Journal of Catalysis 283 (2011) 108–118

Contents lists available at SciVerse ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Oxo/imido heterometathesis of *N*-sulfinylamines and carbonyl compounds catalyzed by silica-supported vanadium oxochloride

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ARTICLE INFO

Article history:
Received 2 May 2011
Revised 28 July 2011
Accepted 29 July 2011
Available online 31 August 2011

Keywords:
Heterometathesis
Heterogeneous catalysis
N-sulfinylamine
Imine
Imido
Vanadium
Silica-supported

ABSTRACT

A series of silica-supported vanadium oxo complexes has been prepared via water-free grafting $VOCl_3$ onto the silica surface. The obtained materials have been characterized with Raman, diffuse reflectance FTIR (DRIFT) and UV–vis, ^{51}V solid-state NMR and X-ray photoelectron spectroscopies, elemental analysis and N_2 physisorption. The samples with a low vanadium loading (1–5%) have been found to be comprised primarily of the isolated tetrahedral d^0 units $(\equiv SiO)V(=O)Cl_2$, whereas the materials with a higher vanadium content are contaminated with a significant amount of d^1 vanadium species. The silica-supported vanadium complexes act as heterogeneous catalysts for oxo/imido heterometathesis between *N*-sulfinylamines and carbonyl compounds affording imines and SO_2. Grafting $VOCl_3$ onto silica leads to a dramatic enhancement of its catalytic activity. A novel water-free express method for preparation of imines of wide range of aldehydes and some ketones has been developed. Noteworthy, this is the first example of transition metal mediated heterometathetical imidation of ketones.

1. Introduction

Olefin metathesis has already become a powerful practical tool of modern organic synthesis [1,2]. Since the middle sixties, the olefin metathesis catalysts have passed the long way from the first examples of ill-defined heterogeneous systems to a varied stock of well-defined homogeneous catalysts. In recent years, having successfully combined both directions, Basset, Copéret, and others have developed a new generation of highly efficient well-defined heterogeneous olefin metathesis catalysts based on Schrock carbene complexes via grafting a molecular precursor of a determinate structure onto the surface of an inorganic support [3–7]. The immobilized olefin metathesis catalysts displayed the activity and stability superior to their homogeneous analogs, especially in metathesis of functionalized olefins bearing polar substituents [5–7]. Application of the grafting methodology to some other transition metal complexes has recently led to the discovery of well-defined heterogeneous catalysts for such nontrivial processes as polyolefin depolymerization [8], nitrogen activation at ambient temperature [9], alkane metathesis [10], and other related transformations [11].

Catalytic *heterometathesis* (i.e., carbon–heteroatom and heteroatom–heteroatom multiple bonds metathesis) is quite a novel class of transition metal mediated reactions. Although numerous stoichiometric heterometathetical transformations as well as [2 + 2] cycloadditions across M=O, M=N and other metal–ligand multiple bonds were described in literature [12–15], only a few examples of transition metal catalyzed heterometathesis, mainly imido-transfer reactions, were reported to date. These are metathesis of imines [16–20], carbodiimides [21–23], diphosphenes [24], and nitriles [25,26]; condensation of isocyanates and *N*-sulfinylamines into carbodiimides [27,28] and sulfurdiimines [29], respectively; imidation of dimethylformamide with *N*-sulfinylamines affording formamidines [29] and metathetical imido-deoxygenation of aldehydes with isocyanates [20], *N*-sulfinylamines [30] and iminophosphoranes [31,32]. Among them, only two examples, namely imine metathesis [20] and condensation of isocyanates into carbodiimides [33] catalyzed by CH_3ReO_3/Nb_2O_5 and $VOCl_3/SiO_2$ respectively, belong to heterogeneous catalysis.

Since heterometathesis implies transformations of the polar substrates, heterometathesis catalysts immobilized on polar inorganic supports could be expected to exhibit a higher activity

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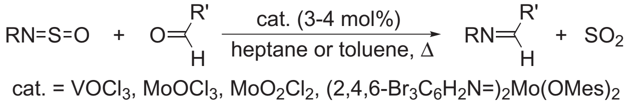
doi:10.1016/j.jcat.2011.07.011



Scheme 1. Oxo/imido heterometathesis between aldehydes and *N*-sulfinylamines.

as compared to their homogeneous analogs, especially in nonpolar media. Herein, we apply this hypothesis to the heterometathesis reaction between aldehydes and *N*-sulfinylamines that has been recently shown in our group to be catalyzed by the vanadium and molybdenum oxo- and imido complexes in hydrocarbon solvents (Scheme 1) [30]. $VOCl_3$ grafted onto silica ($VOCl_3/SiO_2$) was chosen as a model catalytic system to compare its activity with that of unsupported $VOCl_3$. This system was selected since it is generally accepted that, at least at low loadings, vanadium oxide species on the silica are composed of isolated tetrahedral $(\equiv SiO)_nV(=O)X_{3-n}$ units (where X = Hal, OR, etc. and $n = 1, 2, 3$) [33–47], whose structure closely resembles the structure of the tetrahedral vanadium oxo complexes in solution. This structural similarity suggests that silica-supported vanadium oxochloride could be involved in the same heterometathetical transformations as molecular $VOCl_3$. In addition, silica-supported vanadium oxo complexes were extensively studied in recent decades and diverse physical techniques were found suitable for their characterization.

This work demonstrates convincingly that the immobilization of $VOCl_3$ on the silica support dramatically enhances its catalytic activity; $VOCl_3/SiO_2$ is shown to be a highly efficient catalyst for express water-free preparation of imines of wide range of aldehydes and some ketones.

2. Experimental

2.1. Instrumentation

If not otherwise stated, all manipulations were carried out under an argon atmosphere using standard Schlenk techniques. NMR spectra were recorded using Bruker AMX 400 and Avance 300 spectrometers. Infrared spectra were registered with Specord M80 and M82 spectrophotometers. Elemental analyses were performed in the Laboratory of Microanalysis of INEOS RAS. The amount of chemisorbed vanadium was determined by X-ray fluorescence analysis.

Nitrogen adsorption–desorption isotherms were measured at 77 K using an ASAP 2000 instrument (Micromeritics). The samples were preheated for 3 h in a vacuum at 200 °C before the measurements. The specific surface area was calculated by the BET method. The pore size and the pore size distribution were calculated by the BJH method using the desorption isotherm branch.

Raman spectra in the 100–1200 cm^{-1} region were recorded using a Laser Raman spectrometer LabRAM (Horiba Jobin Yvon) equipped with a cooled CCD detector and a microscope. The excitation was accomplished by the red 632.8 nm line of a He-Ne laser with an output power less than 5 mW. The samples for the analysis were transferred into capillary tubes and sealed under argon.

UV–vis diffuse reflectance spectra (UV–vis DRS) in the 260–800 nm region were recorded using a Hitachi M-340 UV–vis–NIR spectrophotometer equipped with a R-10A integrating sphere accessory using a homemade Schlenk-type quartz cell under argon. A disk of pressed MgO powder was used as a reference sample.

FTIR diffuse reflectance (DRIFT) spectra were recorded in the 6000–400 cm^{-1} range at a data point resolution of 4 cm^{-1} with a Nicolet "Protege" 460 spectrometer equipped with a diffuse reflectance attachment developed at IOC RAS [48]. To obtain a satisfactory signal-to-noise ratio, 500 scans were collected per spectrum. The catalysts were placed in an ampule (supplied with a CaF_2 window) in air and immediately evacuated at 350 °C for 2 h. The probe molecule CD_3CN was adsorbed at ambient temperature and the saturation vapor pressure of 96 Torr.

X-ray photoelectron spectra (XPS) were measured using a XSAM-800 spectrometer (Kratos) with Mg Kα nonmonochromatic radiation; the Mg Kα source was operated at 90 W. The spectra were measured under the conditions of a constant relative energy resolution in steps of 0.1 eV at ambient temperature and $\sim 4 \times 10^{-10}$ Torr pressure. The spectral lines recorded were fitted with a Gauss profile or a sum of Gauss profiles after the subtraction of the linear background. The energy scale of the spectrometer was calibrated using the standard procedure; the following binding energies were used: Cu $2p_{3/2}$, 932.7 eV; Ag $3d_{5/2}$, 368.3 eV; and Au $4f_{7/2}$, 84.0 eV. The XPS spectra were referenced to the C—/C—H component of the C 1s spectrum of adventitious carbon, assuming its binding energy to be 285.0 eV.

The ^{51}V NMR spectra of solid samples were recorded at 297 K using a Bruker Avance II 300 spectrometer operating at a frequency of 78.94 MHz. The spin system was excited by a one-pulse sequence using short pulses (pulse width, 2.0 μs; dead time, 6.0 μs; number of scans, 10,000). Exponential multiplication with a 100-Hz line broadening was used. The ^{51}V NMR chemical shifts were referenced to an external $VOCl_3$ solution in $CDCl_3$. The chemical shifts of solid-state signals in static ^{51}V NMR spectra were measured with an accuracy of ±10 ppm. The solid samples were transferred into NMR tubes equipped with Teflon stopcocks under argon.

2.2. Starting materials

$VOCl_3$ (Strem Chemicals) was distilled under argon, degassed through three freeze–pump–thaw cycles and stored in a Schlenk tube equipped with a Teflon stopcock. Tri(*tert*-butoxy)silanol $(^tBuO)_3SiOH$ and polyhedral oligomeric silsesquioxane trisilanol $^iBu_7Si_7O_9(OH)_3$ (^{i}Bu-POSSH$_3$) were purchased from Aldrich. The corresponding vanadyl complexes $[(^tBuO)_3SiO]_3VO$ [49] and [^{i}Bu-POSS]VO [50] were prepared according to the previously reported procedures. Reagent grade solvents were dried by refluxing over sodium/benzophenone ketyl (tetrahydrofuran and diethyl ether), sodium (toluene and *n*-heptane), phosphorus pentoxide (chloroform), and calcium hydride (dichloromethane) and distilled prior to use. $CDCl_3$ was dried over phosphorus pentoxide and stored over activated 4 Å molecular sieves in a Schlenk tube equipped with a Teflon stopcock. Details for organic compounds used are given in Supplementary material.

Silica gel 60 for column chromatography (Merck®; surface area, 480–540 m^2/g; particle size, 63–200 μm; mean pore size, 60 Å) was used as a support in all experiments. The designations for the silicas used are as follows. **Silica-25** was just outgassed in a vacuum (10^{-2} Torr) at ambient temperature for 10 min. **Silica-300** was preheated at 300 °C in air for 2 h and cooled down to ambient temperature in a vacuum (10^{-2} Torr). This procedure is supposed to remove only physically adsorbed water without significant dehydroxylation [51]. **Silica-500** was preheated at 500 °C in a vacuum (10^{-2} Torr) for 12 h.

2.3. Catalyst preparation

Silica-supported vanadium catalysts were prepared via impregnation of silica with $VOCl_3$ in dry *n*-heptane. A typical procedure for **5V/SiO$_2$-300** preparation: $VOCl_3$ (0.30 ml, 3.2 mmol) was added to a vigorously stirred suspension of **silica-300** (3.92 g, 65.3 mmol) in 30 ml of *n*-heptane. The mixture was stirred at room temperature (RT) for 5 h, and then, all volatiles were removed in a vacuum. The resulting material was twice washed with boiling *n*-heptane

Table 1
Designations and elemental analysis data of silica-supported vanadium catalysts.

Heterogeneous catalyst	Support[a]	V (mol%)[b]	V (wt.%)[c]	Cl/V[c] atomic ratio
10V/SiO$_2$-25	Silica-25	10	7.1	0.4
1V/SiO$_2$-300	Silica-300	1	0.9	1.5
5V/SiO$_2$-300	Silica-300	5	3.9	1.3
10V/SiO$_2$-300	Silica-300	10	6.4	1.0
2V/SiO$_2$-500	Silica-500	2	1.4	2.0
5V/SiO$_2$-500	Silica-500	5	3.3	1.7

[a] The designations of silicas are explained in Section 2.2.
[b] Nominal value.
[c] Determined from elemental analysis.

(1 h reflux followed by filtering or decanting) and dried at RT in a vacuum yielding 4.25 g of white powder. For the designations of the catalysts, see Table 1. Calcined samples were prepared by heating the sample for several hours at 500 °C in a quartz tube in a flow of air flowing through a column filled with dry Al_2O_3. Preheated silicas, and all the heterogeneous catalysts were stored in Schlenk flasks under argon.

2.4. Catalytic tests

A Schlenk flask was charged with the catalyst, and a certain volume of a freshly prepared 0.15 M *n*-heptane solution of benzaldehyde and *N*-sulfinyl-2,4,6-trichloroaniline (1:1) was added under argon. The reactor was equipped with a backflow condenser, purged with argon, and heated under reflux (98 °C) for 20 min. Then, the reaction mixture was cooled down for ~1 min, the internal standard (C_6Me_6) was added (if the heterogeneous catalyst was used, it was filtered off before), and the conversion was determined from ^{1}H NMR spectra.

When the test reaction was carried out for a longer time (>20 min), it was followed with IR spectroscopy by taking aliquots from the reaction mixture and monitoring the benzaldehyde carbonyl (1712 cm^{-1}) and imine C=N (1648 cm^{-1}) bands. The substrate to catalyst molar ratio was calculated with respect to the total vanadium amount in the sample determined from elemental analysis.

2.5. Preparation of imines

The detailed procedures for the synthesis of imines **1a–15a**, **1b–5b** (Tables 4 and 5) as well as their spectral characteristics and elemental analysis data are given in Supplementary material.

2.6. Stoichiometric reactions of surface complexes

2V/SiO$_2$-500 (558 mg, ~0.15 mmol V) was placed into a Schlenk flask, and then, *n*-heptane (10 ml) and *N*-sulfinyl-2-trifluoromethylaniline (0.23 ml, 1.5 mmol) were added. The mixture was stirred for 20 min under reflux and then filtered via a cannula filter, and the residue was dried at 50 °C in a vacuum (7.5×10^{-4} Torr). The purple powder was obtained (580 mg). Elemental analysis: V, 1.45%; N, 0.45%; C, 2.85%; F, 2.01%; S $\leqslant$ 0.1% (V:N:C:F = 0.9:1:7.4:3.3).

A portion of the material obtained (102 mg, ~0.03 mmol V) was placed into a Schlenk flask. *n*-Heptane (4 ml) and benzaldehyde (0.06 ml, 0.6 mmol) were added. The mixture was heated under reflux for 20 min and then cooled down, filtered, and washed with 20 ml of a pyridine–heptane (1:10) mixture. The filtrate was evaporated in a vacuum, and an internal standard (C_6Me_6) was added. *N*-benzylidene-2-trifluoromethylaniline (~50% to the initial vanadium content in the sample) was identified in ^{1}H, ^{19}F NMR, and IR spectra [52]. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.05 (d, ^3J = 7.9 Hz, 1H), 7.27 (t, ^3J = 7.7 Hz, 1H), 7.45–7.56 (m, 4H), 7.68 (d, ^3J = 7.7 Hz, 1H), 7.91–7.95 (m, 2H), 8.37 (s, 1H, C*H*=N); ^{19}F NMR (282 MHz, CDCl$_3$): δ 17.51 (s); IR (*n*-heptane): ν 1636 cm^{-1} (C=N).

3. Results and discussion

3.1. Catalyst preparation

Most grafting techniques are based on the interaction of the surface hydroxyl groups of the support with metal chlorides, alkoxides, amides, alkyls, etc., leading to a substitution of one or several ligands. Interaction of $VOCl_3$ with the silica surface is depicted in Scheme 2.

In this work, immobilization was accomplished via impregnation of the support with a certain amount of $VOCl_3$ in excess of *n*-heptane followed by evaporation of volatiles in a vacuum. This water-free grafting procedure is usually referred to as atomic layer deposition (ALD) [45]. It is believed that aggregation and formation of oligomeric vanadia species and V_2O_5 crystallites can thus be avoided providing a better dispersion of the precursor on the surface. A series of heterogeneous catalysts with different $VOCl_3$ loadings (1–10 mol%) were prepared using silicas dehydroxylated under different conditions. Their designations and elemental analysis data are summarized in Table 1.

All the manipulations were carried out in the inert atmosphere since the catalysts, substrates (*N*-sulfinylamines), and intermediates (imido complexes) are sensitive to moisture. The exposure of the catalysts to air leads to an immediate color change from initial white or beige (or gray for **10V/SiO$_2$-25**) to yellow or orange caused by hydrolysis of V—Cl bonds (the chlorine loss was confirmed by elemental analysis). After air exposure for several days, the samples finally become green, which is typical of fully hydrated supported vanadia [41,42,45–47].

On the other hand, we focused primarily on the synthetic laboratory application of our catalysts and hence tried to simplify the techniques used as much as possible and to avoid the procedures that are not commonly used in organic laboratories (e.g., calcination). The same reason accounts for the choice of Merck silica gel 60 as a widespread and easily available sorbent for column chromatography.

3.2. Catalyst characterization

A number of physicochemical techniques were applied to characterize the obtained materials. The influence of the grafting

$$n \equiv SiOH + VOCl_3 \longrightarrow (\equiv SiO)_nV(=O)Cl_{3-n} + nHCl$$

Scheme 2. Interaction of $VOCl_3$ with surface hydroxyl groups of silica.

Table 2
Textural characteristics of the supports and immobilized materials.

Heterogeneous catalyst	BET surface area (m^2/g)	Surface density (V/nm^2)	Pore size (Å)	Pore volume (cm^3/g)
Silica-300	467	–	49	0.72
1V/SiO$_2$-300	451	0.24	48	0.69
5V/SiO$_2$-300	425	1.08	47	0.62
10V/SiO$_2$-300	423	1.79	44	0.58
10V/SiO$_2$-25	405	2.07	48	0.59
Silica-500	500	–	49	0.71
2V/SiO$_2$-500	480	0.34	48	0.68
5V/SiO$_2$-500	477	0.82	45	0.60

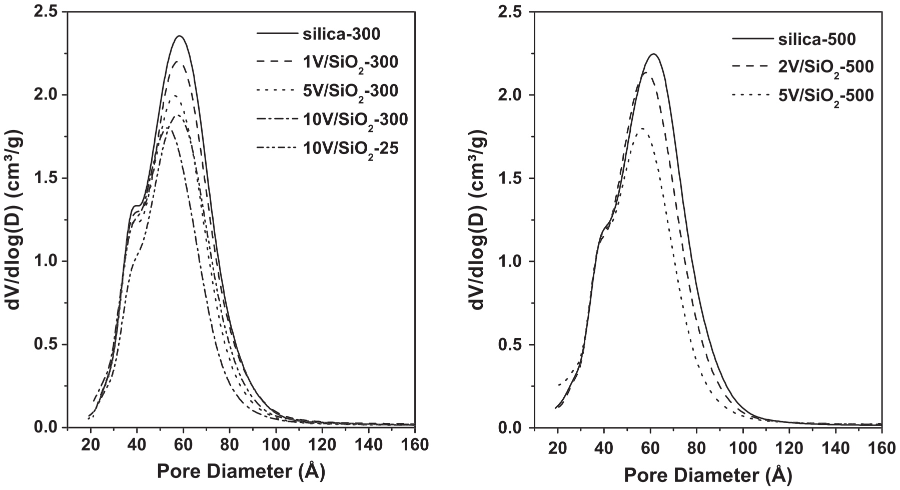


Fig. 1. Pore size distribution profiles of the supports and immobilized materials.

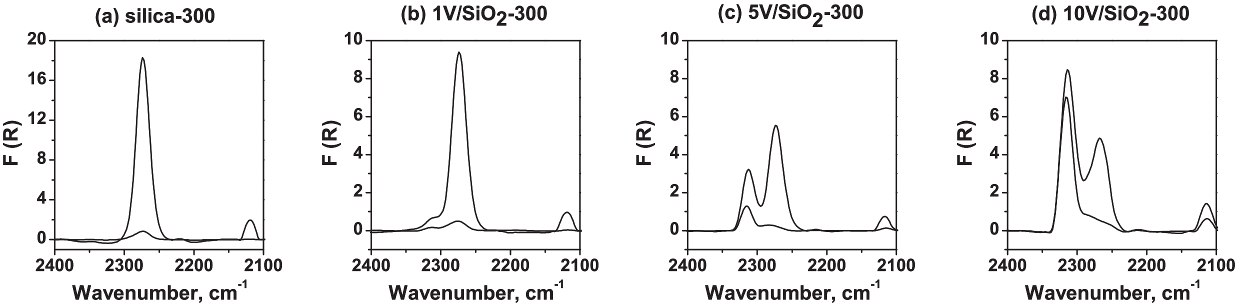


Fig. 2. DRIFT spectra of the C≡N stretching vibration region of: (a) **silica-300**, (b) **1V/SiO$_2$-300**, (c) **5V/SiO$_2$-300** and (d) **10V/SiO$_2$-300** after adsorption and desorption of CD$_3$CN.

process on the porous structure of the support was estimated using N$_2$ physisorption. The nature of the surface acidic sites was probed by the adsorption of CD$_3$CN monitored by DRIFT spectroscopy. The structure of vanadium centers was investigated with Raman, UV–vis DRS, XPS, and ^{51}V solid-state NMR spectroscopies.

The textural characteristics of the parent supports and immobilized materials are given in Table 2, and the pore size distribution profiles are presented in Fig. 1. It is clear that the porous structure of the support is not strongly affected by grafting. As should be expected, a gradual decrease in the surface area, pore size, and pore volume is observed with increasing vanadium loading.

Fig. 2 demonstrates the DRIFT spectra of **silica-300**, **1V/SiO$_2$-300**, **5V/SiO$_2$-300**, and **10V/SiO$_2$-300** in the region of C≡N stretching vibrations after adsorption of CD$_3$CN (upper curves) and after removal of adsorbed CD$_3$CN upon evacuation for 100 min (lower curves). Only one band at 2273 cm^{-1} was observed in the spectrum of the parent support, while two bands at 2313–2315 cm^{-1} and 2267–2273 cm^{-1} were found in the spectra of the vanadium-containing samples. Note that the spectrum of **1V/SiO$_2$-300** exhibits the first of these two bands as a low-intensity shoulder. The band at 2115 cm^{-1} in all spectra is due to the bending vibrations of C—D bonds of CD$_3$CN.

The C≡N vibration at 2267–2273 cm^{-1} belongs to CD$_3$CN molecules adsorbed on moderate Brönsted acidic sites (BAS). This band is blue shifted by 14–20 cm^{-1} compared to the C≡N vibration frequency in the free CD$_3$CN molecule in the gas phase at 2253 cm^{-1} [53–55]. These sites are the surface hydrogen-bonded silanol groups. This was confirmed by DRIFT spectra in the region of silanol stretching vibrations (Fig. 3). The broad Si—OH band in the spectrum of **silica-300** indicates that the parent support does not contain isolated silanols. Yet, Fig. 3 clearly demonstrates partial consumption of silanol groups caused by grafting and appearance of the band at ~3740 cm^{-1} characteristic of isolated Si—OH. The interaction of hydrogen-bonded hydroxyl groups with CD$_3$CN was also confirmed by the red shift of Si—OH bands. It should be noted that the acidity of hydrogen-bonded OH groups increases in parallel with the V content. The red shifts of OH groups in the spectra of **1V/SiO$_2$-300**, **5V/SiO$_2$-300**, and **10V/SiO$_2$-300** are equal

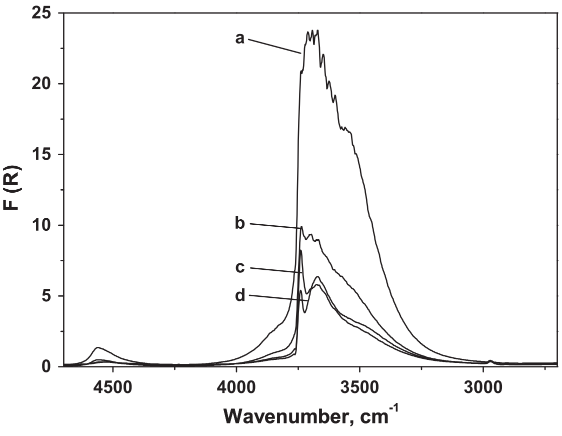


Fig. 3. DRIFT spectra of the silanol stretching vibration region of: (a) **silica-300**, (b) **1V/SiO$_2$-300**, (c) **5V/SiO$_2$-300**, (d) **10V/SiO$_2$-300**.

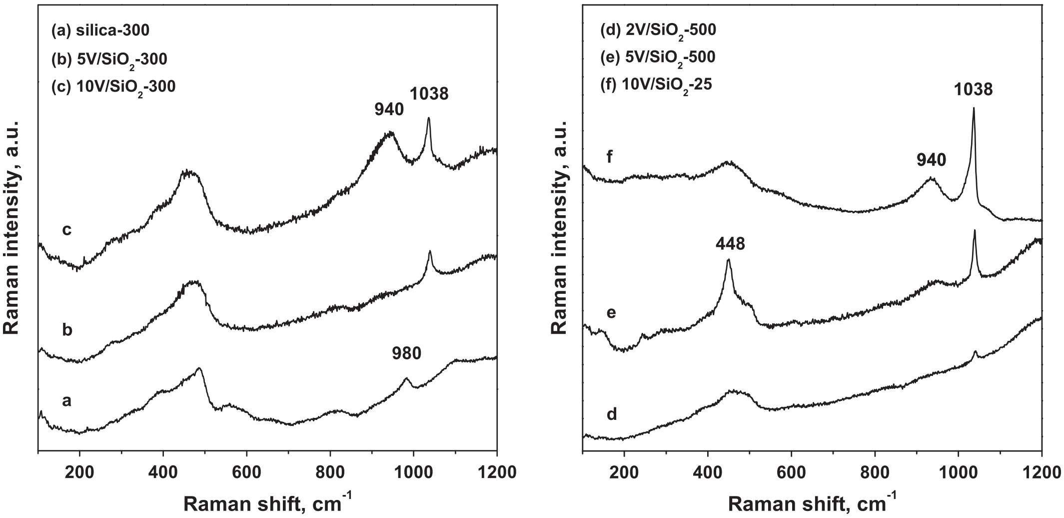


Fig. 4. Raman spectra of: (a) **silica-300**, (b) **5V/SiO$_2$-300**, (c) **10V/SiO$_2$-300**, (d) **2V/SiO$_2$-500**, (e) **5V/SiO$_2$-500** and (f) **10V/SiO$_2$-25**.

to 273, 283 and 315 cm^{-1}, respectively, whereas for **silica-300** it equals to 300 cm^{-1}.

The 2313–2315 cm^{-1} band (Fig. 2b–d) corresponds to the C≡N vibration of CD_3CN molecules adsorbed on strong Lewis acidic sites (LAS) (vanadium cations); the blue shift is 60–62 cm^{-1} [53–55]. The increase in the concentration of vanadium is accompanied by increasing relative intensity of the 2313–2315 cm^{-1} band. The desorption curves show that the adsorption on LAS is more stable than on BAS. In particular, evacuation for 100 min at ambient temperature appears insufficient to fully remove CD_3CN adsorbed on vanadium cations, whereas CD_3CN adsorbed on hydroxyl groups is almost completely removed.

Application of DRIFT spectroscopy to vanadium oxides grafted to silica entails significant difficulties, since the silica is virtually nontransparent in the spectral region below 1200 cm^{-1} and the V═O bands appear to be totally disguised by the intense Si—O—Si fundamental modes. Conversely, Raman spectroscopy is widely used for characterization of surface vanadium oxo species on various oxide supports since the latter are very weak Raman scatters [46,47].

The Raman spectra of **silica-300** and the samples **5V/SiO$_2$-300**, **10V/SiO$_2$-300**, **2V/SiO$_2$-500**, **5V/SiO$_2$-500** and **10V/SiO$_2$-25** are shown in Fig. 4 (only silica bands were observed for **1V/SiO$_2$-300** possibly because of the low vanadium concentration). The silica support exhibits Raman features at ~400, ~490, ~570, ~800, and 980 cm^{-1}. The 980 cm^{-1} band is associated with Si—OH stretching mode of the surface hydroxyls [42,44]. This band is absent in the spectra of the vanadium-containing samples, thus providing an additional proof of silanol groups being consumed during grafting in agreement with the DRIFT data.

The common feature of all spectra is a sharp band at 1038 cm^{-1} which is always present in Raman spectra of dehydrated silica-supported vanadium oxides. There is an unanimous agreement among all researchers that it should be attributed to the V═O stretching vibration of the tetrahedrally coordinated d^0 vanadium centers bearing an oxo ligand (cf. 1034 cm^{-1} for liquid $VOCl_3$) [40–47]. The majority of the researchers consider these centers as isolated, though there is an opinion that Raman spectroscopy may not be reliable in discriminating the monomeric and polymeric vanadyl species [40]. Anyway, the V—O—V vibrations that usually appear as intense bands in the 200–300 and 500–800 cm^{-1} region [41,42,46,47] were not observed in the spectra of our samples, thus supporting the presence of isolated structures. We also did not observe Raman bands attributed to V_2O_5 crystallites (these typically are at 994, 697, 518, 404, 303, 284, and 144 cm^{-1} [42,46]). The sharp band at 448 cm^{-1} in the spectrum of **5V/SiO$_2$-500** (Fig. 4e) corresponds to the V—Cl vibration (cf. 411 cm^{-1} for $VOCl_3$). It was not observed in the spectra of other samples, since they contain less chlorine, and the corresponding band is apparently masked by the intense bands of the support.

An intense broad band centered at ~940 cm^{-1} was observed in the Raman spectra of the samples with a high vanadium loading (**10V/SiO$_2$-25** and **10V/SiO$_2$-300**). The origin of this band will be discussed below.

UV–vis diffuse reflectance spectroscopy further proves the presence of isolated tetrahedral vanadyl units on the surface of **1V/SiO$_2$-300**, **5V/SiO$_2$-300**, **2V/SiO$_2$-500**, and **5V/SiO$_2$-500.** It appears that the materials with a higher vanadium content (**10V/SiO$_2$-25** and **10V/SiO$_2$-300**) have a more complex structure. All UV–vis DRS spectra of our samples (Fig. 5) are dominated by the intense charge-transfer $O^{2-} \rightarrow V^{5+}$ band in the region below 400 nm. For **10V/SiO$_2$-300** and **10V/SiO$_2$-25** (Fig. 5c and d), an additional band (or several bands) is apparently present in the 400–800 nm region as a shoulder on the low energy side of the main CT band. The position of the CT band maximum for surface vanadia species is known to be strongly dependent on the vanadium coordination number and degree of polymerization of vanadium centers [40,42–44]. Polymerization and change of the coordination number of vanadium atoms from 4 to 5 or 6 that usually occur at high loadings or after hydration give rise to a significant red shift of the

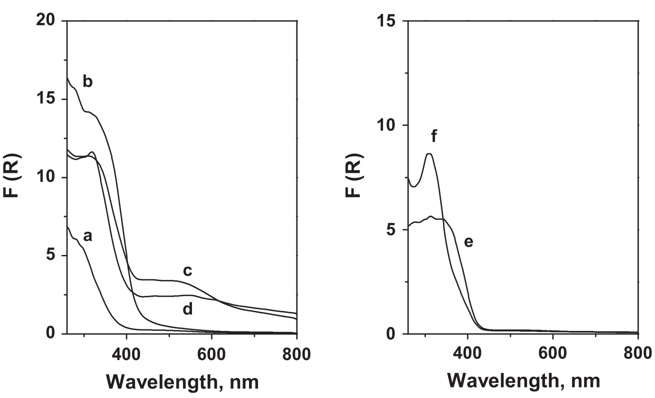


Fig. 5. UV–vis DRS spectra of: (a) **1V/SiO$_2$-300**, (b) **5V/SiO$_2$-300**, (c) **10V/SiO$_2$-300**, (d) **10V/SiO$_2$-25**, (e) **2V/SiO$_2$-500** and (f) **5V/SiO$_2$-500**.

CT band to 400–500 nm. The CT bands in the region below 400 nm are attributed to isolated tetrahedral $(\equiv SiO)_3V{=}O$ units. The surface complex $(\equiv SiO)V({=}O)Cl_2$ described by Rice and Scott also exhibited similar UV–vis DRS spectrum [33].

The complications in the structure of the samples with a higher vanadium content (**10V/SiO$_2$-25** and **10V/SiO$_2$-300**), which manifested themselves as the appearance of the additional Raman band at 940 cm^{-1} and the absorbance in the visible region, were hypothesized as a result of a partial reduction of the vanadium centers to yield the d^1 configuration. This assumption was confirmed by X-ray photoelectron spectroscopy. The XPS spectra of **5V/SiO$_2$-300** and **10V/SiO$_2$-25** are shown in Fig. 6. The V $2p_{3/2}$ peak of **5V/SiO$_2$-300** was fitted with a single Gauss profile at a binding energy (E_{be}) of 519.0 eV (Fig. 6a) and assigned to the V^{5+} state. The V $2p_{3/2}$ peak of **10V/SiO$_2$-25** was fitted with a sum of two Gauss profiles at $E_{be} = 519.0$ and $E_{be} = 517.6$ eV (Fig. 6b) related to V^{5+} and V^{4+} states with relative intensities ca. 2:1. The full width at half maximum of all the peaks is 1.9 eV. Therefore, the appearance of the features discussed above in the Raman and UV–vis spectra can be correlated with the presence of d^1 vanadium centers, whereas the samples that do not contain the reduced vanadium species in significant amounts do not display these features. The absorbance in the visible region thus should be attributed to the d–d transitions of the reduced vanadium atoms and the Raman band at 940 cm^{-1} results from the corresponding V=O vibration. It was found that all the catalysts underwent similar slow transformations when they were kept under argon for several months. The reduction of V^{5+} can be slowed down or even completely prevented by keeping the samples in the dark. The samples with a higher vanadium loading were affected by this process already at the preparation stage. The indications of partial reduction of $VOCl_3$ during immobilization [36] or further evolution of surface vanadium and other metal chlorides [35] were mentioned earlier in a number of studies where the immobilized complexes were not hydrolyzed or annealed to remove the ligands. It was also reported that silica-supported vanadia could be reduced with HCl evolved during grafting [37].

Summarizing all the above characterization data, we can conclude that the catalytic centers of **1V/SiO$_2$-300**, **5V/SiO$_2$-300**, **2V/SiO$_2$-500**, and **5V/SiO$_2$-500** that are not contaminated with reduced vanadium species are composed of isolated tetrahedral d^0 units of a general structure $(\equiv SiO)_nV({=}O)Cl_{3-n}$. The values of n can be determined from the elemental analysis. The values of the Cl/V atomic ratio for all the catalysts are presented in Table 1. Three independent processes can lead to the chlorine loss: (a) substitution of Cl with the surface hydroxyl groups according to Scheme 2, (b) partial hydrolysis with adsorbed water that should be taken into account for the catalysts with **silica-300** and especially with **silica-25** as supports, and (c) reduction of vanadium observed for the catalysts with a high vanadium loading (10 mol%). Thus, **10V/SiO$_2$-25** has the least chlorine content because of the actions of all three factors. **10V/SiO$_2$-300** contains on the average 1 chlorine per 1 vanadium atom. The Cl/V ratio of **1V/SiO$_2$-300**, **5V/SiO$_2$-300**, and **5V/SiO$_2$-500** lies between 1 and 2, and **2V/SiO$_2$-500** has exactly 2 chlorine atoms per 1 vanadium atom. Therefore, we believe that **2V/SiO$_2$-500** is comprised of single mono-grafted $(\equiv SiO)V({=}O)Cl_2$ units, **1V/SiO$_2$-300**, **5V/SiO$_2$-300**, and **5V/SiO$_2$-500** likely contain the admixtures of the other mononuclear tetrahedral vanadyl surface species, e.g., $(\equiv SiO)_2V({=}O)Cl$ and $(\equiv SiO)_3V{=}O$, whereas the structures of **10V/SiO$_2$-25** and **10V/SiO$_2$-300** may be very complex and will not be discussed further.

These assignments correlate with the ^{51}V NMR spectra of **2V/SiO$_2$-500**, **5V/SiO$_2$-500**, and **5V/SiO$_2$-300** solid samples (Fig. 7). The spectra show a broad resonance ($\Delta\nu_{1/2} \approx 10$ kHz) at −378, −370, and −395 ppm, respectively. The line shape is somewhat distorted, most likely due to the chemical shift anisotropy determined in [36]. The signal position and shape are close to those in the static ^{51}V NMR spectrum of silica-supported $VOCl_3$ [36]. The isotropic chemical shift measured in the ^{51}V MAS NMR spectrum of the same sample (−295 ppm [36]) is consistent with that reported for $(\equiv SiO)V({=}O)Cl_2$ species by other authors [34,56]. Bis- and tris-siloxy units $(\equiv SiO)_2V({=}O)Cl$ [56] and $(\equiv SiO)_3V({=}O)$ [41] were reported to show the isotropic chemical shifts of −540 and −710 ppm, respectively. No such signals were detected in the MAS NMR spectra of silica-supported $VOCl_3$ in [36]. Thus, on the basis of the literature data, the signals in the spectra of

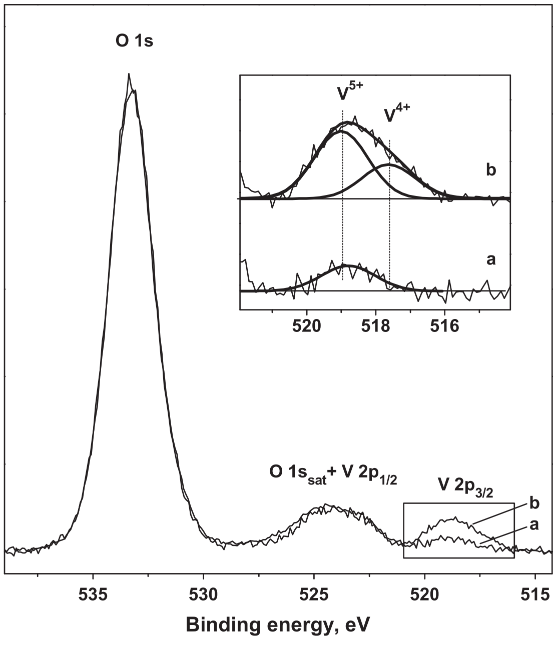


Fig. 6. XPS spectra of: (a) **5V/SiO$_2$-300** and (b) **10V/SiO$_2$-25**.

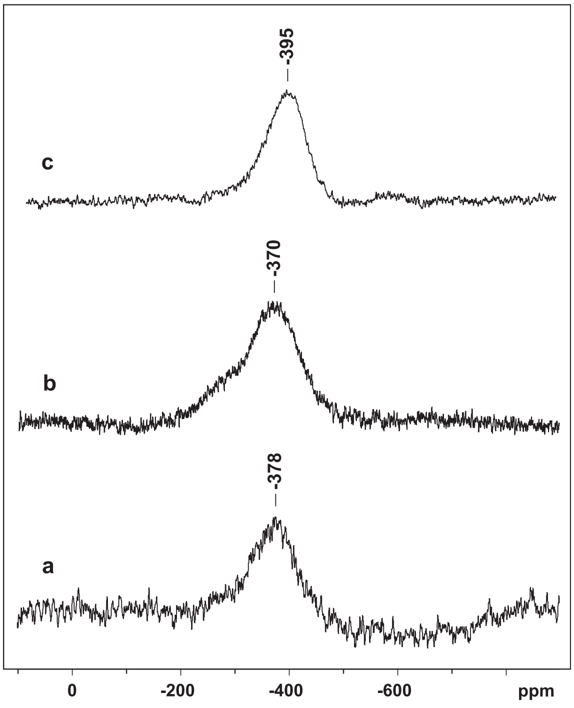


Fig. 7. ^{51}V solid-state NMR spectra of: (a) **2V/SiO$_2$-500**, (b) **5V/SiO$_2$-500** and (c) **5V/SiO$_2$-300**.

2V/SiO$_2$-500, **5V/SiO$_2$-500**, and **5V/SiO$_2$-300** can be assigned to the vanadium monosiloxy dichloro species ($\equiv$SiO)V($=$O)Cl$_2$ bound to the support through one Si—O—V bond with the vanadium atom in a distorted tetrahedral local environment, which is consistent with the conclusions made on the basis of other techniques.

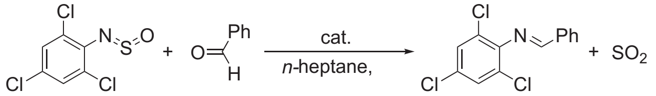
According to some early works [37,38], the interaction of excess gaseous VOCl$_3$ with silica leads to a mixture of mono-, bis-, and tris-grafted vanadyl units depending on the temperature of silica dehydroxylation, mono-grafted units being formed on silica preheated at 500 °C and higher. Other authors reported on the exclusive formation of a monosiloxy complex, irrespective of the temperature of the support pretreatment [33–36]. We conclude that under our experimental conditions, single mono-grafted species ($\equiv$SiO)V($=$O)Cl$_2$ are unambiguously formed on **silica-500** at low vanadium loadings. These surface complexes still dominate on **silica-300**, but the presence of other forms in minor amounts cannot be excluded. The increase in the vanadium loading leads to a partial reduction of the vanadium atoms already at the stage of preparation.

3.3. Catalytic activity tests

The reaction between benzaldehyde and *N*-sulfinyl-2,4,6-trichloroaniline in boiling *n*-heptane (batch reactor) was used to probe the catalytic activity of the silica-supported catalysts and their homogeneous analogs (Table 3). The turn over frequencies presented in Table 3 were measured after 20 min of the reaction. It should be noted that the substrates selected do not interact in the absence of the catalyst and less than 5% of imine was detected in the reaction mixture after 5 h of reflux with parent SiO$_2$.

The reactions with 5 mol% of the catalysts were duplicated no less than three times. The test reaction reaches a quantitative conversion within 20 min with any of the heterogeneous catalysts used. However, it takes about 7 h to achieve a quantitative conversion when unsupported VOCl$_3$ is used. In contrast to homogeneous VOCl$_3$, the supported catalysts display a reasonably high activity even at room temperature: a 70–80% conversion was achieved in 1.5 h (5 mol% of V). Thus, the immobilization of VOCl$_3$ onto the silica surface apparently leads to a dramatic enhancement of its catalytic activity in the studied oxo/imido heterometathesis reaction.

Table 3
Catalytic activities of the homogeneous and heterogeneous vanadium catalysts in the test reaction[a]:



Catalyst	Catalyst/substrate (mol% of V)	Conversion (%)	TOF[b] (h^{-1})
SiO$_2$	–	Traces	–
VOCl$_3$	5	20	12
[(^{t}BuO)$_3$SiO]$_3$VO	5	0	–
[^{i}Bu-POSS]VO	5	0	–
10V/SiO$_2$-25	5	⩾95	60
1V/SiO$_2$-300	5	⩾95	60
5V/SiO$_2$-300	5	⩾95	60
10V/SiO$_2$-300	5	⩾95	60
2V/SiO$_2$-500	5	⩾95	60
5V/SiO$_2$-500	5	⩾95	60
10V/SiO$_2$-25	1	17	51
1V/SiO$_2$-300	1	30	90
5V/SiO$_2$-300	1	21	63
10V/SiO$_2$-300	1	20	60
2V/SiO$_2$-500	1	40	120
5V/SiO$_2$-500	1	25	75

[a] Reaction conditions: refluxing *n*-heptane (98 °C), 20 min.
[b] TOF = (moles of imine produced)/[(moles of V) × time].

Interestingly, [(^{t}BuO)$_3$SiO]$_3$VO and [^{i}Bu-POSS]VO that are often used as molecular models to mimic silica-supported vanadyl species do not display any catalytic activity at all (no imine was observed in the reaction mixture after 5 h of reflux). This finding excludes the idea that the high activity of silica-supported VOCl$_3$ arises from the unique electronic properties of the siloxy ligands.

A series of catalytic tests with 1 mol% of catalysts were carried out to reveal the effects of the vanadium loading and the support pretreatment on the catalytic activity and to rank the activities of the heterogeneous catalysts. It was found that the catalysts prepared with the silica pretreated at higher temperatures displayed a higher catalytic activity compared to the samples with the same vanadium content on less-dehydroxylated silica. The catalysts with the lower vanadium loading display the higher specific activity in the series prepared with the same silica. Thereby, **2V/SiO$_2$-500** exhibited the highest activity whereas **10V/SiO$_2$-25** was the least active. The low activity of the samples with higher vanadium contents is probably related to the presence of V(d^1) and their lower stability. Thus, with 1 mol% of **2V/SiO$_2$-500**, the test reaction reaches a quantitative conversion in 2 h; while it practically stops in 4–5 h at a ca. 75–80% conversion when 1 mol% of **10V/SiO$_2$-25** is used. Moreover, the activity of the catalysts that were stored for months without light protection is considerably lower than their initial activity. This observation confirms the idea that the presence of reduced vanadium disfavors the high catalytic performance.

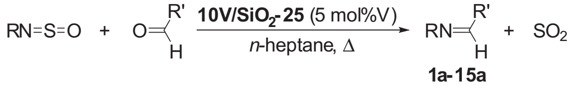
3.4. Imidation of aldehydes

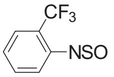
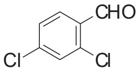
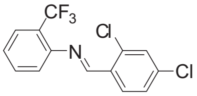
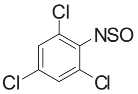
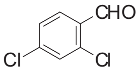
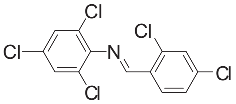
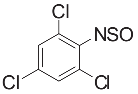
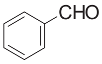
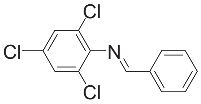
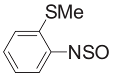
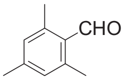
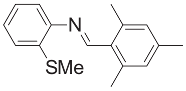
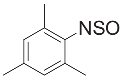
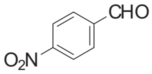
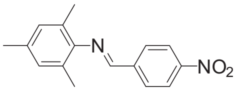
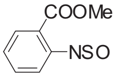
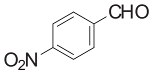
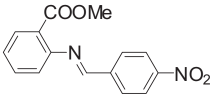
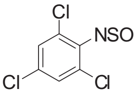
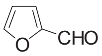
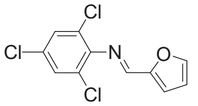
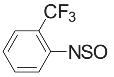
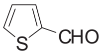
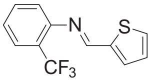
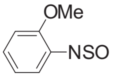
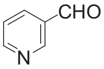
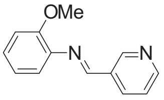
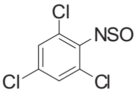
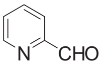
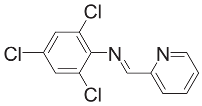
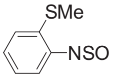
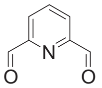
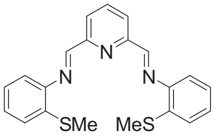
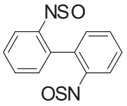
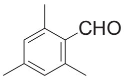
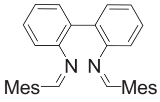
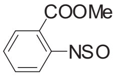
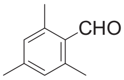
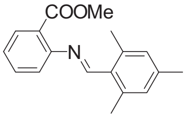
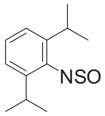
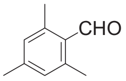
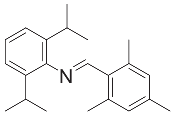
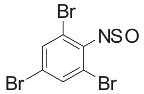
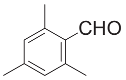
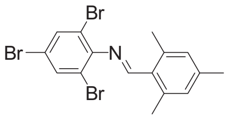
In order to estimate the scope of applicability of the heterogeneously catalyzed oxo/imido heterometathesis reactions, a wide range of both aldehydes and *N*-sulfinylamines was tested (Table 4). **10V/SiO$_2$-25** (5 mol%) was used for all aldimine syntheses despite its poorest catalytic activity in the series of vanadium surface complexes described above. The reason for this selection is that its preparation procedure is the most simple, and this makes this catalyst more attractive from the standpoint of express laboratory application. Some syntheses were also duplicated with other heterogeneous catalysts, with the reaction time being reduced.

At room temperature the oxo/imido heterometathesis proceeds fast only for couples of highly reactive sterically unhindered *N*-sulfinylamines and aldehydes (Table 4, entry **1a**). In the other cases, the reaction is to be preferentially performed under reflux to rapidly produce the aldimines in a high yield. The *N*-sulfinylamines having electron-withdrawing substituents (Table 4, entries **1a**–**3a**, **7a**, **8a**) turned out to be more reactive than aniline derivatives bearing electron-donating groups (Table 4, entries **4a**, **9a**, **11a**). Imidation of well-coordinating aldehydes, e.g., containing a pyridine core (Table 4, entries **9a**–**11a**), is more difficult in comparison with imidation of other aldehydes. Sterically hindered aldehydes like mesitaldehyde (Table 4, entries **4a**, **12a**, **13a**) react more slowly; however, even in combination with sterically hindered *N*-sulfinylanilines bearing such bulky *o*-substituents as *i*-propyl groups or bromine atoms (Table 4, entries **14a**, **15a**), azomethines can be obtained in a high yield at prolonged reaction times. It should be noted that neither pyridinecarboxaldehydes nor couples of sterically hindered reagents enter into the same reaction in the presence of molecular VOCl$_3$.

Thus, the water-free method based on VOCl$_3$/SiO$_2$ catalyzed imidation of aldehydes with *N*-sulfinylamines is suitable for the fast preparation of a wide range of imines of aromatic and heterocyclic aldehydes. This method is especially useful for the synthesis

Table 4
Imidation of aldehydes with *N*-sulfinylamines.



№	*N*-sulfinylamine	Aldehyde	Aldimine	Reaction Time	Isolated Yield (%)
1a				30 min[a]	97
2a				20 min	85
3a				20 min	96
4a				1 h	94
5a				1 h	95
6a				1 h 45 min	95
7a				30 min	84
8a				40 min	98
9a				1.5 h	91
10a				2 h	90
11a				5 h	81
12a				1 h 20 min	94
13a				15 h	80
14a				26 h	73
15a				36 h	62

[a] At room temperature.

of azomethines from poorly nucleophilic anilines that are difficult to access by classic acid-catalyzed condensation of primary amines with aldehydes.

3.5. Imidation of ketones

Only few reports on the stoichiometric imido-transfer reactions from transition metal imides to ketones have been reported. Primarily, these examples are restricted to the imido complexes of titanium and zirconium that are characterized by pronounced oxophilicity. As far as transition metal catalyzed heterometathetical ketone imidation is concerned, to the best of our knowledge, there is no report on the processes of such type to date. Much higher activity of the vanadium heterogeneous catalysts compared to their homogeneous analog $VOCl_3$ encouraged us to probe ketones as a carbonyl component in the oxo/imido heterometathesis reaction under consideration. Here, we report the first examples of ketone imidation (Table 5), where **5V/SiO$_2$-300** was used as a catalyst in loading of 10 mol% to reach a high conversion of the reagents in a reasonable period of time.

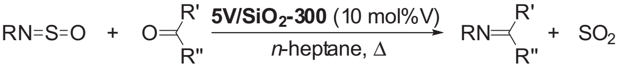
We found that highly reactive *o*-monofluorinated ketones, e.g. 2-fluoroacetophenone, react readily (Table 5, entry **1b**), whereas in other cases, prolonged heating was necessary to obtain ketimines in a high yield. Aside from *N*-sulfinyl-2-trifluoromethylaniline, the variety of reactive *N*-sulfinylamines turned out to be limited to *N*-sulfinylanilines having no *o*-substituents. This indicated that the reaction is sensitive to the steric factor. It should be noted that homogeneous catalysis by using molecular $VOCl_3$ is not efficient in imido-deoxygenation of ketones with *N*-sulfinylamines. Thus, grafting $VOCl_3$ onto the silica surface not only leads to the enhancement of its catalytic activity, but also allows one to considerably expand the scope of applicability of the catalytic reaction.

3.6. Leaching and recycling

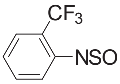
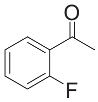
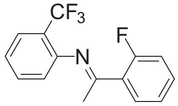
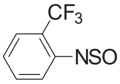
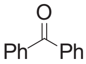
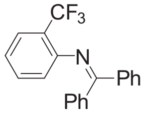
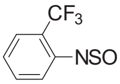
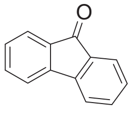
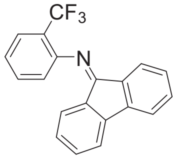
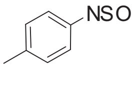
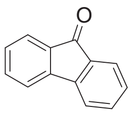
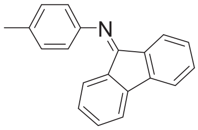
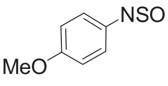
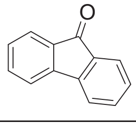
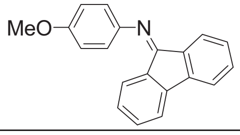
All the catalysts were always twice washed with boiling *n*-heptane after grafting to model the conditions of the heterometathesis reaction studied. However, this procedure seems to be not necessary, since in most cases, the amount of vanadium grafted found by elemental analysis was consistent with that initially introduced into the grafting procedure. It is not surprising, since the polar vanadium species, even in a physisorbed state, should exhibit more affinity to silica rather than to an aliphatic solvent. Chemically bound vanadium requires at least a stoichiometric amount of a protic reagent to cleave V—O—Si bonds, such a cleavage being often observed in oxidation reactions where hydroperoxides, alcohols, or other protic substrates are involved. Indeed, treatment of the catalysts with MeOH followed by filtration led to a significant loss of vanadium in the sample. We also performed a simple leaching test under reaction conditions [57]. The test reaction was carried out in the presence of 1 mol% **5V/SiO$_2$-300**, and the catalyst was filtered off after 20 min. The procedure was accomplished under argon, and the reaction mixture was maintained under reflux during the filtration. The filtrate was monitored for further reaction up to 10 h after filtration, and no reaction was observed. However, this does not exclude leaching, as we know that vanadium complexes are of low catalytic activity in homogeneous media. Therefore, the crude product of the reaction was subjected to elemental analysis and was found to contain less than 0.005% of vanadium.

The activity of all heterogeneous catalysts studied lowers significantly already after the first catalytic run. Washing the catalysts

Table 5
Imidation of ketones with *N*-sulfinylamines.



1b-5b

№	*N*-sulfinylamine	Ketone	Ketimine	Reaction Time	Isolated Yield (%)
1b				1.5 h	95
2b				18 h	52
3b				12 h	90
4b				12 h	96
5b				12 h	94

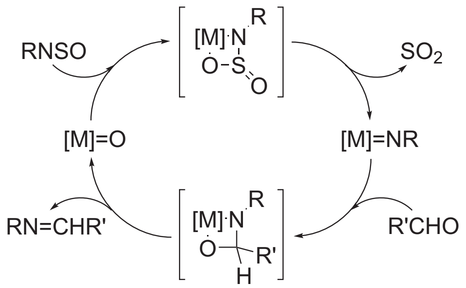
after the reaction with boiling heptane, CH_2Cl_2, etc., or heating in a vacuum did not restore their initial activity. However, calcination at 500 °C in a stream of air followed by heating in a vacuum at the same temperature led to the materials with the activity close to that of the initial catalyst. Obviously, such a treatment has to be accompanied by some structural changes of the initial catalyst (e.g., the resulting material does not contain chlorine according to elemental analysis). These changes and their influence on the catalytic behavior are currently being under investigation.

3.7. Mechanistic considerations and stoichiometric reactions of surface complexes

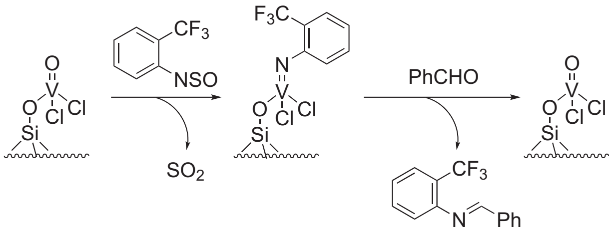
The idea of the catalytic activity of surface vanadium oxo complexes in heterometathetical imidation of carbonyl compounds was initially suggested on the basis of the mechanism taken from the molecular catalysis (Scheme 3) [30]. The two steps of this cycle—imidation of the transition metal oxo complex with *N*-sulfinylamine [58–64] and imido group transfer from the imido complex to an aldehyde [14,15,20,65–68]—are well-documented stoichiometric heterometathesis reactions. To demonstrate that the heterogeneous reaction follows the same route, we carried out the stoichiometric reactions involved in the catalytic cycle step by step (Scheme 4).

3.7.1. Imidation of the surface oxo complex with N-sulfinylamine

The sample of **2V/SiO$_2$-500** was allowed to react with an excess of *N*-sulfinyl-2-trifluoromethylaniline in *n*-heptane (reflux, 20 min). The purple product was obtained after removal of the solvent and desorption of the excess of sulfinylamine in a vacuum at 50 °C. The elemental analysis revealed that the stoichiometry of the reaction was approximately 1 ± 0.1 imido ligand per vanadium atom (average of several experiments). It was also confirmed that no sulfur remained in the solid product, which excludes *N*-sulfinylamine being only coordinated to the metal center or physisorbed on the surface and suggests the formation of the surface imido complex. It should be mentioned that heterometathetical imidation of grafted oxo complexes with isocyanates (with liberation of CO_2) had already been introduced for tantalum [69], rhenium [70] and vanadium [33] surface oxo species.



Scheme 3. The catalytic cycle of oxo/imido heterometathesis between aldehydes and *N*-sulfinylamines.



Scheme 4. Stoichiometric heterometathesis reactions of vanadium surface complexes.

3.7.2. Reaction of the surface imido complex with an aldehyde

The obtained material was introduced into the reaction with an excess of benzaldehyde in *n*-heptane in the absence of *N*-sulfinylamine (reflux, 20 min). The imine formed was not observed in the solution by IR directly after the reaction, as it was physisorbed on the surface or coordinated to vanadium. Therefore, the mixture was filtered and washed with various eluents (pyridine–heptane (1:10) mixture, triethylamine, etc.) to desorb the product. The imine band at 1636 cm^{-1} appeared in the IR spectrum of the filtrate. The amount of imine desorbed was determined from the NMR spectrum with an internal standard in the range 35–65% of the initial vanadium amount in the sample (it is dependent on the eluent). No free aniline or other compounds apart from *N*-benzylidene-2-trifluoromethylaniline and benzaldehyde were observed in the mixture according to ^{1}H and ^{19}F NMR.

We also analyzed the filtrate obtained after refluxing the catalyst **2V/SiO$_2$-500** with excess of benzaldehyde, filtering, and washing it with py–heptane mixture (1:10) and did not detect any products of benzaldehyde transformation. And finally, when the catalyst treated with benzaldehyde is subjected to prolonged heating in a vacuum (100 °C/7.5×10^{-4} Torr) to remove benzaldehyde and then *N*-sulfinylamine is added, no imine formation is observed. This observation confirms that in the absence of *N*-sulfinylamine, benzaldehyde is only adsorbed or coordinated to vanadium as a ligand.

Although alternative mechanisms cannot be excluded at this point, these data suggest that the homogeneous and heterogeneous oxo/imido heterometathesis reactions follow the same general sequence of the stoichiometric steps. However, the activation effect of the support that is observed in the latter case indicates that some details of the heterogeneous reaction are apparently different. The activation could arise from various factors. First of all, the immobilization of the catalytically active species on the surface should prevent them from decomposition via kinetic stabilization. On the other hand, the polar substrates in nonpolar media are able to concentrate in the near-surface layer due to a strong adsorption, which should increase the reaction rate. This is confirmed by changing the solvent for more polar toluene, in which the reaction proceeds slower than in heptane. Furthermore, the adsorption could also cause an activation of the substrates by enhancing their polarization, e.g., via hydrogen bonding between the carbonyl oxygen and remaining silanol groups close with vanadium centers, etc. These hypotheses are currently under investigation.

4. Conclusion

A series of silica-supported vanadium catalysts were prepared via water-free grafting $VOCl_3$ onto the silica surface. The materials obtained were characterized with Raman, diffuse reflectance FTIR (DRIFT) and UV–vis, ^{51}V solid-state NMR and X-ray photoelectron spectroscopies, elemental analysis and N_2 physisorption. It was found that at low vanadium loadings (1–5%), the catalyst surface is mainly comprised of the isolated tetrahedral d^0 units $(\equiv SiO)V(=O)Cl_2$, whereas the materials with higher vanadium concentrations contain significant admixtures of reduced vanadium species.

The activities of the heterogeneous catalysts in oxo/imido heterometathetical imidation of carbonyl compounds with *N*-sulfinylamines were found to be significantly higher than the activity of homogeneous $VOCl_3$. Thus, it can be concluded that the immobilization of the heterometathesis catalysts on the heterogeneous support indeed dramatically enhances their catalytic activity, as it was predicted.

On the basis of the heterogeneous catalysts obtained, a novel water-free express method for the preparation of organic imines of a wide range of aldehydes and some ketones was developed. Noteworthy that we report on the first successful example of transition metal mediated heterometathetical imidation of ketones. The simplicity of the catalyst preparation and product isolation procedures makes this method especially attractive for easy preparation of azomethines from poorly nucleophilic anilines that are difficult to access by classic acid-catalyzed condensation of primary amines with aldehydes.

It is important to note that the synthetic potential of heterometathesis reactions is not limited to imidation of aldehydes and ketones. It is possible that the most intriguing catalytic heterometathesis processes (e.g., catalytic imidation of CO_2, CO, nitro and nitroso compounds, synthesis of asymmetric carbodiimides, cyclic azomethines metathesis polymerization, etc.) may lie not in the field of homogeneous catalysis by transition metal complexes but in the field of well-defined heterogeneous catalysis.

Acknowledgments

This work was partially supported by the Russian Foundation for Basic Research (Grant 07-03-00939). The authors thank the Laboratory of Microanalysis of INEOS RAS; S. Bukalov and L. Leites for the registration and discussion of the Raman spectra; A. Naumkin and I. Volkov for the registration and discussion of the XPS spectra; A. Smirnov for the N_2 physisorption measurements.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcat.2011.07.011.

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