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# Molecular Modelling of Supported Metal Catalysts: $SiO_2$-grafted $[\{(\eta^3\text{-}C_4H_7)_2Rh\}_2V_4O_{12}]$ and $[\{Rh(C_2Me_5)\}_4V_6O_{19}]$ are Catalytically Active in the Selective Oxidation of Propene to Acetone

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$SiO_2$-grafted $[\{(\eta^3\text{-}C_4H_7)_2Rh\}_2V_4O_{12}]$ and $[\{Rh(C_5Me_5)\}_4V_6O_{19}]$, as molecular models of supported Rh catalysts characterized by EXAFS, FTIR and TPD studies, exhibit high catalytic activities for the selective oxidation of propene to acetone.

Organometallic oxide clusters such as $[\{(\eta^3\text{-}C_4H_7)_2Rh\}_2(V_4O_{12})]$, cubane-type $[\{M(C_5Me_5)\}_4Mo_4O_{16}]$ and $[\{M(C_5Me_5)\}_4V_6O_{19}]$ (M = Rh, Ir) are of interest as models of the infinite layer structures of $MoO_3$ and $V_2O_5$ crystals, which have been used as heterogeneous catalysts for the oxidation of organic compounds.[1] They have multifunctional properties and synergistic effects on reactivity owing to the heterometallic centres. Furthermore, they are potential molecular models[2] relevant to metal-supported catalysts whose catalytic activity and selectivity are affected by localized metal–support bonding. In this study, novel organometallic oxide clusters such as $[Bu^n{}_4N_2[\{(\eta^3\text{-}C_4H_7)_2Rh\}_2(V_4O_{12})]$ and $[\{Rh(C_5Me_5)\}_4V_6O_{19}]$ were used as molecular precursors for grafting organometallic oxide clusters onto a silica surface. These attached multicentred metal oxide clusters were well characterized by EXAFS (extended X-ray absorption fine structures), FTIR (Fourier transform infrared) and TPD (temperature-programmed desorption) studies, showing the 'vanadate tetramer and hexamer' oxide cluster frameworks capped by rhodium species, which remained grafted to the surface with silanol–Rh ligand interactions. We report here that the resulting $SiO_2$-attached $Rh_2V_4O_{12}$ and $Rh_4V_6O_{19}$ clusters exhibit higher catalytic activities for the selective oxidation of propene to acetone.

$[Bu^n{}_4N]_2[\{(\eta^3\text{-}C_4H_7)_2Rh\}_2(V_4O_{12})]$ and $[\{Rh(C_5Me_5)\}_4V_6O_{19}]$ were synthesized and purified by the literature methods,[3,4] and were impregnated at 300 K onto $SiO_2$ (Aerosil 200, Japan Aerosil Co.; surface area 200 $m^2\ g^{-1}$; dehydrated by evacuation at 573 K). $SiO_2$ was mixed with the $CH_2Cl_2$ solution of both cluster compounds, followed by removal of the solvent. The mass loading of the cluster in each sample was 15–20% (*m*/*m*) with respect to silica. The impregnated material (0.4 g) was mounted into the microreactor and treated by thermal activation *in vacuo* or by exposure to 13.3 kPa of $O_2$ at 353–413 K, resulting in $SiO_2$-grafted samples, denoted as $Rh_2V_4O_{12}/SiO_2$ **1** and $Rh_4V_6O_{19}/SiO_2$ **2**.

The IR spectra (recorded on a Shimadzu FT-IR 8100M IR spectrometer wtih a resolution of 2 $cm^{-1}$) of $[Bu^n{}_4N]_2[\{(\eta^3\text{-}C_4H_7)_2Rh\}_2(V_4O_{12})]$ on silica gave bands at 3078 and 3056 $cm^{-1}$, characteristic of the stretching ν(C–H) of $(\eta^3\text{-}C_4H_7)_2Rh$ groups capping the precursor cluster, which decreased gradually with increasing evacuation temperature up to 413 K, along with a considerable suppression of the 3765 $cm^{-1}$ sharp band due to isolated silanol groups on the silica support. On the other hand, the IR bands at 2990, 2962, 2919 and 2875 $cm^{-1}$ due to ν($CH_3$/$CH_2$) of the counter-cation $[Bu^n{}_4N]^+$ remained unchanged below 450 K. Similarly, it was found by IR observation that the ($C_5Me_5$) ligand in $[\{Rh(C_5Me_5)\}_4V_6O_{19}]/SiO_2$ was partially eliminated by thermal evacuation at 423 K and under an $O_2$ atmosphere at 373 K.

TPD studies were performed using 0.2 g of the sample, *e.g.* $[Bu^n{}_4N]_2[\{(\eta^3\text{-}C_4H_7)_2Rh\}_2(V_4O_{12})]/SiO_2$ and $[Rh(acac)(\eta^3\text{-}C_4H_7)_2]/SiO_2$ (acac = acetylacetone) which were charged in microreactor and heated by flowing He from 300 to 600 K with a heating rate of 2 K $min^{-1}$. Desorbed species were detected by gas chromatography using a TCD detector with VZ-7 column, coupled with mass spectroscopy (ANELVA Co, AQP-100). In the TPD spectra shown in Fig. 1, it was found that 2-methylpropene, derived from *ca.* 50% of the $\eta^3\text{-}C_4H_7$ ligands bound to $Rh_2V_4O_9$ and Rh(acac) moieties on the silica surface, was evolved at 350–413 K, and all completely desorbed below 450 K. Other species such as $CH_4$, $C_3H_6$ and but-2-enes were formed on $[Bu^n{}_4N]_2[\{(\eta^3\text{-}C_4H_7)_2Rh\}_2(V_4O_{12})]/SiO_2$ (Fig. 1A) at temperatures >450 K. These products were associated with Hofmann degradation[5] of the $[Bu^n{}_4N]^+$ counter-cation.

Rh and V–K-edge EXAFS spectra were measured in the transmission mode at BL-10B or BL-7C of the Photon Factory in the National Laboratory for High Energy Physics. The spectra were analysed with a curve-fitting method using the program of EXAFS2 (Research Center for spectroscopy, The University of Tokyo) with theoretical parameters, as previously reported.[6] The FT peaks of the Rh–C and Rh–O contributions were obtained from the raw Rh-edge EXAFS data for $[Bu^n{}_4N]_2[\{\eta^3\text{-}C_4H_7)_2Rh\}_2(V_4O_{12})]/SiO_2$ with a $k^3$-weighting over the range $3.5 < k < 15$ Å$^{-1}$. When the sample was evacuated at 413 K, the intensity of the Rh–C peak decreased (*R* = 2.17 Å, C.N. = 3.2) to 50% of that in the precursor sample (*R* = 2.19 Å, C.N. = 5.6), whereas the C.N. of the Rh–O (*R* = 2.07 Å) bonds increased relative to the precursor sample from 1.8 to 2.1, possibly owing to surface attachment of the capped

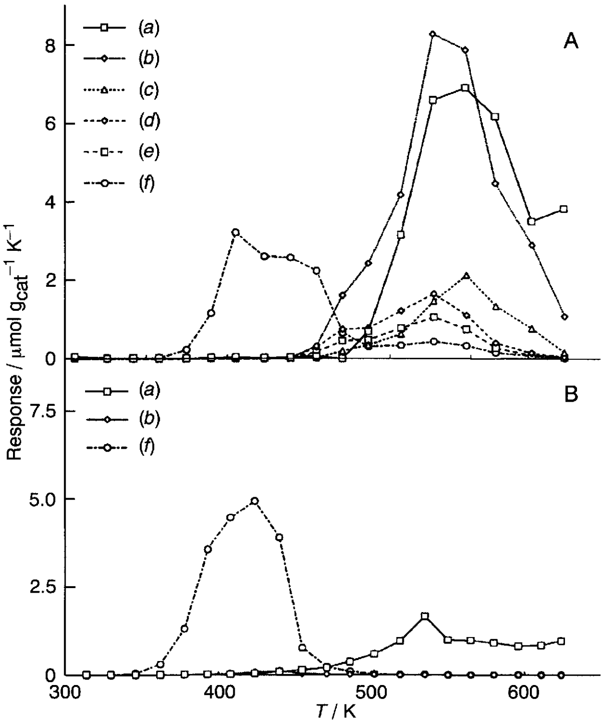

**Fig. 1** TPD patterns of: A, $[Bu^n{}_4N]_2[\{(\eta^3\text{-}C_4H_7)_2Rh\}_2(V_4O_{12})]$; and B, $[Rh(acac)(\eta^3\text{-}C_4H_7)_2]$ impregnated on $SiO_2$ gel. Yields are given of: (*a*) 2-methylpropene; (*b*) methane; (*c*) propane; (*d*) butane; (*e*) *trans*-but-2-ene; and (*f*) *cis*-but-2-ene.

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$(\eta^3\text{-}C_4H_7)_2Rh$ with silanol groups. Table 1 shows structural parameters for $k^3$ weighted V–K-edge EXAFS of $Rh_2V_4O_{12}/SiO_2$ **1** and $Rh_4V_6O_{19}/SiO_2$ **2** before and after the thermal activation *in vacuo* or in an $O_2$ atmosphere of 13.3 kPa. When sample **1** was evacuated at 300–413 K, the intensity and shape of the FT peaks of V=O and V–O remained unchanged, which agrees well with those of the precursor cluster, *i.e.* $[Bu^n{}_4N]_2[\{(\eta^3\text{-}C_4H_7)_2Rh\}_2(V_4O_{12})]$ in the crystalline state. When **1** was evacuated at 513 K, the resulting FT spectra were changed substantially, to resemble that of the conventional $V_2O_5/SiO_2$ which was prepared by calcination of ammonium vanadate on silica. The V–O–M contributions to the EXAFS oscillation of samples **1** and **2** were observed at 2.99 and 2.74 Å, respectively. The V–O–M contributions decreased when the sample was evacuated above 413 K. Accordingly, the results of FTIR, EXAFS and TPD studies suggest that the chair-form vanadate tetramer and the hexamer clusters capped with $(\eta^3\text{-}C_4H_7)_2Rh$ and $Rh(C_5Me_5)$ groups were grafted with Rh end-on to silica surface, as depicted in Scheme 1; the vanadium oxide ($V_4O_{12}$ and $V_6O_{19}$) cluster frameworks remain basically unchanged, at least by thermal activation *in vacuo* or under 13.3 kPa $O_2$ below 413 K.

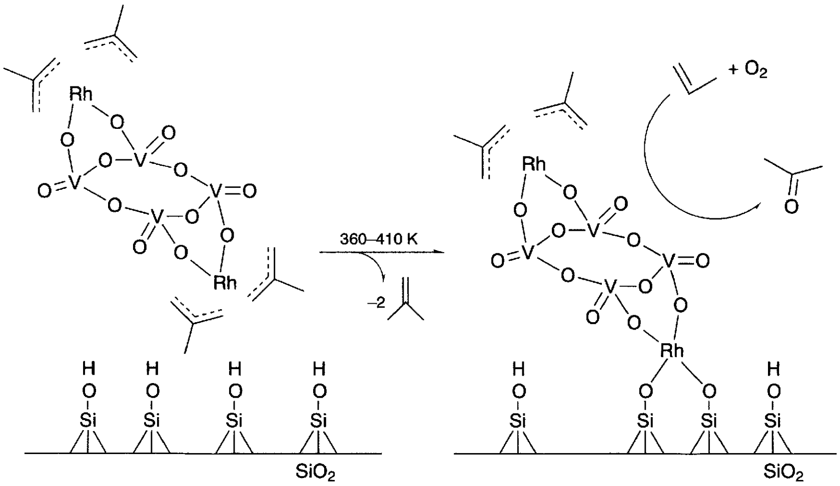
The oxidation of propene was carried out at 313–413 K by using a closed circulating system equipped with a Pyrex glass reactor of volume 206 ml. A mixture of propene (13.3 kPa) and oxygen (13.3 kPa) was admitted onto the samples of **1** and **2**. Products consisting of acetone and $CO_2$ were quantitatively analysed (gas chromatography; Shimadzu GC-8A) using TCD with TCP 20%/Uniport R for oxygenates such as acetone and a Porapak Q column for propene, $O_2$ and $CO_2$. It was interesting to find that although propene oxidation occurred negligibly on both Rh-capped vanadium oxide cluster compounds in the crystalline state, acetone was produced catalytically with higher selectivities (43–85 mol%) on **1** and **2** grafted onto a silica surface.

As shown in Table 2, **2** exhibited higher selectivities towards acetone than **1**. By contrast, the oxidation of propene to acetone over $Rh(acac)(\eta^3\text{-}C_4H_7)_2/SiO_2$ gave poor selectivities and conversions with a higher activation energy of 73.7 kJ $mol^{-1}$. Nevertheless, a negligible amount of acetone was obtained in the reaction on $[V_{10}O_{28}]/SiO_2$ derived from the non-Rh capped vanadate dodecamer cluster and the conventional $V_2O_5/SiO_2$ under the similar reaction conditions. These results suggest that the coordinately unsaturated Rh sites capped with vanadium

**Table 1** Structural parameters of V–K-edge EXAFS for $[Bu^n{}_4N]_2[\{(\eta^3\text{-}C_4H_7)_2Rh\}_2(V_4O_{12})]/SiO_2$ and $\{Rh(C_5Me_5)\}_4V_6O_{19}/SiO_2$ before and after thermal activation *in vacuo* and under an $O_2$ atmosphere

| Sample | FT peaks | C.N.[a] | $R^b$/Å | R factor (%) |
|---|---|---|---|---|
| $[Bu^n{}_4N]_2[\{(\eta^3\text{-}C_4H_7)_2Rh\}_2(V_4O_{12})]/BN^c$ | V=O | 1.0 | 1.65 | 13.3 |
| | V–O | 3.0 | 1.82 | |
| $[Bu^n{}_4N]_2[\{(\eta^3\text{-}C_4H_7)_2Rh\}_2(V_4O_{12})]/SiO_2$ impregnation | V=O | 1.2 | 1.65 | 7.2 |
| | V–O | 3.7 | 1.84 | |
| After evac. (413 K) | V=O | 1.0 | 1.64 | 6.5 |
| | V–O | 3.1 | 1.84 | |
| Exposure to $O_2$ (413 K) | V=O | 1.0 | 1.64 | 15.4 |
| | V–O | 3.3 | 1.83 | |
| Exposure to $O_2$ (523 K) | V=O | 0.7 | 1.65 | 10.4 |
| | V–O | 2.1 | 1.84 | |
| $\{Rh(C_5Me_5)\}_4V_6O_{19}/BN$ | V=O | 1.0 | 1.62 | 5.2 |
| | V–$O_b$ | 4.0 | 1.88 | |
| | V–$O_c$ | 1.0 | 2.31 | |
| $\{Rh(C_5Me_5)\}_4V_6O_{19}/SiO_2$ impregnation | V=O | 1.0 | 1.60 | 8.3 |
| | V–$O_b$ | 4.0 | 1.88 | |
| | V–$O_c$ | 2.2 | 2.29 | |
| After evac. (373 K) | V=O | 1.2 | 1.62 | 4.2 |
| | V–$O_b$ | 3.5 | 1.86 | |
| | V–$O_c$ | 1.2 | 2.28 | |

[a] C.N. = normalized coordination number. [b] $R$ = interatomic distance. [c] BN = boron nitride.



**Scheme 1**

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**Table 2** Catalytic performance of $SiO_2$-grafted vanadate tetramer and hexamer capped with Rh and other impregnated materials ($p_{C_3H_6} = p_{O_2} = 13.3$ kPa; reaction temp. = 343 K)

| | Formation of acetone in propene oxidation | | | |
|---|---|---|---|---|
| | | | Activation energy[b]/kJ mol$^{-1}$ | |
| Catalyst | TOF/s$^{-1}$ | Selectivity[a]/mol% | Acetone | $CO_2$ |
| $[Bu^n_4N]_2[\{(\eta^3\text{-}C_4H_7)_2Rh\}_2(V_4O_{12})]/SiO_2$ | $2.3 \times 10^{-6}$ | 41 | 47 | 36 |
| $\{Rh(C_5Me_5)\}_4V_6O_{19}/SiO_2$ | $1.7 \times 10^{-6}$ | 85 | 45 | 62 |
| $Rh(acac)(\eta^3\text{-}C_4H_7)/SiO_2$ | $0.6 \times 10^{-6}$ | 13 | 74 | 29 |
| $[Bu^n_4N]_3(V_{10}O_{28}H_3)/SiO_2$ | $0.1 \times 10^{-6}$ | 54 | — | — |
| $V_2O_5/SiO_2$ | $< 10^{-8}$ | *ca.* 0 | — | — |

[a] Selectivity to acetone. [b] Activation energy for acetone and $CO_2$ formation.

oxide cluster frameworks are associated with the selective catalysis for propene oxidation to give acetone. The catalytic activity and selectivity for acetone formation decreased substantially on exceeding the activation temperature of 513 K, possibly owing to the degradation of Rh capped vanadate clusters. For the Arrhenius plots in propene oxidation on $Rh_2V_4O_{12}/SiO_2$, the activation energies obtained were 46.8 kJ mol$^{-1}$ for acetone production and 35.5 kJ mol$^{-1}$ for $CO_2$ production, respectively.

As recently reported by Mimoun *et al.*,[7,8] allyl–Rh complexes catalysed the selective oxidation of alk-1-enes to 2-ketones in solution, the activity of which was strongly retarded by water. Actually, we found that acetone formation from propene oxidation on **1** and **2** was not affected or suppressed by the addition of water. These results indicate that this reaction was not a Wacker-type reaction likely to occur on the conventional binary acidic Mo–Co oxides and redox-cycle catalysed by $CuCl_2$–$PdCl_2$ in solution. By contrast, acetone is formed by a direct reaction between propene and $O_2$ through a peroxy intermediate. Schwartz *et al.*[9] also recently reported that acetone was formed with higher selectivities on the surface-grafted Rh species derived from Rh(π-allyl)$_3$ impregnated on $Al_2O_3$. In summary, we suggest that a coordinatively unsaturated Rh site accommodated by $V_4O_{12}$ and $V_6O_{19}$ cluster frameworks as supporting oxide modelling is responsible for the selective oxidation of propene to acetone, possibly owing to a bifunctional role[10] played by Rh and vanadate cluster moieties.

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## Footnote

† On leave from Chisso Co., Minamata, Kumamoto 867, Japan.

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