnation, 2,3,7: precursor–oxygen cycle number for vanadia and titania growth.
[b] Irreversibly adsorbed volume at 27 Pa.
[c] Onset reduction peak temperature.
[d] Maximum reduction peak temperature.
[e] Full width at half maximum of the reduction peak.
[f] Average oxidation state.
[g] Titanium amount.
[h] Negligible or zero.

and Fig. 1). However, in the less dispersed impregnated catalyst I-2V3TiSi, the vanadia crystals decreased the acidity.

Well dispersed, both ALD and impregnated vanadia catalysts supported on high surface area 7TiSi showed large NH_3 adsorption capacities, i.e. a great number and strength of surface acid sites. The highest number of strong acid sites of I-2V7TiSi compared to that of A-2V7TiSi (and of 7TiSi) is likely due to the greater attachment of surface vanadia on crystalline (and surface) titania species than on silica species (Table 1 and Fig. 1). The strong Lewis acidity of pure titania support was masked by the deposition of vanadia, the decrease in the number of acid sites was pronounced especially in the case of the highly dispersed ALD sample A-2VTi (Table 1 and Fig. 1).

3.3. Reducibility

The reducibility of the ALD and impregnated catalysts, measured in terms of decreasing reduction temperatures T_{onset} and T_{max} (Table 1), improved with increasing titania loading. In the case of catalysts supported on titania/silica, these temperatures were ~10 K lower and the TPR profiles (Fig. 2) narrower for the ALD samples, indicating an easier reduction and a higher uniformity of gas-phase deposited surface species [14]. Smaller differences in the reducibility were detected, however, between the ALD and impregnated, pure titania-supported samples with lower vanadia coverage (Table 1).

The reduction peak width increased with titania content in the bilayered catalysts (Table 1) in agreement with the

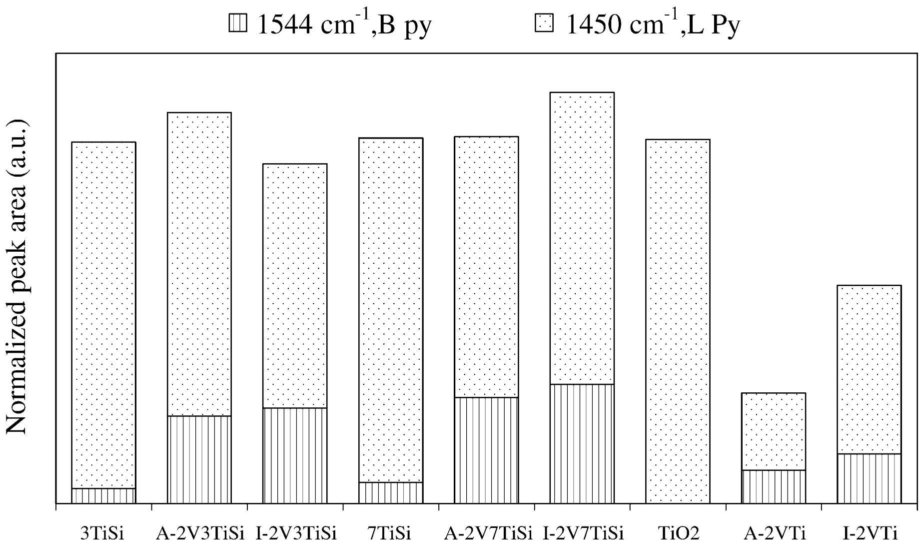

Fig. 1. Relative Lewis and Brønsted acid site distributions of the catalysts obtained by pyridine adsorption infrared spectroscopy after desorption at 353 K.

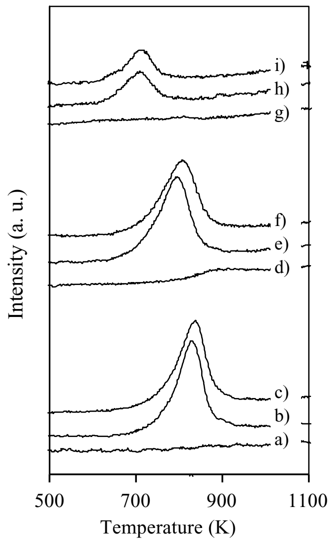

Fig. 2. Temperature programmed reduction profiles of the catalysts: (a) 3TiSi, (b) A-2V3TiSi, (c) I-2V3TiSi, (d) 7TiSi, (e) A-2V7TiSi, (f) I-2V7TiSi, (g) TiO_2, (h) A-2VTi and (i) I-2VTi.

literature [6]. Broader peak widths for 7TiSi-supported samples, compared to those of samples supported on 3TiSi (or on pure titania), suggest the presence of more than one type of surface vanadia species [2]. This heterogeneity arises from the association of the vanadia with both dispersed titania species and crystalline TiO_2 [2]. The average oxidation state of vanadium after reduction was independent of the preparative method, however (Table 1).

3.4. Activity and o-xylene adsorption capacities

The selective oxidation of *o*-xylene was used as a test reaction to probe the surface properties of the catalysts. In general, vanadia/titania catalysts are the most active for this reaction, whereas vanadia/silica catalysts suffer from the deactivation phenomena [5,15]. The activity of the catalysts, expressed by conversion of *o*-xylene at 598 K, was higher for the titania-supported than for the bilayered catalysts (Table 2). The conversion increased with temperature in a more or less marked way depending on the sample. The most active catalysts A-2VTi (Fig. 3) and I-2VTiSi attained higher than 80% conversion at the highest temperature, whereas the conversion was within the 40–60% range for the other catalysts.

Selectivity to the main important oxidized product, i.e. phthalic anhydride, attained its maximum of ∼20% at 598 K (Table 2) with the most performing catalysts A-2VTi (Fig. 3) and I-2VTi. The particular structure features, e.g. increased V–O–Si linkage density, decreased the PA selectivity and increased slightly the *o*-tolualdehyde and phthalide selectivity (maximum 4%) of the bilayered catalysts especially with titania submonolayer quantities. The silica component of the catalysts, even when covered by a titania layer seemed to have a negative effect on the activity of

Table 2
Adsorption site information and catalytic test results of the catalysts

Catalyst	Microcalorimetry of *o*-xylene adsorption at 313 K					*o*-Xylene oxidation at 598 K	
	V_t (μmol *o*-xylene/$g_{catalyst}$)[a]	V_{irr} (μmol *o*-xylene/$g_{catalyst}$)[b]	Adsorption site number (μmol *o*-xylene/$g_{catalyst}$)			Conversion (%)	Selectivity to PA[c] (%)
			60 kJ/mol < Q < 100 kJ/mol	100 kJ/mol < Q < 120 kJ/mol	120 kJ/mol < Q < 150 kJ/mol		
3TiSi	221	80	8.2	4.1	10.5	33	–[d]
A-2V3TiSi	266	165	8.6	4.3	11.7	26	6
I-2V3TiSi	202	108	6.1	3.0	6.5	46	9
7TiSi	244	106	19.1	4.3	6.4	19	–
A-2V7TiSi	243	91	7.3	3.6	5.4	40	2
I-2V7TiSi	287	139	11.2	5.6	8.4	34	4
TiO_2	223	88	10.2	5.1	7.6	11	–
A-2VTi	129	83	6.6	1.2	1.8	69	19
I-2VTi	163	147	28.5	9.1	9.7	55	16

[a] Total adsorbed volume at 27 Pa.
[b] Irreversibly adsorbed volume at 27 Pa.
[c] Phthalic anhydride.
[d] Negligible or zero.

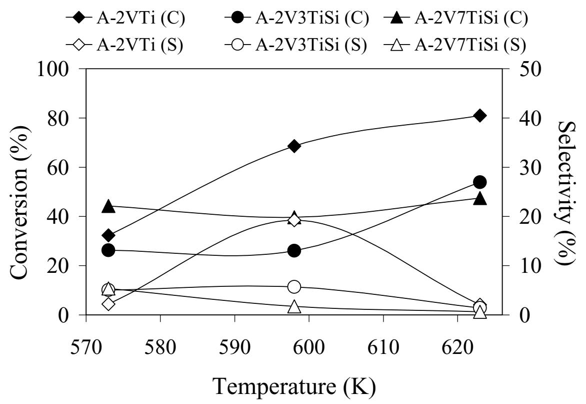

Fig. 3. Conversion of *o*-xylene and selectivity to phthalic anhydride of the ALD catalysts at temperature range of 573–623 K.

the catalysts. Nevertheless, for the $V_2O_5/TiO_2/SiO_2$ catalysts, intermediate values of the T_{max} reduction temperature comparing to the pure V_2O_5/TiO_2 and V_2O_5/SiO_2 catalysts [14], and thus optimal V^{IV}/V^{V} equilibrium could be a factor maintaining a good selectivity to PA at high reaction temperature of 623 K [5,15].

A reversed trend of the activity with the number of strong, mainly Lewis acid sites of catalysts measured by NH_3 adsorption microcalorimetry (Table 1) and pyridine adsorption FTIR spectroscopy (Fig. 1), was observed. It has been suggested in the literature [5,15] that *o*-xylene is retained efficiently on the strong Lewis acid sites, which facilitate the formation of non-volatile by-products via reaction between adsorbed species. Indeed, the most acidic catalysts I-2V7TiSi showed deactivation (and coke formation) as the temperature increased.

Moreover, microcalorimetry measurements showed that both the total adsorbed amount of *o*-xylene and the number of strongly interacting surface sites (V_{irr}) were inferior in the ALD catalyst to those found in the impregnated equivalent, with exception of the 3TiSi-supported catalysts (Table 2). The medium and strong strength *o*-xylene adsorption sites, with an evolved heat (Q) between 100 and 150 kJ/mol, and particularly the strong strength adsorption sites between 120 and 150 kJ/mol (Table 2), seemed to be the most detrimental for the catalytic activity. The vanadia catalysts, I-2V3TiSi, A-2V7TiSi, A-2VTi, possessing a smaller number of these sites and being less acidic, were detected to be more active and selective than their counterparts on the same support (Table 2).

4. Conclusions

The method of preparation significantly affected the characteristics of the $V_2O_5/TiO_2/SiO_2$ catalyst, especially at low titania concentrations. Atomic layer deposited vanadia species were highly dispersed and attached both on the titania surface species and on the exposed silica support. The corresponding vanadia deposited by impregnation was more firmly localized onto titania but was present partly as V_2O_5 crystallites that decreased the catalyst surface area. The better dispersion of active species in the ALD samples was verified by the acidity measurements. The number of strong, mainly Lewis acid sites increased in the ALD catalysts with submonolayer titania coverage. In the catalysts with high titania content, the ALD vanadia species masked the acidity better than the species prepared by impregnation. Reduction characteristics further confirmed the higher dispersion and uniformity of vanadia in the bilayered ALD catalysts. However, the presence of strong surface acid and *o*-xylene adsorption sites decreased the activity of the catalysts in the test reaction of *o*-xylene oxidation. Among the catalysts based on pure titania or bimetallic supports containing high titania amounts, *o*-xylene conversion was better on the highly dispersed ALD catalysts than on the impregnated analogs.

Acknowledgements

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