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

Pavel A. Zhizhko [a,b], Anton A. Zhizhin [a], Dmitry N. Zarubin [a,*], Nikolai A. Ustynyuk [a], Dmitry A. Lemenovskii [b], Boris N. Shelimov [c], Leonid M. Kustov [c], Olga P. Tkachenko [c], Gayane A. Kirakosyan [d]

[a] *A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov str. 28, 119991 Moscow, Russia*
[b] *Chemistry Department, Moscow State University, Vorob'evy Gory 1, 119992 Moscow, Russia*
[c] *N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky Prospect 47, 119991 Moscow, Russia*
[d] *N.S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninsky Prospect 31, 119991 Moscow, Russia*

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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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* Corresponding author. Fax: +7 499 135 50 85.
E-mail address: zaroubine@ineos.ac.ru (D.N. Zarubin).

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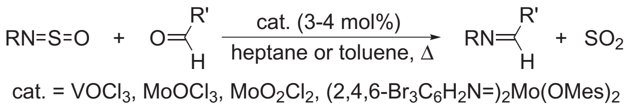

Scheme 1. Oxo/imido heterometathesis between aldehydes and *N*-sulfinylamines.

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