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Studies on the Interaction of Vanadia with Modified Silica Supports and Catalytic Activity for Oxidative Dehydrogenation of Propane: Effect of Support Modification by Al^{3+}, Zr^{4+} or Y^{3+}

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Detailed structural studies of vanadia supported on SiO_2 and modified SiO_2 ($Si_{0.8}M_{0.2}O_{2\pm\delta}$ where M = Al^{3+}, Zr^{4+} and Y^{3+}) were carried out using different techniques such as powder XRD, IR spectroscopy and ^{29}Si, ^{27}Al and ^{51}V MAS NMR spectroscopy. All samples except vanadia impregnated on Zr^{4+} or Y^{3+} modified SiO_2 existed as amorphous phases. A crystalline phase of ZrO_2 was seen in Zr^{4+} modified SiO_2 and YVO_4 was seen in Y^{3+} modified SiO_2 after vanadia impregnation. Based on ^{29}Si MAS NMR and IR spectroscopic studies it was concluded that substitution of Si^{4+} by M results in the breakage of the Si–O–Si network and formation of silicon structural units with Si–O–M type linkages. Unlike all other modified SiO_2, the silicon structural units remained unaffected in Al^{3+} modified SiO_2 before and after vanadia impregnation. A profound change in the interaction of vanadia with the support was observed when the SiO_2 support was modified with different cations and in all cases the V^{5+} preferentially interacted with the substituted cations. Two types of vanadia species, viz. the octahedral and tetrahedral V^{5+}, were present in vanadia impregnated silica and Al^{3+} modified silica but the amount of tetrahedral V^{5+} was more in the latter. In Zr^{4+} modified silica, V^{5+} was present in a crystalline environment which is the V^{5+} dissolved in the ZrO_2 phase. Vanadia impregnated on Y^{3+} modified silica exhibited very little chemical shift anisotropy indicating a symmetric environment around V^{5+} in YVO_4. The catalytic activity for the selective oxidation of propane to propene was tested on these supported catalysts. Vanadia supported on Zr^{4+} modified silica showed maximum selectivity whereas vanadia on silica and Al^{3+} modified silica showed comparable selectivity for propene formation. Vanadia on Y^{3+} modified silica did not show the formation of propene at all.

Introduction

Supported vanadia catalysts are widely used for selective oxidation of hydrocarbons[1–4] and for the reduction of NO_x by ammonia.[5,6] It is well known that the catalytic activity of vanadia catalysts varies with the supporting oxides. The reason for the observed change in the catalytic activity has been attributed to a vanadia-support interaction, which varies with the nature of the support. Different factors influencing the interaction are the acidity of the support, the concentration of vanadia as well as pretreatment conditions etc.[7–10] Thus, different types of vanadia species exist on different supports such as isolated tetrahedral vanadium ions, polymeric species, 2D layers of vanadium oxide or V_2O_5 crystallites.[11–15] It has been demonstrated that isolated vanadia species possessing VO_4 coordination predominate at low surface coverage of vanadia whereas at higher surface coverage both isolated and polymerised species may be observed on the surface of the support. A monolayer of vanadia is formed on the support when the surface coverage is 7–8 V atoms per nm^2.[2,16] However, in the case of V_2O_5 supported on SiO_2, only isolated vanadia species may be observed on the surface and the maximum attainable surface coverage is less than 3 V atoms per nm^2. Hence it is of interest to modify the SiO_2 support by partial substitution of Si^{4+} by Al^{3+}, Zr^{4+} or Y^{3+} and to see whether the support modification improves the dispersion of vanadia on the surface and also to study the structure of the resultant vanadia species. Because the catalytic activity and turnover frequency of a reaction changes with the type of VO_x species, which in turn depends on the nature of support, it is useful to study the interaction of vanadia with this modified support. To the best of our knowledge, the variation of the nature of the interaction of vanadia with the silica support when it is modified with different cations has not been reported so far.

In the present work SiO_2 was modified by partial substitution of the Si^{4+} by Al^{3+}, Zr^{4+} or Y^{3+} and vanadia was loaded on these supports as well as on SiO_2. All supports and vanadia impregnated supports were investigated by various spectroscopic and diffraction techniques such as powder XRD, infrared and NMR spectroscopy to see whether there would be any change in the interaction of vanadia with the modified silica support compared with the

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unmodified one. The activity of these supported vanadia materials as catalysts for the oxidative dehydrogenation of propane to propene has been examined in order to deduce the dependence of the product selectivity on the type of surface vanadia species.

Results and Discussion

Figure 1 shows the powder XRD patterns of SiO_2, VS, SA, VSA, SZ, VSZ, SY and VSY ($Si_{0.8}M_{0.2}O_{2\pm\delta}$, M = Al^{3+}, Zr^{4+} and Y^{3+} represented as SA, SZ and SY, respectively). It can be seen from the figure that the XRD patterns of SiO_2, VS, SA, VSA, SZ and SY oxides show broad peaks centred around 22°, which is characteristic of amorphous silica. However, after vanadia impregnation, samples VSZ and VSY exhibited crystalline phases. The VSZ sample exhibits a pattern with three peaks centred around 30.3, 50.2 and 59.9°, which can be matched with the tetragonal phase of ZrO_2 (JCPDS card no. 17-0923). The presence of this phase was further confirmed from the XRD pattern of the sample heated at 650 °C for 18 h. This clearly showed peaks corresponding to the tetragonal phase of ZrO_2. It is known that V_2O_5 stabilises the tetragonal phase of ZrO_2.[2] The XRD pattern of VSY indicates a crystalline phase, the peak positions of which were found to be matching those of YVO_4. The three most intense peaks seen at 25.0, 33.6 and 49.8° are due to the YVO_4 phase (JCPDS card no. 17–0341). Table 1 gives the total surface area of SiO_2, all modified silica supports before and after vanadia impregnation and the amount of vanadia on these supports (% V_2O_5 on the support by weight, wt.-%). The surface area was found to decrease with vanadia impregnation and this is in agreement with the previous report.[12]

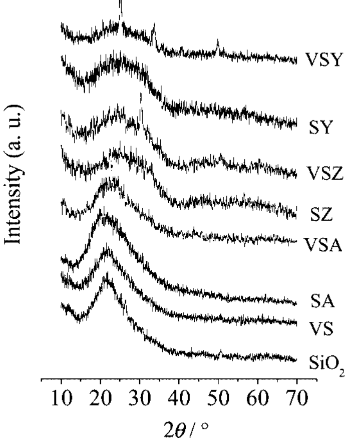

Figure 1. Powder X-ray diffraction patterns of SiO_2, modified silica samples and vanadia impregnated samples.

Since the XRD patterns of these samples indicate poor crystallinity, it was not possible to ascertain whether the Al^{3+}, Zr^{4+} and Y^{3+} cations had really substituted the Si^{4+} sites. Since ^{29}Si NMR spectroscopy can give information regarding the local coordination of Si^{4+} and Si–O–Si bonding in SiO_2, MAS NMR spectra of these samples were recorded. Figure 2 shows the ^{29}Si MAS NMR spectra of SiO_2, the modified silica support and modified supports impregnated with vanadia. For the SiO_2 and VS samples, a clear asymmetry was observed in their spectra indicating that more than one type of silicon structural unit (Q^n, where "n" represents the number of SiO_4 tetrahedra attached to Si^{4+}) is present in these samples. The peaks of all modified supports and vanadia containing supports are broad and showed varying amounts of asymmetry indicating the presence of different types of Q^n structural units within them.

Table 1. Total surface area and wt.-% of V_2O_5 on different supports.

Support	wt.-% V_2O_5 on the support	Surface area [$m^2 g^{-1}$]
SiO_2	–	73
VS	9.7	69
SA	–	72
VSA	9.7	47
SZ	–	173
VSZ	8.0	128
SY	–	125
VSY	8.0	75

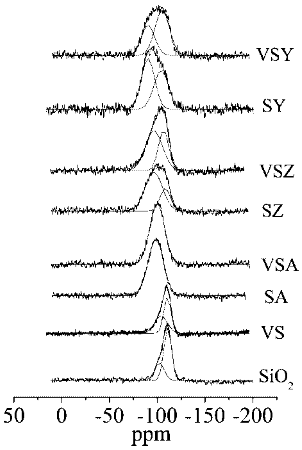

Figure 2. Deconvoluted ^{29}Si MAS NMR spectra of SiO_2, modified silica samples and vanadia impregnated samples.

However, the spectra of the SA and VSA samples are identical, with a peak maximum around –99 ppm indicating that no significant change occurs in the vicinity of the SiO_4 tetrahedra upon vanadia impregnation. A downfield shift seen in the spectra of SA and VSA with respect to SiO_2 indicates that Al^{3+} units have substituted Si^{4+} ion thereby forming an Si–Al mixed oxide.

In order to characterise the different structural units in detail, all spectra except those of SA and VSA were deconvoluted based on a Guassian fit and it was found that these patterns mainly consist of Q^4 and Q^3 structural units of silicon. The peak positions of the Q^4 and Q^3 units and their relative ratios are given in Table 2. It can be seen that the ratio of Q^3 to Q^4 is more for VS than that for SiO_2 indicating that V^{5+} modifies the Si–O–Si network. Similarly, the ratio of Q^3 to Q^4 is more in all modified supports compared with in SiO_2 indicating that incorporation of Al^{3+}, Zr^{4+} or

Y^{3+} in silica results in the breakage of Si–O–Si linkages. The spectra of SA and VSA could be satisfactorily fitted only as a single Gaussian peak with a peak maximum around –99 ppm characteristic of Q^3 structural units. This establishes that V^{5+} has no direct interaction with silicon structural units in the alumino-silicate network. Had there been any direct interaction between the silicon and vanadium structural units, this would have been reflected in the relative concentration of Q^n structural units and their chemical shift values but this was not observed in the present study. It was observed, however, that a downfield shift occurs for the peaks corresponding to the Q^4 and Q^3 structural units in the spectra of modified silica supports compared with that of SiO_2 (see Table 2) and this has been attributed to the decreased Si–O–Si chain length brought about by the modification.

Table 2. Fitted peak positions of Q^4 and Q^3 units present in different samples and their relative ratios.

Sample	Chemical shift [ppm] Q^4	Q^3	$Q^3/(Q^4+Q^3)$
SiO_2	–110·9	–102.0	0.29
VS	–110·6	–103.9	0.46
SA	–	–99.0	≈ 1.0
VSA	–	–99.9	≈ 1.0
SZ	–108.0	–96.0	0.73
VSZ	–106.7	–96.5	0.65
SY	–104.1	–90.4	0.54
VSY	–105.2	–90.5	0.38

To obtain more information regarding the silicon structural units attached to OH groups in these samples, $^1H\rightarrow^{29}Si$ cross polarisation (CP) MAS NMR spectra were recorded and these are shown in Figure 3. A comparison of a single pulse spectrum and a CPMAS NMR spectrum of pure SiO_2 reveals that even in unmodified SiO_2, Q^3 and Q^2 structural units exist in the form of Si–OH linkages.

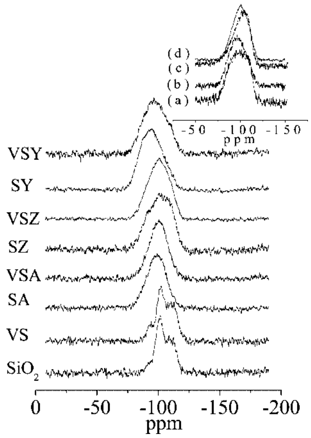

Figure 3. $^1H\rightarrow^{29}Si$ CP MAS NMR spectra of SiO_2, modified silica samples and vanadia impregnated samples. Inset shows the ^{29}Si single pulse and CP MAS NMR spectra, respectively, for VSY (a and b) and VSZ (c and d).

A careful observation of the VS sample revealed a slight increase in the intensity of the peak corresponding to the Q^2 structural unit and this can be attributed to the breakage of Si–O–Si linkages brought about by the vanadia incorporation in silica. Unlike the single pulse spectra of these samples, the peak corresponding to the Q^2 unit can be clearly seen here due to the sensitivity of the technique to the OH groups attached to the silica structural units. The spectra of SA and VSA obtained from single pulse experiments and CP MAS experiments are exactly identical and can be superimposed over one another. This observation once again suggests that vanadia incorporation does not bring about any change in the vicinity of the SiO_4 tetrahedra and hence vanadia probably interacts with the Al^{3+} of the support. For the SZ and SY samples, the spectra resulting from single pulse and CP MAS spectroscopy are identical, demonstrating that no Si–OH linkages are created by Zr^{4+} or Y^{3+} incorporation in silica. However for the VSZ and VSY samples, the CP MAS spectra showed a slightly different line shape with a downfield shift of the peak maxima over a range of 5–6 ppm compared with that obtained from single pulse experiments (see inset in Figure 3). This can be attributed to the formation of Si–OH (Q^3 type) linkages brought about by the removal of Zr^{4+}/Y^{3+} from the VSZ/VSY samples to form ZrO_2 and YVO_4, respectively.

The ^{27}Al NMR spectra of SA and VSA are shown in Figure 4. A single peak with a chemical shift of 53 ppm with a comparable line shape can be seen indicating that Al^{3+} is in a tetrahedral coordination environment before and after vanadia impregnation. Since there is no Al^{3+} present in an octahedral coordination mode, it can be concluded that the γ-Al_2O_3 phase is not present in these samples. Due to the quadrupolar nature of the Al^{3+} ion, it is less sensitive to the changes in the chemical environment brought about by vanadium incorporation and hence no change in the line shape is to be expected for the VSA sample and such is the case.

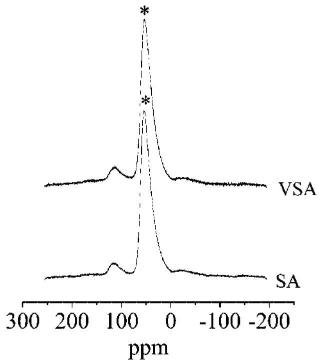

Figure 4. ^{27}Al MAS NMR spectra of SA and VSA samples (the peak marked with an asterisk is the isotropic peak).

The IR spectra of all modified silica samples with and without vanadia impregnation are shown in Figure 5. It can be seen that the spectra of all silica containing samples are somewhat similar to the spectrum of SiO_2. However, some subtle changes can be observed in the spectra of modified silica samples upon closer observation. The IR spectrum of V_2O_5 shows three prominent bands at 472, 810 and

1020 cm^{-1}. The band at 1020 cm^{-1} corresponds to the unshared V=O stretching vibration and the bands located around 810, 472 and 364 cm^{-1} can be assigned to the vibrations of the bound oxygen which are shared by two vanadium atoms.[17,18] The IR spectrum of silica mainly shows three broad bands centred at 1091, 808 and 470 cm^{-1} which can be assigned to the Si–O stretching (antisymmetric stretching of the type ←Si O→ ←Si), Si stretching (symmetric stretching mode of type ←Si O Si→) and Si–O–Si bending of the characteristic groups, respectively.[19,20] Since the peak positions of both V_2O_5 and SiO_2 are close, they overlap and hence IR bands due to V_2O_5 cannot be seen in vanadia impregnated samples. In all substituted silica samples, it can be seen that the band around 1091 cm^{-1} shifts to a slightly lower frequency compared with that in pure SiO_2. This is due to the substitution of some of the Si^{4+} centres by bigger cations which form M–O bonds (M = Al^{3+}, Zr^{4+} and Y^{3+}). This results in a softening of the Si–O bond. A similar effect has been observed for the Si stretching band located around 808 cm^{-1}. A downward frequency shift of the V–O stretch in V_2O_5–MoO_3 has been reported by Hirata et al.[21] due to the softening of this bond arising from the replacement of V^{V} by V^{IV} in this mixed oxide. The IR spectra of reduced V_2O_5 also show a similar effect in the V=O stretching vibration due to the V^{IV} species, the ionic radius of which is larger than V^{V}.[17] In the case of the SZ and SY samples, it can be seen that the band around 1091 cm^{-1} is very broad compared with that in SiO_2 and this is due to the distortion of the Si–O–Si bond brought about by the substitution. However, in the case of VSZ and VSY, a shift in this band to a slightly higher frequency can be observed. This high frequency shift can be attributed to the formation of ZrO_2 and YVO_4 compounds in SZ and SY, respectively, resulting from the removal of Zr^{4+}or Y^{3+} from the silica structure. This observation is in accord with the ^{29}Si MAS NMR spectroscopic results. A weak narrow band around 1630 cm^{-1} present in the IR patterns of all samples except V_2O_5 arises due to the bending vibrations of the OH groups attached to silicon.

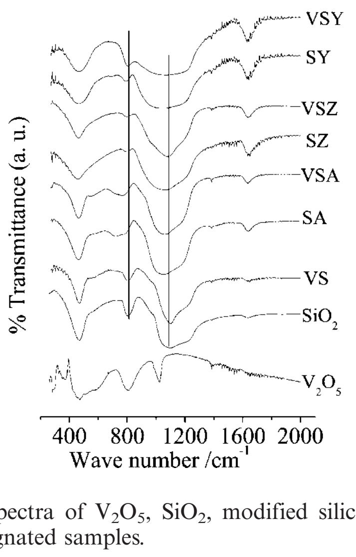

Figure 5. IR spectra of V_2O_5, SiO_2, modified silica samples and vanadia impregnated samples.

^{51}V solid state NMR spectroscopy can give a clear understanding of the state of V^{5+} species on different supports and many such studies have identified different vanadia species such as tetrahedrally or octahedrally coordinated V^{5+} or vanadia crystallites on various supports.[22–28] Figure 6 shows the ^{51}V static and MAS NMR spectra of V_2O_5, VS and VSA. The static pattern of V_2O_5 is similar to that reported in the literature indicating a distorted octahedrally coordinated V^{5+} ion with axial symmetry. The MAS NMR spectrum shows an isotropic peak at δ = –614 ppm with a side band pattern typical of this compound. The static spectrum of VS was found to be different from that of V_2O_5. It consists of two peaks with maxima around –380 and –597 ppm which are similar to those for the "a" (octahedral) and "b" (tetrahedral) type V^{5+} species reported by Eckert and Wachs.[22] The MAS NMR spectrum of this sample consists of an extensive side band pattern superimposed over a weak broad peak. The extensive side band patterns have been attributed to the presence of bulk-like V_2O_5 or a precursor of V_2O_5[22,24] in which vanadium is in a distorted octahedral configuration. The weak broad background arises from the vanadium species existing in the tetrahedral configuration. Hence it can be concluded that both octahedral and tetrahedral V^{5+} are present in this sample. The static spectrum of VSA also showed a similar pattern to that of VS with two peaks centred around –340 and –590 ppm showing the presence of both octahedral and tetrahedral V^{5+}. Unlike the MAS NMR spectrum of VS, the spectrum of the VSA sample clearly showed a side band pattern similar to that of bulk-like V_2O_5 superimposed over a broad peak characteristic of tetrahedral V^{5+} species. From these results it can be inferred that the dispersion of vanadia is better on SA than on SiO_2. The static and MAS NMR spectra of VSZ, VSY and YVO_4 are shown in Figure 7. The static spectrum of VSZ shows two narrow peaks around –495 and –566 ppm having line widths significantly less than those of VS and VSA. The MAS NMR pattern for this sample is characterised by a sharp isotropic peak at δ = –566 ppm along with a number of side bands. Both static and MAS NMR spectroscopic results thus suggest that V^{5+} structural units exist in a highly crystalline environment. However, the XRD pattern revealed that the only crystalline phase present in the sample is ZrO_2. Thus, based on the XRD and NMR results, it can be inferred that in the VSZ sample, the V^{5+} species are dissolved in the ZrO_2 phase. The static spectrum of VSY showed a narrow peak (peak maximum at δ = –682 ppm), which suggests that V^{5+} species exist in a symmetric environment and hence exhibit very little chemical shift anisotropy. Since the VSY sample showed a crystalline phase of YVO_4 in its XRD pattern, the NMR spectrum of YVO_4 was also recorded and is shown in Figure 7. Both the static and MAS NMR spectra of YVO_4 are similar to that of VSY. The MAS spectrum of YVO_4 showed an isotropic peak at –673ppm, which is very close to that of the VSY sample. Hence the peak seen at δ = –663 ppm for VSY can be assigned to the YVO_4 phase. Thus, ^{51}V NMR spectroscopy gives clear evidence for a different type of interaction between vanadia and modified silica compared with unmodified silica. Based on the ^{29}Si, ^{27}Al and ^{51}V NMR results it can be concluded that V^{5+} selectively interacts with the substituted cations and not Si^{4+}. This conclusion is in agreement with the observation of Gao and Wachs[29] who reported a preferential interaction of V cations with Ti, Zr or Al on multilayered metal oxide catalysts such as $V_2O_5/MO/SiO_2$ where M = Ti^{4+}, Zr^{4+} or Al^{3+}. Similarly, a preferential interaction of Cr^{n+} with alumina compared with silica has been reported where the Cr^{n+} is adsorbed as a chromate ion.[30]

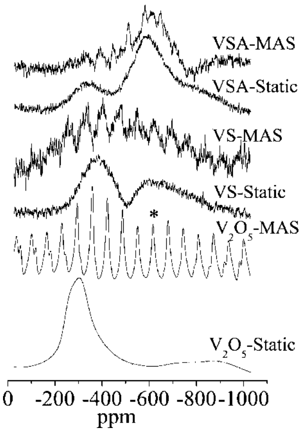

Figure 6. ^{51}V static and MAS NMR spectra of V_2O_5, VS and VSA (the peak marked with an asterisk is the isotropic peak).

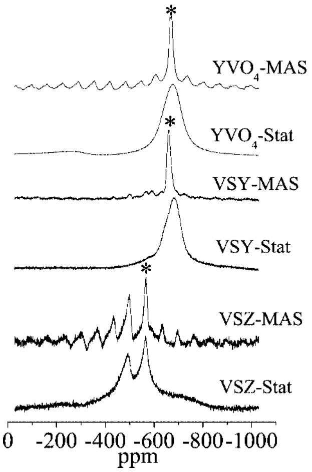

Figure 7. ^{51}V static and MAS NMR spectra of VSZ, VSY and YVO_4 samples (the peak marked with an asterisk is the isotropic peak).

The results of catalytic tests performed on these supported catalysts for the selective oxidation of propane to propene are summarised in Table 3. The products formed during the reactions were mainly propene and CO_2. Small quantities of CH_4 and C_2H_4 were detected and the selectivity for these products was around 1%. CO, if formed during the reaction, was not analysed. It can be seen from Table 3 that the catalytic activity and selectivity of vanadia varies as the silica support is modified with different cations. VSZ showed maximum selectivity for propene formation whereas VSY gave no propene formation at all. Though the C_3H_8 conversion was highest for VS, its selectivity for propene formation was less when compared with VSZ. The selectivity of VSA for catalytic propene formation was comparable with that of VS. These results clearly demonstrate that the product selectivity and catalytic activity depend significantly on the type of vanadia species, which in turn depends on the cations used for the modification of the silica support. The relatively low value of propene selectivity observed for these catalysts could be due to the low flow rate of the reactants. It has been reported that low flow rates result in an increased residence time of the reactants on the catalysts which can lead to the formation of CO_x species from the secondary oxidation of C_3H_6 as observed in the present study.[2]

Table 3. Percentage conversion and selectivity data for oxidative dehydrogenation of propane for various V_2O_5 supported catalysts at 550 °C.

No.	Catalyst	C_3H_8 conversion [%]	C_3H_6 selectivity [%]
1	VS	51	14
2	VSA	34	12
3	VSZ	36	23
4	VSY	26	–

The salient feature of this study is that the interaction of vanadia with the support varies when the SiO_2 is modified by substitution of just 20% of the Si^{4+} by different cations. This change in the interaction of vanadia with the modified support has a significant impact on its catalytic activity and selectivity for the oxidative dehydrogenation of propane to propene.

Conclusions

The interaction of vanadia with silica supports varies as the silica is modified with cations such as Al^{3+}, Zr^{4+}or Y^{3+}. A preferential interaction of V^{5+} with Al^{3+}, Zr^{4+}or Y^{3+} cations present in SiO_2 occurs in these samples. Vanadia present on unmodified SiO_2 contains two types of V^{5+} species which are tetrahedrally and octahedrally coordinated. Bulk-like V_2O_5 with a distorted octahedral configuration is the predominant species on unmodified SiO_2 whereas on Al^{3+} modified SiO_2, both tetrahedral and octahedral V^{5+} species can be clearly seen. On Zr^{4+} modified silica, V^{5+} becomes dissolved in the ZrO_2 phase. On Y^{3+} modified silica, vanadia reacts with Y^{3+} forming the YVO_4 phase. Catalytic tests conducted for the oxidative dehydrogenation of propane indicated that the catalytic activity and selectivity of vanadia varies with support modification. This is due to the presence of different types of surface vanadia species on these catalysts formed by the selective interaction of V^{5+} with the cations present in modified silica.

Experimental Section

Samples of $Si_{0\cdot8}M_{0\cdot2}O_{2\pm\delta}$ (M = Al^{3+}, Zr^{4+} and Y^{3+} represented as SA, SZ and SY, respectively, in the text) were prepared by the coprecipitation technique. Aqueous solutions of aluminium nitrate, zirconium oxychloride and yttrium nitrate were used for the preparation of the SA, SZ and SY samples. Each of these solutions, with the required ratio of cations, was mixed thoroughly with sodium silicate solution and precipitated using ammonia solution (pH ≈ 8). The precipitates, after filtering, were washed thoroughly and dried in an oven for nearly 10 h. This was followed by calcination in air at 500 °C for 2 h. Unmodified SiO_2 was prepared by adding ammonia to an aqueous solution of sodium silicate, followed by a similar washing and heating procedure mentioned above. Vanadia was impregnated on these supports (6 atom-% of V) by an impregnation technique. SiO_2 and modified SiO_2 were kept in contact with an aqueous solution of ammonium vanadate and were then dried on a hot plate with constant stirring followed by heating in air at 500 °C for 2 h (vanadia impregnated on SiO_2, SA, SZ and SY are represented as VS, VSA, VSZ and VSY, respectively, in the text). The surface areas of these samples were measured using the BET technique with nitrogen as the adsorbing gas. Since a second phase of YVO_4 was seen in the VSY sample, YVO_4 was prepared for comparison purposes. YVO_4 was prepared by mixing ammonium vanadate and yttrium oxide thoroughly in the correct stoichiometric ratio and heating in air at 800 °C for 6 h. V_2O_5 obtained from Fluka was used for recording NMR and IR spectra.

Powder X-ray diffraction patterns of these samples were recorded using a Philips PW1820-X-ray diffractometer coupled with a PW 1729 generator, which was operated at 30 kV and 20 mA. A graphite crystal monochromator was used for generating monochromatic Cu-K_α radiation. IR spectra were recorded as KBr pellets using a Bomem MB102 FTIR machine having a range of 200–4000 cm^{-1}. NMR spectra were recorded with a Bruker Avance DPX 300 spectrometer at basic frequencies of 78.206, 59.6214 and 78.9005 MHz for ^{27}Al, ^{29}Si and ^{51}V, respectively. Spectra were recorded using 7 mm zirconia rotors packed with the sample. Different spinning speeds of 5 kHz, 4 kHz and 3 kHz were employed to identify the isotropic peaks. A typical 90° pulse duration for recording ^{27}Al NMR spectra was 3.5 μs and a delay time of 5 s was used. ^{51}V MAS spectra were recorded with a 90° pulse duration of 3.5 μs and a delay time of 4 s. Experiments were also carried out by varying the 90° pulse duration from 1 μs to 3 μs with a view to establishing any line distortion brought about by the satellite transitions of the quadrupolar ^{51}V nuclei. However, it was observed that the line shapes were unaffected by the different pulse durations. For recording ^{29}Si MAS NMR spectra, a 90° pulse duration of 4.0 μs and a delay time of 5 s were employed. Delay times were varied from 5 s to 20 s to see whether there would be any change in the line shape of the spectra since the ^{29}Si nucleus has a long relaxation time. For $^{1}H\rightarrow^{29}Si$ cross polarisation (CP) MAS NMR experiments, a contact time of 5 μs and delay time of 6 s were employed. Around 4000 scans were recorded for each sample in order to obtain NMR patters with reasonable signal to noise ratios. All ^{29}Si, ^{27}Al and ^{51}V NMR chemical shifts are expressed with respect to tetramethylsilane, aqueous $[Al(H_2O)_6]^{3+}$ and $VOCl_3$, respectively.

A preliminary test of the catalytic activity of these supported catalysts for the selective oxidation of propane to propene was carried out in a tubular quartz reactor of 25 cm length and 0.7 cm internal diameter using a fixed bed. A quantity of 200 mg of catalyst was used for each experiment and the reactant gas mixture had a composition of C_3H_8:O_2:He as 1.06:1.09:97.85 (by volume). The reaction was studied at 550 °C using a continuous flow method with a flow rate of 20 $cm^3\,min^{-1}$ of the reactant mixture. The effluent gas mixture was analysed online by an automatic gas sampling valve connected to a gas chromatograph (CIC, GC2011) equipped with a porapak Q column and a thermal conductivity detector. The hydrocarbons formed were also analysed in an FID mode using a porapak R column.

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