# Creation, characterisation and performance of vanadyl active sites in microporous and mesoporous silica-based catalysts for the selective oxidation of hydrocarbons

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We here describe how to design vanadium-centred active sites at the inner surfaces of both well defined microporous and well defined mesoporous siliceous hosts. Each type of vanadia–silica catalyst has been extensively characterised (in regard to surface area, pore size and hydrophobicity) and X-ray absorption spectroscopy establishes the active site for these conversions to be a vanadyl group. These centres are catalytically active under mild conditions for both the epoxidation of a typical alkene and the selective oxidation of a typical alkane. Placing methyl groups in the vicinity of this active site significantly enhances the catalytic performance towards epoxidation.

# Introduction

Two recent experimental developments now make it feasible to engineer atomically well defined active sites in inorganic solids for processes such as the selective oxidation of hydrocarbons. First, the ready preparation of both microporous (pore diameters in the range 3–20 Å) and mesoporous (20–500 Å) high-area siliceous solids into (or onto) which a wide variety of transition-metal ions may be incorporated.<sup>1–3</sup> Second, relatively ready access to synchrotron radiation which, coupled with appropriate catalytic reaction cells and detection systems, enable the local environment of a metal-ion centred active site to be determined by *in situ* X-ray absorption spectroscopy (XAS).<sup>4–8</sup>

One of us has previously described<sup>3,9,10</sup> the preparation and characterisation of a large family of so-called amorphous, microporous mixed oxides, designated typically AMM- $X_n^{Me}Si_ySi$  (where X is the incorporated metal ion, *n* is the mol.% of the metal ion with respect to silicon and *y* is the percentage of silicon atoms which contain a methyl functionality). It has also been shown<sup>11,12</sup> how the so-called MCM-41 mesoporous silica may be functionalised with organometallic precursors and converted to well defined, single-site heterogeneous catalysts. This is particularly true of Ti<sup>IV</sup>-based epoxidation catalysts, that may be prepared and fully characterised<sup>13</sup> by XAS during both preparation and use.

Apart from titanium-based alkene oxidation catalysts, vanadium-containing systems have attracted much of the attention for both alkane oxidation and alkene epoxidation catalysis. Recognising the power and further scope for vanadium-based catalysts in the selective oxidation of hydro-carbons,<sup>14,15</sup> we set about engineering and characterising, in atomic detail, the catalytically active sites situated inside both the AMM- and MCM-type microporous and mesoporous siliceous environments, respectively. Our other aims were to assess and to modify the catalytic performance of these related yet contrasting catalysts, for both the epoxidation of cyclo-

hexene and the partial oxidation of cyclohexane, as summarised in Scheme 1.



# Experimental

# Synthesis

Synthesis of AMM-V<sub>5</sub><sup>Me</sup>Si<sub>50</sub>Si. The microporous amorphous silica host (designated AMM-V<sub>5</sub><sup>Me</sup>Si<sub>50</sub>Si), with a V:<sup>Me</sup>Si : Si ratio of 5:50:45 was synthesised by a sol–gel procedure, the transition metal being incorporated into the bulk material during preparation. In a typical synthesis, 744 mg of V<sup>v</sup> trisisopropoxide was added to a stirred solution of 6.85 ml of tetraethoxysilane, 5.80 ml methyltrisethoxysilane and 11.3 ml ethanol. This was followed by slow addition of 2.82 ml 8 M HCl. The sol, which gelled after *ca.* 4 days, was dried at room temperature for an additional 6 days before being calcined. The calcination procedure involved heating the gel from room temperature to 65 °C at a rate 0.1 °C min<sup>-1</sup>, holding the temperature at this level for 5 h.

Synthesis of AMM-V<sub>5</sub>Si. A similar procedure was adopted, with the exception that 13.70 ml tetraethoxysilane was used and no methyltrisethoxysilane. Gel formation took considerably longer to occur, in this case ca. 6 days.

Synthesis of MCM-41. This was synthesised using the method of Rey et al.<sup>16</sup> 5 g Degussa Aerosil 200 silica was slowly added to a solution of 21.3 g hexadecyl trimethyl ammonium bromide that had been thoroughly mixed and stirred with 28.75 ml water and 7.90 ml tetramethyl ammonium hydroxide (25 wt.% solution in water). Once all the silica was added, the resulting gel was stirred vigorously for at least 1 h, before being transferred to a polypropylene bottle, sealed and placed in an oven at 90 °C for 24 h. The solidified mixture was then mixed thoroughly with distilled water, filtered off and washed with copious amounts of water to remove as much surfactant as possible. The solid was then calcined by first heating under nitrogen to 550 °C at a rate of 5 °C min<sup>-1</sup> and holding the temperature at 550 °C for 1 h. The gas was then changed to dry oxygen and the temperature held constant for a further 6 h before cooling.

Synthesis of V<sub>2</sub>↑PMCM-41 and V<sub>4</sub>↑PMCM-41. 2 g of calcined MCM-41 was dehydrated under vacuum for 2 h at 200 °C and allowed to cool to 40 °C. The solid was then mixed thoroughly with 75 ml anhydrous chloroform under an argon atmosphere to which 0.17 g (or 0.34 g for the 4% catalyst) VCp<sub>2</sub>Cl<sub>2</sub> was subsequently added. After 1 h, 1 ml triethylamine was added, and the mixture stirred under argon at 40 °C for 16 h. The pale-brown coloured solid was filtered off and washed with 250 ml chloroform. The calcination procedure involved heating the sample under nitrogen to 550 °C at a rate of 5 °C min<sup>-1</sup> and, after 30 min, changing the gas to oxygen and holding the temperature at 550 °C for a further 3 h. The active catalyst so formed was white when fresh from the oven, but gradually changed colour to yellow/orange on exposure to the atmosphere. We note that a similar procedure for synthesising a comparable catalyst has been reported.<sup>17</sup>

Synthesis of  $V_2 \uparrow^{Me}$ MCM-41. 0.5 g  $V_2 \uparrow$ MCM-41 (2%) was dehydrated under vacuum for 2 h at 200 °C. Once cooled to 40 °C, a solution of 0.075 ml chlorotrimethylsilane (Me<sub>3</sub>SiCl) in 50 ml anhydrous chloroform was added, under an argon atmosphere, and stirred at 40 °C for 16 h. The remaining green solid was separated by filtration and washed with 250 ml chloroform.

#### Characterisation

**X-Ray diffraction.** All the MCM-41 based catalysts were characterised by XRD (Cu-K $\alpha$ ) employing a Siemens D-500 diffractometer. They all showed the peaks characteristic of the hexagonal form of MCM-41, with no evidence for extra-framework formation of vanadium oxide or vanadate phases.

**IR spectroscopy.** *In situ* **IR** studies were performed using a Perkin Elmer 1725X spectrometer employing a previously reported *in situ* cell.<sup>18</sup>

XAS. In situ V K-edge XAS were recorded on station 8.1 at the CLRC Daresbury Laboratory Synchrotron Radiation Source, operating with a beam energy of 2 GeV and an average current of ca. 200 mA. A double-crystal Si(111) monochromator was employed, offset to 50% of maximum beam intensity for harmonic rejection. In a typical experiment 80 mg of the catalyst was pelletised and loaded into the in situ cell described in an earlier publication.<sup>18</sup> The catalysts were calcined in pure oxygen at 550 °C prior to the roomtemperature data collection. Spectra were obtained in fluorescence mode using a Canberra 13 element solid state fluorescence detector. Four spectra were collected and averaged for each sample. EXCALIB (to add all the data sets and convert the raw data to energy vs. absorption coefficient), EXBROOK (for pre- and post-edge background subtraction) and EXCURV92 (for detailed curve fitting analysis) suite of programs were used to analyse the XAS. X-Ray absorption near-edge structure (XANES) data presented in this work were obtained using the EXBROOK program. The curvefitting procedure was carried out using the data without Fourier filtering and the curved wave theory and multiple scattering approach were adopted for the detailed extended X-ray absorption fine structure (EXAFS) data analysis.

**Hydrophobicity measurements.**<sup>9</sup> The hydrophobicity index,<sup>19</sup> HI, is the ratio of the masses of competitively adsorbed octane and water. The higher the HI the more hydrophobic the catalyst. In order to determine the HI for these catalysts, the material (150 mg) was heated, prior to the measurement to  $250 \,^{\circ}$ C in a constant stream of Ar. For the adsorption experiment a stream of Ar, kept at a constant temperature of  $30 \,^{\circ}$ C, was saturated with equal masses of octane and water. The unadsorbed gases were measured by gas chromatography (GC) over a period of several h in order to determine the adsorbed quantities of water and octane.

Argon physisorption. These measurements were collected on an Omnisorb 360 (Coulter) apparatus. The samples were outgassed, prior to the measurement, at 523 K and  $10^{-4}$  mbar for 12 h. Adsorption isotherms were recorded using a static volumetric technique with a starting pressure of 5 Torr, which was increased by a factor of 1.05 for every dosage step. Ar was adsorbed at a temperature of 87.4 K. The pore-size distributions were calculated for the microporous samples using the Horvath–Kawazoe model while, for the mesoporous materials the Barrett–Joyner–Halenda theory was applied.<sup>20</sup>

#### Catalysis

**Cyclohexane oxidation reactions.** The catalysts were heated to a temperature of 400 °C for 5 h in a constant stream of Ar to remove all traces of water. A 3 M solution of TBHP in nonane (2 ml) was mixed with cyclohexane (6.48 ml) giving a cyclohexane to TBHP ratio of 6:1. The mixture was degassed before use by bubbling Ar through it overnight. 20 mg of the catalyst and the reaction mixture were added to a glass microreactor equipped with a magnetic stirrer, and was heated to 70 °C. Conversion was followed by GC.

Cyclohexene oxidation reactions. These were performed using 2 ml cyclohexene, 1 ml TBHP (80% solution in di-tertbutyl peroxide), 6.5 ml acetonitrile, 0.5 ml mesitylene (as an internal GC standard) and 75 mg catalyst. The reactions were carried out at 30 °C under an argon atmosphere, using undried reagents and catalyst. Since it has been reported that vanadium may leach into solution, even under water-free conditions, causing homogeneous rather than heterogeneous catalysis,<sup>21,22</sup> great care was taken to investigate the nature of our catalytic systems. To prove the heterogeneous character of the reactions, the solid catalyst was either centrifuged and separated (cyclohexane oxidation reactions) or filtered off (cyclohexene oxidation reactions) after 60 min. No further activity was observed in the remaining liquid showing that the results obtained are not due to species leached into solution. In addition, the catalyst was heated with one of the components (i.e. either neat cyclohexane or neat tert-butyl hydroperoxide) for 3 h, after which the solid catalyst was removed by centrifugation. The missing component was then added to the solution and the conversion of the homogeneous mixture followed by GC. No catalysis was observed, and hence the catalytic reactions are truly heterogeneous.

#### **Results and discussion**

The mesoporous silica, MCM-41, was modified with vanadium *via* a vanadocene dichloride precursor, two distinct loadings being used with V : Si ratios of 2 : 100 and 4 : 100. (By analogy with our earlier work<sup>12</sup> on Ti-loaded MCM-41, using titanocene dichloride, these materials are designated





Fig. 1 Vanadium K-edge XANES spectra of (a) VCp<sub>2</sub>Cl<sub>2</sub>, (b) the uncalcined vanadium-modified MCM-41 material, CpV<sub>2</sub>↑MCM-41, (c) NH<sub>4</sub>VO<sub>3</sub> and (d) V<sub>2</sub>O<sub>5</sub>.

 $V_2\uparrow MCM-41$  and  $V_4\uparrow MCM-41$  respectively). XAS was used to characterise the local environment of the vanadium centres. XANES spectra are shown in Fig. 1 and 2, while typical extended EXAFS spectra are shown in Fig. 3. The extracted bond distances and angles can be seen in Table 1. Comparing the XANES spectra (Fig. 1) of the vanadocene dichloride starting material, the uncalcined V↑MCM-41 samples (henceforth referred to as CpV<sub>2</sub>↑MCM-41 or CpV<sub>4</sub>↑MCM-41 depending on the vanadium loading) and other oxide stan-

**Fig. 2** Vanadium K-edge XANES spectra of (a) AMM-V<sub>5</sub>Si, (b) AMM-V<sub>5</sub><sup>Me</sup>V<sub>50</sub>Si, (c)  $V_4\uparrow$ MCM-41, (d)  $V_2\uparrow$ MCM-41 and (e)  $V_2\uparrow$ <sup>Me</sup>MCM-41.

dards, notably ammonium vanadate  $(NH_4VO_3)$  and vanadium pentoxide  $(V_2O_5)$ , it is clear that, firstly, vanadium centres are oxidised to the 5+ state during the grafting procedure and, secondly, there exists a vanadyl bond which gives rise to an intense pre-edge feature.<sup>23</sup> The best fit to the EXAFS spectrum of  $CpV_2\uparrow MCM$ -41 involved a Cp ligand still attached to the vanadium centre, a vanadyl moiety, V=O, and two links to the surface in the form of V-O-Si bonds. On calcination of both the MCM-41 supported

Table 1 Structural data for the catalysts determined by in situ vanadium K-edge EXAFS analysis

Catalyst	Number and type of of atoms	Distance /Å <sup>a</sup>	$2\sigma^2/\text{\AA}^2$	Angle /degrees
AMM-V <sub>5</sub> Si	10	1.54	0.007	
5	3 O	1.75	0.010	
	1.5 Si	3.15	0.013	140
	1.5 Si	3.31	0.013	160
AMM-V <sub>5</sub> <sup>Me</sup> Si <sub>50</sub> Si	1 O	1.57	0.003	
5 50	3 O	1.75	0.007	
	1.5 Si	3.15	0.012	141
	1.5 Si	3.30	0.012	160
V <sub>2</sub> ↑MCM-41	1 0	1.56	0.001	
21	3 O	1.76	0.003	
	1.5 Si	3.16	0.009	140
	1.5 Si	3.30	0.009	159
V₄↑MCM-41	1 0	1.55	0.003	
+1	3 O	1.76	0.006	
	1.5 Si	3.16	0.011	140
	1.5 Si	3.29	0.001	158
V <sub>2</sub> ↑ <sup>Me</sup> MCM-41	1 0	1.55	0.001	
21	3 O	1.74	0.007	
	1.5 Si	3.15	0.014	142
	1.5 Si	3.30	0.014	161
$O = V(OSiPh_3)_3^b$	1 0	1.572		
1 3/3	3 O	1.743 1.745 1.739		
	3 Si	3.260 3.349 3.312		

<sup>a</sup> Typical errors in EXASF-derived bond distances are ca. ±0.02 Å. <sup>b</sup> Single-crystal X-ray diffraction data taken from ref. 24.



**Fig. 3** (a) Vanadium K-edge EXAFS spectra and (b) associated Fourier transforms of  $V_2 \uparrow MCM$ -41. (-----) Experimental spectrum, (....) theoretical best fit. The inset shows the immediate atomic environment around the vanadium centres.

materials in oxygen, the intense pre-edge feature in the XANES region is retained, while EXAFS reveals that the Cp ligand is no longer present and an extra V-O-Si link has been created, *i.e.* a V<sup>V</sup> centre with a short (1.55 Å) vanadyl bond and three longer V-O-Si linkages to the MCM-41 surface, with V-O distances of 1.77 Å. Such a vanadium environment has recently been characterised crystallographically by Feher and Walzer,<sup>24</sup> as a vanadyl centre attached to a silsesquioxane cage via three V-O-Si bonds. The reported bond distances of this soluble analogue are almost identical to those reported here for the silica-supported species. The loading of vanadium does not appear to alter the nature of the active sites, there being no evidence for the formation of V-O-V links. From the resolution of the EXAFS technique, this means that the amount of vanadium existing as dimeric and oligomeric species is less than ca. 10% of the total amount of vanadium present. On methylation of the  $V_2$  MCM-41 catalyst, this supported vanadyl species again does not seem to be affected. With the AMM materials (both methylated and non-methylated), the same vanadium environment is also present. Thus, from analysis of the XANES (Fig. 2) and the EXAFS spectra (Fig. 3), all the catalysts contain the same type of vanadium centre, *i.e.* a supported vanadyl site, as shown in the inset to Fig. 3. Further evidence supporting the fact that  $V^{v}$  centres are involved comes from EPR spectroscopy, which shows that there is no detectable signal for the MCM-41 supported materials, while a very weak resonance (consistent with the presence of small amounts of  $V^{IV}$  centres)<sup>25</sup> is observed for the methylated AMM- $V_5^{Me}Si_{50}Si$  catalyst.

Surface areas and pore volumes, as deduced from the adsorption isotherms, are listed in Table 2 and shown in Fig. 4. *T*-plot analysis of the sorption data confirm that the MCM-41 materials do not contain any micropores. The HIs for  $V_4\uparrow$ MCM-41 and AMM- $V_5^{\text{me}}Si_{50}Si$  are very similar (1.6 and 1.7, respectively), but when  $V_2\uparrow$ MCM-41 was methylated using Me<sub>3</sub>SiCl, as described in the Experimental section, to form  $V_2\uparrow^{\text{Me}}MCM$ -41, its hydrophobicity rose dramatically to 3.9, demonstrating the large influence of the methyl groups on the nature of the surface. The non-methylated AMM- $V_5Si$  catalyst has the smallest value of 0.2. The lower values for the AMM materials are almost certainly a result of their smaller pore sizes which interact more with the probe molecules (octane and water) compared to the larger pore MCM-41 based catalysts.

Both the vanadium-modified AMM and MCM-41 materials were tested for catalytic performance using mild conditions. They are catalytically active towards the oxidation of cyclohexane and cyclohexene in the presence of *tert*-butyl hydroperoxide (see Tables 3 and 4). In the oxidation of cyclohexane, all the catalysts show almost identical selectivity, with cyclohexanol and cyclohexanone being the major products. This similarity is rather surprising in view of the distinctly different pore sizes involved. In order to confirm that this similarity in selectivity is not due to any leached metal ions, we carried out an independent experiment by filtering off the

 Table 2
 Physical characteristics of the silica-based catalysts

	$\frac{Surface\ area}{/m^2\ g^{-1}}$	Pore size /Å	Hydrophobicity index
AMM-V <sub>5</sub> Si	497	8.5 <sup>a</sup>	0.2
AMM-V5 <sup>Me</sup> Si50Si	541	6.5 <sup>a</sup>	1.7
V₄↑MCM-41	673	$28.8^{b}$	1.6
$V_2^{\uparrow Me}MCM-41$ (2%)	—	—	3.9

Maximum of the pore-size distribution as determined by: <sup>*a*</sup> Horvath–Kawazoe method and <sup>*b*</sup> BJH method.



**Fig. 4** Argon adsorption isotherms of  $V_4\uparrow MCM-41$  and AMM- $V_5^{Me}Si_{50}Si$ . The inset shows the Barrett–Joyner–Halenda and the Horvath–Kawazoe treatment, respectively, and the pore-size distribution in each material.

Table 3 Oxidation characteristics for cyclohexane after 70 h at  $70 \,^{\circ}C^a$ 

	Conversion to cyclohexanol (%)	Conversion to cyclohexanone (%)	Conversion to other products (%)
V₂↑MCM-41	0.60	1.93	1.3
V₄́↑MCM-41	0.65	1.91	0.8
V <sub>2</sub> <sup>↑Me</sup> MCM-41	0.58	1.93	0.9
AMM-V <sub>5</sub> Si	0.90	1.97	0.8
AMM-V <sub>5</sub> <sup>Me</sup> Si <sub>50</sub> Si	0.94	2.14	0.9

 $^a$  6.5 ml cyclohexane, 2 ml TBHP (3 M solution in nonane), 20 mg catalyst.

catalyst at 70 °C and continuing the reaction. There was no further catalytic conversion of cyclohexane, and furthermore, ICP chemical analysis yielded no evidence for any leached vanadium in the liquid phase, obtained after catalytic experiments (once again the catalyst was filtered at 70 °C). Thus it is clear from these two tests that the catalytic conversion is effected only by the solid catalyst. Neither a higher concentration of vanadium MCM-41 catalyst nor a more hydrophobic character of the MCM-41 surface had an influence on the



Fig. 5 Total cyclohexane conversion *versus* time, in the presence of either  $V_4\uparrow MCM$ -41 ( $\blacksquare$ ) or AMM- $V_5^{Mc}Si_{50}Si( \bullet)$ .



Fig. 6 Schematic illustration, based on X-ray absorption and the other data presented herein, of the nature of the catalytically active site in (left) V $\uparrow$ MCM-41; (right) AMM-V<sub>5</sub><sup>Me</sup>Si<sub>50</sub>Si and (centre) V $\uparrow$ <sup>Me</sup>MCM-41.

Table 4	Oxidation	characteristics	for cyclol	hexene after	6 h at 30	$^{\circ}C^{a}$
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reaction rate. However, the initial rates of reaction are notably different, with the MCM-41-supported samples giving a faster initial rate relative to the AMM materials (see inset of Fig. 5). Since the selectivities and final conversions are comparable, the initial rate difference must be attributed to the more efficient diffusion in the mesopores of the MCM-41 material. For the cyclohexene epoxidation reaction, the catalysts show different degrees of both activity and selectivity, with the nonmethylated catalysts causing significant "ring-opening" of the cyclohexene oxide to cyclohexan-1,2-diol. In the case of V<sup>Me</sup>MCM-41, the oxidation rate is significantly enhanced compared to the non-methylated V<sup>MCM-41</sup>, attributable to the former's higher hydrophobicity, and the epoxide selectivity is simultaneously dramatically increased. This enhancement in selectivity is also observed with AMM-V5<sup>Me</sup>Si50Si compared to AMM-V<sub>5</sub>Si. Therefore, the methyl groups in both the AMM and MCM-41 vanadium-modified materials not only confer additional hydrophobicity, but also block acidic centres responsible for the hydrolysis that converts the epoxide to the diol. In contrast to the  $V_2\uparrow MCM-41$  and  $V_2\uparrow^{Me}MCM-41$ catalysts, however, the AMM-V<sub>5</sub><sup>Me</sup>Si<sub>50</sub>Si catalyst is not more active than the non-methylated catalyst. It is unclear precisely why this should be so, although it is possible that the methyl groups will increase steric effects within the micropores (consistent with the experimentally determined pore sizes, as listed in Table 2) which may hinder the passage of cyclohexene through the methylated material to a greater extent. Since the completion of this work we have seen the paper of Tatsumi et al.<sup>26</sup> who also detail the effects of hydrophobicity introduced by methyl groups on the oxidation catalysis.

These results indicate that differences in selectivity are due to the presence of methyl groups which, somehow, significantly reduce the acid-catalysed ring opening of cyclohexene oxide to the diol, and are not due to differences in the transition state caused by steric constraints. In order to confirm this, an acidic vanadyl-exchanged ZSM-5 catalyst was employed in a cyclohexene epoxidation reaction. The resulting diol to epoxide ratio of *ca.* 10:1 was the highest of all the catalysts studied.

## Conclusions

In summary, we find that two quite different preparations of vanadium-containing silica-based, high-area meso- and microporous solids (as illustrated in Fig. 6), which are both catalytically active in the selective oxidation of two distinct types of hydrocarbons, have a vanadyl group as the active centre, as depicted in Fig. 3. Although all the catalysts behave similarly towards cyclohexane oxidation, there are distinct differences in their mode of action towards epoxidation of cyclohexene, the most important being the presence of methyl groups on the catalyst surface and their consequent effects on the product selectivity. Plausible mechanisms for hydrocarbon oxidation at a V=O active centre have previously been proposed, suggesting that alkoxyl radicals are responsible for alkane oxidation and a heterolytic, non-radical mechanism is

	Conversion to epoxide (selectivity) (%)	Conversion to cyclohexan-1,2-diol (selectivity) (%)	Conversion to other products (selectivity) (%)
V₂↑MCM-41	1.57 (44.07)	1.78 (49.97)	0.21 (5.96)
V₄↑MCM-41	1.25 (34.88)	2.06 (57.53)	0.27 (7.59)
V <sub>2</sub> ↑ <sup>Me</sup> MCM-41	3.54 (72.84)	0.99 (20.46)	0.33 (6.70)
AMM-V <sub>5</sub> Si	1.00 (39.32)	0.95 (37.52)	0.59 (23.16)
AMM-V <sub>5</sub> <sup>Me</sup> Si <sub>50</sub> Si	1.32 (79.33)	0.21 (12.42)	0.14 (8.25)

<sup>a</sup> 6.5 ml acetonitrile, 2 ml cyclohexene, 1 ml TBHP, 0.5 ml mesitylene (internal GC standard), 75 mg catalyst.

involved in alkene epoxidation.<sup>27-29</sup> Our results are consistent with these mechanistic interpretations.

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## References

- (a) T. Blasco, A. Corma, M. T. Navarro and J. Perez-Pariente, J. Catal., 1995, 156, 65; (b) I. W. C. E. Arends, R. A. Sheldon, M. Wallau and U. Schuchardt, Angew. Chem., Int. Ed. Engl., 1997, 36, 1144; (c) J. M. Thomas, Philos. Trans. R. Soc. London A, 1990, 333 173
- (a) M. S. Rigutto, R. Deruiter, J. P. M. Niederer and H. van Bekkum, Stud. Surf. Sci. Catal. A-C, 1994, 84, 2245; (b) J. M. 2 Thomas, Angew. Chem. Int. Ed. Engl., 1994, 33, 913; (c) J. M. Thomas, Faraday Discuss., 1996, 105, 1; (d) R. Hutter, D. C. M. Dutoit, T. Mallat, M. Schneider and A. Baiker, J. Chem. Soc., Chem. Commun., 1995, 163.
- 3 W. F. Maier, J. A. Martens, S. Klein, J. Heilmann, R. Parton, K. Vercruysse and P. A. Jacobs, Angew. Chem., Int. Ed. Engl., 1996, 35, 180.
- J. W. Couves, J. M. Thomas, D. Waller, R. H. Jones, A. J. Dent, 4 G. E. Derbyshire and G. N. Greaves, Nature (London), 1991, 354, 465.
- 5 J. M. Thomas and G. N. Greaves, Science, 1994, 265, 1675.
- 6
- J. Evans, *Chem. Soc. Rev.*, 1997, **26**, 11. G. Sankar, F. Rey, J. M. Thomas, G. N. Greaves, A. Corma and 7 B. R. Dobson, J. Chem. Soc., Chem. Commun., 1994, 2279.
- L. Aleandri, B. Bogdanovic, C. Dürr, S. C. Huckett, D. J. Jones, U. Kolb, M. Lagarden, J. Rozière and U. Wilczok, Chem. Eur. J., 1997, **3**, 1710.

- S. Klein and W. F. Maier, Anaew, Chem., Int. Ed. Engl., 1996, 35. 9 2230
- 10 S. Klein, S. Thorimbert and W. F. Maier, J. Catal., 1996, 163, 476.
- (a) T. Maschmeyer, F. Rey, G. Sankar and J. M. Thomas, Nature 11 (London), 1995, 378, 159; (b) R. D. Oldroyd, J. M. Thomas and G. Sankar, Chem. Commun., 1997, 2025.
- R. D. Oldroyd, J. M. Thomas, T. Maschmeyer, P. A. MacFaul, 12 D. W. Snelgrove, K. U. Ingold and D. D. M. Wayner, Angew. Chem., Int. Ed. Engl., 1996, 35, 2787.
- J. M. Thomas, Chem. Eur. J., 1997, 3, 1557. 13
- (a) J. Haber, ACS Symp. Ser., 1996, 638, 20; (b) R. Kozlowski, R. 14 F. Pettifer and J. M. Thomas, J. Chem. Soc., Chem. Commun., 1983, 438; (c) B. K. Hodnett, Catal. Rev. Sci. Eng., 1985, 27, 373.
- 15 P. L. Gai-Bayes and K. Kourtakis, Science, 1995, 267, 661.
- F. Rey, G. Sankar, T. Maschmeyer, J. M. Thomas, R. G. Bell and 16 G. N. Greaves, Top. Catal., 1996, 3, 121.
- R. Neumann and A. M. Khenkin, Chem. Commun., 1996, 2643. 17
- 18 P. A. Barrett, G. Sankar, C. R. A. Catlow and J. M. Thomas, J. Phys. Chem., 1996, 108, 8977.
- 19 C. H. Berke, A. Kiss, P. Kleinschmit and J. Weitkamp, Chem. Ing. Tech., 1991, 63, 623.
- 20 J. Seifert and G. Emig, Chem. Ing. Tech., 1987, 59, 475.
- 21 M. J. Haanepen and J. H. C. va Hooff, Appl. Catal. A., 1997, 152, 183
- 22 M. J. Haanepen, A. M. Elemans-Mehring and J. H. C. van Hooff, Appl. Catal. A, 1997, 152, 203.
- (a) R. Kozlowski, R. F. Pettifer and J. M. Thomas, J. Phys. Chem., 1983, 87, 5176; (b) J. Wong, F. W. Lytle, R. P. Messmer 23 and D. H. Maylotte, Phys. Rev. B, 1984, 30, 5596.
- F. J. Feher and J. F. Walzer, Inorg. Chem., 1991, 30, 1689. 24
- Z. Luan, J. Xu, H. He, J. Klinowski and L. Kevan, J. Phys. 25 Chem., 1996, 100, 19595.
- 26 T. Tatsumi, K. A. Koyano and N. Igrashi, Chem. Commun., 1998, 325
- 27 P. R. H. P. Rao, A. V. Ramaswamy and P. Ratnasamy, J. Catal., 1993, 141, 604.
- A. O. Chong and K. B. Sharpless, J. Org. Chem., 1977, 42, 1587. 28
- E. P. Talsi, V. D. Chinakov, V. P. Babenko and K. I. Zamaraev, 29 J. Mol. Catal., 1993, 81, 235.

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