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Atomic layer deposition and surface characterization of highly dispersed titania/silica-supported vanadia catalysts

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Abstract

The atomic layer deposition (ALD) method using surface-saturating gas–solid reactions was applied to modify a highly dispersed titania/silica support with submonolayer amounts of vanadia. The surface properties and acidity of the $V_2O_5/TiO_2/SiO_2$ materials were examined relatively to the corresponding silica and titania supported samples. The surface area, porosity and amorphous nature of the support were not affected by vanadia, which was present in the form of highly dispersed isolated species on titania/silica, as detected by Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). Microcalorimetry measurements showed that the vanadia species interacted with both the titania overlayer and the silica surface, confirming the observed V–O–Ti bonding Raman features. The surface reactivity towards ammonia was strongly enhanced by the modification, as probed by adsorption microcalorimetry and XPS. The superiority of the ALD method for the preparation of bilayered vanadia/titania/silica catalysts was demonstrated by examining for comparison a series of aqueous-phase impregnated catalysts.

Keywords: Atomic layer deposition; Titania/silica-supported vanadia catalysts; Dispersion; Acidity

1. Introduction

In order to benefit from the combined advantages of titania and silica, binary TiO_2/SiO_2 materials have been widely used as supports for vanadia catalysts [1–8]. Highly dispersed titania/silica is preferred to the mixed titania–silica oxide in order to have a strong and direct interaction between surface TiO_x and VO_x on silica [1,3,5,6].

The atomic layer deposition (ALD) method is a gas phase preparation technique based on surface-saturating precursor adsorption on support, allowing a high dispersion of the deposited species on the catalyst [9–12]. The principle and use of the ALD technique for the coating of porous carriers have been reviewed in the literature [9–12]. In the present contribution, the ALD method was applied to prepare highly dispersed vanadia submonolayers on titania-modified silica by consecutive surface reactions of vanadyl triisopropoxide ($VO(OPr^i)_3$) and oxygen. An effort was devoted to provide understanding of how controlled modification of the chemical properties of the support by active species changed the surface characteristics and acidity of the material. For comparison, vanadia overlayers were deposited also onto silica and titania carriers. In addition, a series of samples was prepared by a standard impregnation method. The catalysts were examined by N_2 adsorption, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and adsorption microcalorimetry.

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2. Experimental

2.1. Catalyst preparation

The depositions of vanadia onto SiO_2, TiO_2 and highly dispersed TiO_2/SiO_2 supports were carried out in a fixed-bed flow-type ALD reactor [10] (F-120, ASM Microchemistry Ltd.), following a procedure similar to that presented in Ref. [13]. In this typical ALD procedure, the volatilized precursor is transported in nitrogen flow downward through the heated bed of support kept in a vacuum of 1–10 kPa. The surface-saturating reaction of precursor with the support adsorption sites is followed by a nitrogen purge and a calcination treatment [9–13].

The precursor used for the vanadia deposition was $VO(OPr^i)_3$ from Strem Chemicals, Inc. (purity >98%). The silica and titania employed were EP10 from Crosfield Ltd. and P25 from Degussa (75% anatase, 25% rutile), respectively. The high surface area titania/silica (2.7 wt.% of Ti or 1.2 Ti atoms/$nm^2_{support}$) was prepared similarly by ALD by letting the $Ti(OPr^i)_4$ precursor (Acros Organics, purity >98%) react with the silica surface for 5 h at 413 K [14]. Considering that the maximum dispersion of titania on silica is ~4 Ti atoms/$nm^2_{support}$ [15], the titania/silica sample possessed a 1/3 monolayer coverage.

The supports were pretreated in air for 16 h at 873 K (SiO_2) or 773 K (TiO_2 and TiO_2/SiO_2) in a muffle furnace and subsequently in the ALD reactor for 3 h at 383 K (SiO_2), 623 K (TiO_2) and 373 K (TiO_2/SiO_2), respectively. The chemisorption of $VO(OPr^i)_3$ on the support was performed at 383 K (5 h) for silica and at 363 K (8 h) for titania and titania/silica. The solids were subsequently purged under nitrogen flow at the same temperature for 2 h and calcined under oxygen flow at 773 K for 11 h. The ALD catalyst are designated in the text by A-VSi, A-VTi and A-VTiSi.

The conventional aqueous-phase impregnated catalysts were prepared with solutions of ammonium metavanadate (Strem Chemicals, purity 99%) and oxalic acid (Prolabo, purity 99%) [13]. After drying for 24 h at 383 K, the solids were calcined in oxygen at 773 K for 11 h. The impregnated catalyst are designated in the text by I-VSi, I-VTi and I-VTiSi.

2.2. Catalyst characterization

The vanadium content of the samples was determined by ICP-AES in a Spectroflame-ICP instrument. The BET specific surface area (S_{BET}) and pore volume and diameter of the catalysts were determined by nitrogen adsorption at 77 K after heat pretreatment under vacuum for 3.5 h at 623 K. The XRD measurements were collected in a Bruker D5005 diffractometer between 3° and 80° (2θ), employing Cu Kα radiation. Raman spectra were obtained using a Dilor XY spectrometer coupled to an Olympus BH-2 microscope. The excitation was provided by the 514.5 nm line of an Ar^+ ion laser (Spectra Physics) employing a laser power of 80 mW. The samples were dehydrated for 0.5 h at 673 K under oxygen flow in a specially designed cell, and the spectra acquisitions were performed, without the sample contacting air, within the wavenumber region from 100 to 1100 cm^{-1} with a resolution of 3.0 cm^{-1}.

The XPS spectra were acquired at room temperature with a SSI 301 instrument using a monochromatic and focused (spot diameter 600 μm, 100 W) Al Kα radiation source. The residual pressure in the spectrometer chamber was 5×10^{-8} Pa during data acquisition. The pass energy of the analyzer was fixed at 50 eV for high-resolution spectra and at 150 eV for quantitative analyses. A flood gun (5 eV) was used to control the charge effects. The Si 2p or Ti $2p_{3/2}$ lines at 103.5 or 458.8 eV, respectively, were used as internal references for calibration of binding energies (BEs). The BEs were determined by fitting the experimental bands to theoretical Gaussian (80%) and Lorentzian (20%) bands with a least-squares algorithm using a nonlinear baseline. Appropriate Scofield factors were applied for quantitative analyses [16]. The samples were pretreated under helium at 673 K, exposed to NH_3 at 353 K and subsequently desorbed for 1 h under helium at 353 K.

The microcalorimetric experiments of NH_3 adsorption were performed in a heat flow calorimeter (C80 from Setaram) coupled to a conventional volumetric apparatus. The samples were activated for 12–14 h in air and for 2 h under vacuum at 673 K. Consecutive small ammonia gas (Air Liquide, purity >99.9%) pulses were introduced onto the catalyst kept at 353 K until an equilibrium pressure of ~133 Pa was reached [17]. A readsorption was carried out at 353 K after outgassing the samples for 0.5 h at the same temperature in order to determine the chemisorbed uptake (V_{irr}).

3. Results and discussion

3.1. Dispersion, structure and crystallinity of the catalysts

3.1.1. Chemical composition, surface area/porosity and XRD determinations

An ALD cycle of precursor binding and oxidation onto silica, titania and titania/silica resulted in vanadium contents of 2.9 wt.% (A-VSi), 0.8 wt.% (A-VTi) and 2.4 wt.% (A-VTiSi) throughout the support bed, respectively (Table 1). The slight difference in density of bonding sites between pure silica and titania/silica (TiSi) supports [3,18] resulted in a smaller surface concentration of vanadium on the latter support (Table 1). No notable effect on the specific surface area and porosity of the silica or TiSi supports was detected upon deposition of vanadium oxide by ALD (Table 1). However, in the case of impregnated catalysts I-VSi and I-VTiSi, a decrease in S_{BET} was observed in addition to the slight pore plugging occurring in I-VTiSi (Table 1).

The presence of V_2O_5 crystal particles with a diameter larger than ~4–5 nm in the catalysts was examined by XRD. Highly dispersed vanadia on titania displayed only the XRD features of the support. A weak sign of V_2O_5 presence was observed at $2\theta = 26.2°$ (1 1 0) [19] for the I-VSi sample (Fig. 1(b)), whereas no XRD peaks were detected for the ALD prepared A-VSi or A-VTiSi samples (Fig. 1(a) and (c), respectively). I-VTiSi presented a weak peak at $2\theta =\sim 25.3–25.5°$ (Fig. 1(d)), arguably resulting from TiO_2 anatase ($2\theta = 25.3°$, (1 0 1)) [20], V_2O_5 ($2\theta = 26.2°$, (1 1 0)) [19] or vanadium suboxide V_6O_{13} ($2\theta = 25.4°$, (1 1 0)) [21] agglomeration contributions. Carrying out the impregnation in acidic solution could have caused a partial dissolution of titania [22], and the calcination under humid conditions may have led to crystallization of amorphous titania particles [18,23].

3.1.2. Dispersion and structure analysis by XPS

Information about the relative dispersion of supported vanadia species as well as indications about the oxidation degree of vanadium in the catalysts were acquired by XPS. Andersson [24] has reported the V $2p_{3/2}$ line positions for several vanadium oxides by standardizing the spectra to the O 1s signal at 529.6 eV. Since the standardization method used in this study assigns the O 1s peak at 529.9 eV for V_2O_5 (Aldrich, purity 99.99%), i.e. allows a shift of 0.3 eV in V $2p_{3/2}$ signals toward higher BEs [25], the reference V $2p_{3/2}$ peak positions for V_2O_5, V_6O_{13}, V_2O_4 and V_2O_3 could be fixed at 516.9, 516.6, 515.9 and 515.7 eV, respectively.

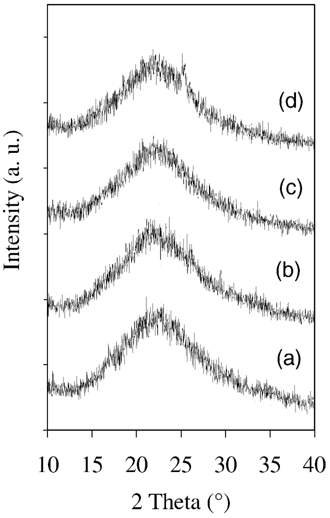

Fig. 1. XRD spectra ($2\theta = 10–40°$) of vanadia catalysts supported on SiO_2 and TiO_2/SiO_2: (a) A-VSi; (b) I-VSi; (c) A-VTiSi; (d) I-VTiSi.

The V $2p_{3/2}$ BEs of 516.5 ± 0.3 eV for the silica or titania/silica-supported samples and of ~515.9 eV for those supported on titania (Table 1) indicated thus the presence of vanadium species in an oxidation state between V^{4+} and V^{5+} in the samples [24–27]. This phenomenon of slight reduction especially of the more reducible, titania containing samples [30] A-VTi, I-VTi and I-VTiSi, can be mainly attributed to the exposure of the samples to the X-ray in UHV conditions [3] and possibly also to the NH_3 adsorption at 353 K before the XPS spectra collection [25] (see Section 3.2.2).

The XPS spectra of the O 1s line for the silica-supported catalysts, A-VSi and I-VSi, were identical and could be divided into two bands centered at 531.0 eV (vanadium bonded oxygen) and 532.7 eV

Table 1
Physico-chemical properties of the supports and vanadium oxide catalysts prepared by ALD and impregnation

Catalyst[a]	Vanadium amount		S_{BET} (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)	XPS: BE (eV)		Atomic ratios		XPS: BE of O 1s (eV) (contribution, %)
	wt.%	atoms/ $nm^2_{support}$				V $2p_{3/2}$	Ti $2p_{3/2}$	XPS: V/Si (Ti/Si)	Chemical analysis: V/Si (Ti/Si)	
SiO_2	–[b]	–	301	1.2	19–20	–	–	–	–	532.8 (100)
A-VSi	2.9	1.2	297	1.2	20	516.6	–	0.020	0.036	531.0 (10), 532.7 (90)
I-VSi	3.6	1.5	286	1.2	20	516.7	–	0.019	0.045	531.0 (10), 532.7 (90)
TiO_2	–	–	55	–	–	–	458.8	–	–	530.0 (90), 531.6 (10)
A-VTi	0.8	1.7	51	–	–	516.0	458.8	0.084[c]	0.013[c]	530.1 (90), 531.6 (10)
I-VTi	0.8	1.7	50	–	–	515.8	458.8	0.062[c]	0.013[c]	530.0 (90), 531.6 (10)
TiSi	2.7[d]	1.2[d]	307	1.2	20	–	459.4	(0.022)	(0.036)	531.1 (10), 532.8 (90)
A-VTiSi	2.4	1.0	295	1.2	20	516.8	459.4	0.018 (0.022)	0.031 (0.037)	531.2 (20), 532.9 (80)
I-VTiSi	2.3	0.9	278	0.95	20	516.3	458.6	0.015 (0.013)	0.030 (0.037)	531.4 (10), 532.7 (90)

[a] A: ALD; I: impregnation.

[b] Negligible or zero.

[c] V/Ti.

[d] Titanium amount.

(Si–O in the SiO_2 lattice) (Table 1) [3,15]. The O 1s spectrum of the pure titania support showed the contributions of both TiO_2 at 530.0 eV and $Ti(OH)_x$ at 531.6 eV [16], and was not much affected by the deposition of a dispersed, low-coverage layer of vanadia by ALD or impregnation (Table 1). The surface V/Si or V/Ti atomic ratios (Table 1) were slightly higher for ALD catalysts than for the impregnated ones, indicating a good relative dispersion of vanadia species deposited in a gas phase.

The relatively high Ti $2p_{3/2}$ peak position (459.4 eV) due to the formation of Ti–O–Si bridging bonds [14,15] in the TiSi support (Table 1) was shifted towards the bulk Ti $2p_{3/2}$ value in the I-VTiSi sample. Along with the ~40% decrease in Ti/Si ratio (Table 1), this indicated the occurrence of some titania agglomeration during the impregnation and calcination procedure, as observed also by XRD measurements. However, the position of the Ti $2p_{3/2}$ line as well as the surface and bulk Ti/Si ratios of the pure support were maintained in the bilayered A-VTiSi catalyst, excluding the possibility of changes in the support dispersion. The O 1s spectra of TiSi, A-VTiSi and I-VTiSi catalysts are presented in Fig. 2. For the TiSi support (Fig. 2(a)), the band maxima at 531.1 and 532.8 eV were due to Ti–O–Si and Si–O–Si bonds, respectively [14,15]. Addition of vanadia by impregnation (Fig. 2(c)) preserved the component ratio of 10/90, only slightly altering the position of the lower band (Table 1). Both vanadia and titania are thought to contribute in the formation of this band at 531.4 eV. However, an additional effect of the deposited vanadia on the support titania submonolayer was illustrated for the A-VTiSi catalyst (Fig. 2(b)) by the doubled contribution (20%) of the band at 531.2 eV.

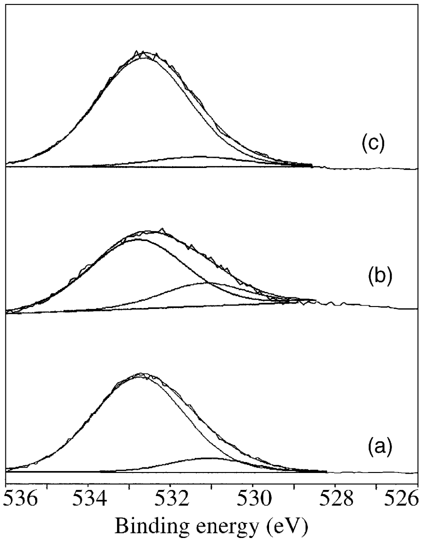

Fig. 2. O 1s XPS spectra of titania/silica and vanadia catalysts supported on TiO_2/SiO_2: (a) TiSi; (b) A-VTiSi; (c) I-VTiSi.

3.1.3. Determination of the nature of the surface species by Raman spectroscopy

The surface analysis was completed by Raman spectroscopy to investigate the vanadia species interaction on the carriers. For the titania supported catalysts, identical support bands at wavenumbers 144, 397, 443, 516, 639 and 788 cm^{-1} [1,15,28,29] appeared. In addition, a sharp but low intensity Raman peak at 1031 cm^{-1} was detected for both I-VTi and A-VTi, indicating the formation of isolated, monomeric vanadyl species [29–31].

Whereas the broad Raman features of highly dispersed TiSi (Fig. 3(a)) were identical to those of the silica support, a stretching ν(V=O) of isolated VO_4 species [1,32,33] gave rise to strong peaks at 1037 and 1041 cm^{-1} for the impregnated samples I-VSi and I-VTiSi (Fig. 3(c)), respectively. These two samples also showed clear features of crystalline V_2O_5, located at ~142, 194, 282, 301, 407, 470, 515, 694 and 994 cm^{-1} [29,32–35]. However, for the ALD samples A-VSi and A-VTiSi (Fig. 3(b)), no typical crystalline V_2O_5 bands were present, but sharp features at 1042 cm^{-1} were detected indicating that the catalysts contained isolated tetrahedral vanadate species possessing one mono-oxo terminal V=O bond in addition

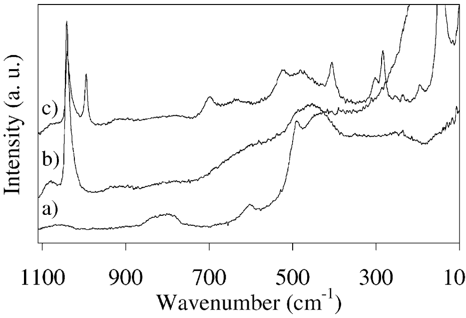

Fig. 3. Raman spectra of titania/silica and vanadia catalysts supported on TiO_2/SiO_2: (a) TiSi; (b) A-VTiSi; (c) I-VTiSi.

to three bridging V–O–Si bonds [1,30,32,33]. The catalysts also showed a broad, rather intense band at ∼440 cm^{-1}, probably due either to the silica support or to poorly crystallized vanadia [32]. Moreover, it is not clear whether the very broad, low intensity band at ∼920 cm^{-1} observed for A-VTiSi (and I-VTiSi) arose from polymeric units of vanadia attached to titania [1,30], from perturbed vibrations of the silica support [32] or from other, unidentified vanadia species [32]. Finally, it has been suggested that the very broad features at ∼248 and ∼640 cm^{-1} are caused by the stretching and bending of V–O–Ti bridging bonds in the surface vanadia–titania interaction [5]. Nevertheless, the band at ∼640 cm^{-1} detected for I-VTiSi could also be due to small amounts of titania anatase crystals present due to the titania layer agglomeration during the calcination [1,5,29]. However, the definite identification of TiO_2 in I-VTiSi by Raman spectroscopy was made difficult by the overlapping positions of intense crystalline V_2O_5 ($\sim 144 \pm 2\,cm^{-1}$) [1,28] and TiO_2 anatase peaks ($\sim 147 \pm 6\,cm^{-1}$) [15,28,29,33,34].

Jehng and Wachs [1] observed similarities in the Raman characteristics of $V_2O_5/TiO_2/SiO_2$ (∼0.7 V and ∼1.8 Ti atoms/$nm^2_{support}$) and V_2O_5/TiO_2 catalysts, which led them to suggest that the vanadia species interacted preferentially with the surface TiO sites. In our bilayered catalysts (Fig. 3), typical features of silica-supported vanadia were also detected along with the indications of V–O–Ti interactions.

3.2. Acidity of the catalysts

3.2.1. Quantitative measurements by adsorption microcalorimetry

Ammonia adsorption microcalorimetry measurements were carried out to determine the number, strength and strength distribution of the surface acid sites of the catalysts [17]. As shown by the total adsorbed volumes (V_T) in Table 2, the deposition of a low amount of vanadia onto titania decreased slightly the acidity of the support [30], whereas rather weak surface acid sites were created by addition of vanadia onto neutral silica by ALD or impregnation [36–38]. The superior ammonia uptakes as well as initial heats of adsorption for A-VSi (106 kJ/mol and 156 μmol $NH_3/g_{catalyst}$, respectively) compared to those for I-VSi (91 kJ/mol and 139 μmol $NH_3/g_{catalyst}$, respectively) are mainly due to the better dispersion of the vanadia species in the former catalyst.

The differential heats (Q_{diff}) of NH_3 adsorption on TiSi, A-VTiSi and I-VTiSi are presented in Fig. 4 vs. ammonia uptake. The acid site strength distributions

Table 2
Acidity data obtained from the calorimetric and XPS measurements of NH_3 adsorption at 353 K

Catalyst[a]	Quantitative calorimetric data		Qualitative and quantitative XPS data	
	V_T[b] (μmol $NH_3/g_{catalyst}$)	$V_{irr}/n(V+Ti)$ ($V_{irr}/n(V+Ti+Si)$)[c] ($g^{-1}_{catalyst}$)	BE of N 1s (eV) (contribution, %)	N/(V + Ti) (N/(V + Ti + Si))
SiO_2	66	–[d]	–	–
A-VSi	156	–	399.9 (50), 401.5 (50)	–
I-VSi	139	–	400.6 (70), 402.2 (30)	–
TiO_2	282	0.014[e]	400.5 (100)	0.033[f]
A-VTi	221	0.011	400.4 (100)	0.027
I-VTi	196	0.009	400.1 (100)	0.028
TiSi	204	0.13[e] (0.005)[g]	400.1 (65), 402.3 (35)	0.14[f] (0.003)[h]
A-VTiSi	318	0.07 (0.005)	400.5 (80), 402.5 (20)	0.27 (0.010)
I-VTiSi	178	0.05 (0.003)	400.2 (100)	0.22 (0.006)

[a] A: ALD; I: impregnation.
[b] Total adsorbed volume at 27 Pa.
[c] Number of strong sites: irreversibly adsorbed volume at 27 Pa/mol of components.
[d] Negligible or zero.
[e] $V_{irr}/n(Ti)$.
[f] N/Ti.
[g] $V_{irr}/n(Ti+Si)$.
[h] N/(Ti + Si).

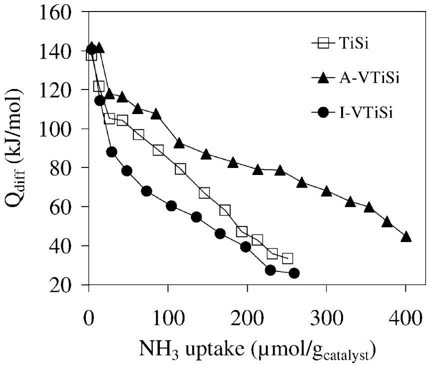

Fig. 4. Differential heats of adsorption of ammonia at 353 K on titania/silica and vanadia catalysts supported on TiO_2/SiO_2 as a function of uptake.

for the samples are shown in Fig. 5. Whereas the initial heats of adsorption (Q_{init}) stayed at a constant value of ∼140 kJ/mol (Fig. 4), the number of acid sites (V_T values) decreased in the order A-VTiSi ≫ TiSi > I-VTiSi (Table 2). The weak, medium and strong strength acid sites of the TiSi support were equally affected and their amount practically doubled when the vanadia layer was deposited by ALD (Fig. 5). The Q_{diff} curve profile of A-VTiSi is parallel to that of TiSi, with heat values higher by ∼20 kJ/mol at the beginning of the adsorption. Once these strong acid sites due to the titania/silica support and vanadia attached to titania were titrated, the chemisorption of ammonia on weak acid sites, i.e. mainly vanadia on silica, produced the second part of the descending curve.

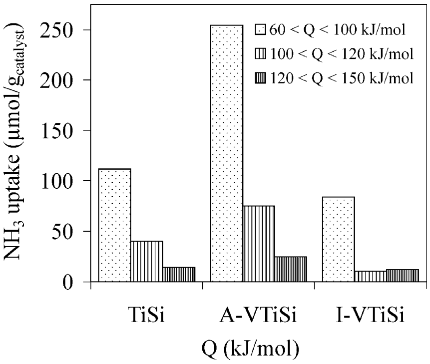

Fig. 5. Acid site strength distribution of titania/silica and vanadia catalysts supported on TiO_2/SiO_2 obtained after ammonia adsorption at 353 K.

When vanadia was added by impregnation, the distribution pattern of the support was altered, and especially the number of sites at Q values between 60 and 120 kJ/mol decreased (Fig. 5). The acidic behavior of I-VTiSi followed that of TiSi at low ammonia uptakes (strong acid sites) (Fig. 4), but started to resemble that of I-VSi at uptakes greater than ∼50 μmol $NH_3/g_{catalyst}$ (medium and weak strength acid sites). Thus, the support contribution can be seen in the presence of medium and strong strength acid sites ($100 < Q < 150$ kJ/mol) (Fig. 5), absent from the silica-supported vanadia sample, and in the difference (∼40 μmol $NH_3/g_{catalyst}$, Table 2) between the total numbers of acid sites V_T of I-VTiSi and I-VSi. It can be estimated that for I-VTiSi, around 1/3 of the vanadium is attached to surface titania species, whereas 2/3 is on the silica support. The lower energy values observed for I-VTiSi compared to the TiSi support (and to A-VTiSi) could be attributed to the agglomeration of both titania and vanadia species during the impregnation process.

These microcalorimetry results support the Raman spectroscopy observations that dispersed vanadia species are bound in A-VTiSi both onto the surface titania species and onto the remaining free surface Si–OH groups. This is also the case for the I-VTiSi catalyst, although the deposition is much more heterogeneous, resulting in more bulk-like vanadia, i.e. less dispersed and acidic vanadia species.

3.2.2. Study of strong and medium strength surface acid sites by adsorption XPS

The presence of surface acid sites and their nature were evaluated also by ammonia adsorption XPS [16]. This XPS technique of probe molecule adsorption has been introduced previously, e.g. by Borade et al. [39] and Huang et al. [40] for the analysis of the acid–base properties of zeolites. The XPS measurements of ammonia adsorption reveal only the strong and medium strength acid sites and does not titrate weak sites, which do not retain ammonia in ultra-high vacuum conditions of the analyses [16].

The XPS spectra of the N 1s line of titania, A-VTi and I-VTi consisted of a single band with maximum at ∼400.3 eV (Table 2), thus indicating the presence of only Lewis surface acid sites [16]. The I-VSi sample showed a N 1s line decomposed into two components at 400.6 eV (Lewis, 70%) and 402.2 eV (Brønsted,

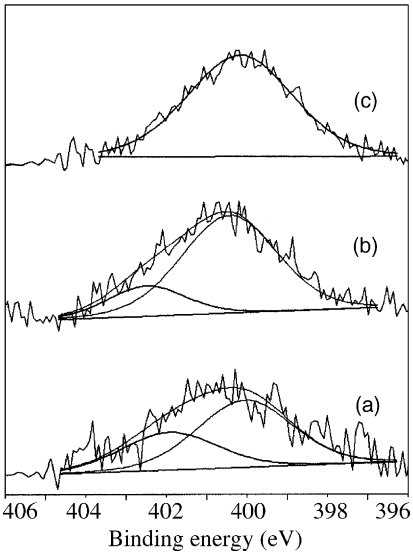

Fig. 6. N 1s XPS spectra obtained after ammonia adsorption at 353 K on titania/silica and vanadia catalysts supported on TiO_2/SiO_2: (a) TiSi; (b) A-VTiSi; (c) I-VTiSi.

30%) [16]. For A-VSi, equal to 50% contributions at maximum values 399.9 and 401.5 eV were observed, indicating that the Brønsted acidity of surface vanadia species was also strong in the ALD prepared catalyst.

The N 1s spectra of TiSi, A-VTiSi and I-VTiSi are presented in Fig. 6. When in bare titania only Lewis acidity is detected [30,41], the titania/silica support, as seen in Fig. 6(a), also showed rather strong Brønsted acid sites (Table 2) [14]. Upon addition of vanadia by ALD, the relative contribution of strong Lewis acid sites increased from 65 to 80%. However, when vanadia was deposited by impregnation, only Lewis acid sites were detected. The absence of strong Brønsted acidity was due to the overall less acidic character of the I-VTiSi catalyst, as observed also by microcalorimetry, and may arise from the change in support nature to a more “titania-like” behavior by agglomeration.

The XPS N/(V + Ti) ratios decreased in the order: A-VTiSi > I-VTiSi > TiSi $\gg$ TiO_2 > I-VTi $\sim$ A-VTi (Table 2). The microcalorimetric $V_{irr}/n(V+Ti)$ bulk ratios, calculated by dividing the irreversibly adsorbed amounts (V_{irr}) by the combined molar quantities of V and Ti, decreased similarly, only at substantially lower values (Table 2). The higher these ratios representing the number of strong acid sites on which ammonia is adsorbed, the more acidic the sample under study [16]. In the bilayered catalysts, the difference in strong acidity was detected in favor of the ALD samples, as seen from the N/(V + Ti + Si) and $V_{irr}/n(V + Ti + Si)$ ratios (Table 2).

4. Conclusion

As expected, the ALD modification of the titania/silica carrier by a submonolayer of vanadia did not affect the surface area or porosity of the material. No crystallinity but highly dispersed isolated vanadia surface species were detected by XRD and by XPS and Raman spectroscopies. However, in the corresponding aqueous-phase impregnated catalyst the addition of vanadia decreased the surface area of the support and led to less dispersed and more crystalline vanadia. Moreover, some agglomeration of the titania interface layer occurred during the impregnation procedure, as verified by XPS. Vanadia–oxygen–titanium interaction was suggested by Raman spectroscopy, and ammonia adsorption microcalorimetric studies confirmed that the vanadia species in the bilayered catalyst were attached to both the titania surface species and the silica support.

The acidic character of the titania/silica support was greatly enhanced by the atomic layer deposited vanadia. The homogeneous alteration of the surface acid site populations confirmed the high dispersion of the vanadia species and indicated that the $VO(OPr^i)_3$ precursor was bound by ALD in equal manners to all support adsorption sites independently of their strength. Both the total number and relative strength of acid sites were higher in ALD $V_2O_5/TiO_2/SiO_2$ catalysts than in the corresponding impregnated ones, as probed by XPS and microcalorimetry of NH_3 adsorption.

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