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Structural and catalytic properties of a novel vanadium containing solid core mesoporous silica shell catalysts for gas phase oxidation reaction

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Abstract. A novel vanadium containing solid core mesoporous silica shell catalyst was synthesized with different Si/V ratios by sol–gel method under neutral conditions. The synthesized materials were characterized by various techniques and gas phase diphenyl methane oxidation reaction. The mesoporosity combined with microporosity are formed by incorporation of octadecyltrichloro silane and triethylamine in the catalyst and it was found out from E-DAX and BET—surface area analysis. The material was found to be nanocrystalline. Vanadium is present as V^{4+} species in as-synthesized samples and convert to V^{5+} on calcination. Most of the vanadium is present in tetrahedral or square pyramidal environment. Incorporation of vanadium in silica framework was confirmed by ^{29}Si MAS NMR analysis. Among the various vanadium containing solid core mesoporous silica shell catalysts, the Si/V = 100 ratio exhibited maximum efficiency towards diphenyl methane to benzophenone gas phase reaction. The optimum condition required for maximum conversion and selectivity was found out from the catalytic studies.

Keywords. Gas phase oxidation; vanadium containing solid core mesoporous silica shell; diphenylmethane.

1. Introduction

Catalytic oxidation of hydrocarbons in general is employed in the manufacture of fine chemicals. In particular, more than 60% of products synthesized by catalytic routes in the chemical industry are obtained by oxidation reaction.[1] In this context, the selective partial oxidation of diphenylmethane to benzophenone is a versatile route for the synthesis of many fine chemicals. Since, benzophenone is widely used as a constituent of synthetic perfumes and as a starting material for the manufacture of dyes, pesticides and drugs (especially anxiolytic and hypnotic drugs). Earlier, synthesis of benzophenone is performed by the oxidation reaction of the diphenylmethane using stoichiometric quantities of oxidizing agents like $KMnO_4$ or $K_2Cr_2O_7$ and by Friedel–Crafts acylation.[2,3] Heterogeneous catalysts are prefered due to the environmentally friendly reasons. The heterogeneous catalysts include vanadium ions or complexes incorporated into the framework or cavities of microporous materials.[4–8] In addition, microporous based molecular sieves have a drawback of smaller pore size, which restricts the accessibility of active sites to large substrate molecules. Thus, it is of interest to carry out the oxidation of diphenylmethane using transition metals containing mesoporous catalysts. In this regard, a new material viz. solid core mesoporus silica shell was recently synthesized with combined micro- and mesoporous material and uniform mesopores.[9]

In the present investigation, synthesis of novel vanadium containing solid core mesoporous silica shell by sol–gel method is established and its application towards vapour phase oxidation of diphenylmethane using CO_2-free air as oxidant. In order to achieve the better activity and selectivity, effect of temperature, time on stream, and vanadium content were studied.

2. Experimental

The vanadium containing solid core mesoporous silica shell was synthesized by sol–gel method using the following procedure. Acetone of 74 ml (99.5%, S D Fine, India) was mixed with 11 ml of tetraethylortho silicate (98%, Aldrich, USA). Triethylamine of 3.3 ml (98%, S D Fine, India) and 2 ml of octadecyltrichlorosilane (98%, Aldrich, USA) were mixed with the above gel. V_2O_5 of 0.102 g (98%, Aldrich, USA) was mixed well with the above mixture. Finally, 10 ml of distilled water was mixed with the above mixture and stirred well for

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2 h. The precipitate is centrifuged to separate the solid and washed with distilled water and dried at 353 K. The as-synthesized sample was subjected to various physicochemical characterizations. A portion of the sample was calcined at 823 K for 8 h and the furnace temperature was raised from room temperature at 1.5 K/min rate. Influence of various silanes on solid core mesoporous silica shell synthesis were studied in similar conditions.

Small angle X-ray diffraction analysis was carried out using Mac Science Co. Ltd., MO3XHF22 instrument in the 1–12° region. The surface elemental analysis, particle size and shape were analysed by a Leica Stereoscan - 440 scanning electron microscope. The copper disc was pasted with carbon tape and the sample was dispersed over the tape. The disc was coated with gold in ionization chamber. Transmission electronmicroscopic (TEM) studies were performed on a JEOL JSM-2000 EX electron microscope operated at 200 kV. The TEM sample was prepared by dipping a Cu grid coated with carbon films by sample suspension with water as solvent (solution was sonicated for 20 min). Thermogravimetry/differential thermal analysis was carried out using Perkin Elmer, S11 Diamond TG/DTA analyzer. Fourier transform infrared spectroscopic analysis was carried out using Perkin Elmer Spectrum one FT-IR Instruments. Electron spin resonance spectra of the as-synthesized and calcined vanadium containing solid core mesoporous silica shell samples were obtained using a Bruker 200D spectrometer. The UV-Vis diffuse reflectance spectra were recorded using a Pye Unichem (SP-8-100) instrument in 200–900 nm regions. Raman spectroscopy carried out using Bruker senterra dispersive Raman microscope of laser light of 532 nm wavelength. Solid State Nuclear Magnetic Resonance spectrum was carried out using Bruker Avance 300 MHz instrument.

Oxidation of diphenylmethane was carried out on a fixed bed down flow quartz reactor with CO_2 free air at atmospheric pressure in the temperature range of 563–713 K. Prior to the reaction, the reactor was charged with 0.5 g of the catalyst and pre-heated in a tubular furnace equipped with a thermocouple. Diphenylmethane was fed into the reactor through a syringe infusion pump at a predetermined flow rate. The product mixture was collected at regular interval of time was filtered through 0.2 μm membrane filter and analysed by HPLC (Shimadzu, CLASS VP model) with a UV detector using a column packed with octadecyl silane with a mobile phase of acetonitrile/ methanol (60:40, v/v) at a flow rate of 1.0 mL min^{-1}. An injection volume of 20 μl was used. After every run, the catalysts were regenerated by passing a stream of pure dry air at a temperature of 773 K for 6 h.

3. Results and discussion

Octadecyltrichlorosilane and triethylamine have given solid core mesoporous silica shell (table 1). However, methyltrimethoxysilane or octyltrimethoxy silane instead of octadecyltrichlorosilane did not give the same. No precipitate was formed. The reason is probably due to the poor hydrolysing rate in the former reagents. Only triethylamine is given nano silica. Introduction of vanadium did not change the product. The small angle X-ray diffraction pattern (figure 1) of the as-synthesized vanadium containing solid core mesoporous silica shell show that it is probably a mesoporous. On calcinations the pattern does not change considerably, however a small line broadening is observed. The sample synthesized only with triethylamine gave amorphous material. Scanning electron

Table 1. Physical properties of mesoporous V – silica.

S. No.	Gel composition	Product composition (2 h)	Particle size	Yield (%)
1.	$0.01V_2O_5$: SiO_2: 0.7 TEA: 0.1ODTCS: 11.5 H_2O: 1.25 Act	SiO_2: $0.02V_2O_5$: 0.3TEA: 0.04ODTCS	500 nm (shell thickness = 50 nm)	100
2.	SiO_2: 0.7 TEA:0.1ODTCS: 11.5 H_2O: 1.25 Act	SiO_2: 0.3TEA: 0.04ODTCS	400 nm (shell thickness = 45 nm)	80
3.	$0.01V_2O_5$: SiO_2: 0.7 TEA: 11.5 H_2O: 1.25 Act	SiO_2: $0.06V_2O_5$: 0.3TEA	600 (no shell)	70
4.	$0.01V_2O_5$: SiO_2: 0.7 TEA: 0.1 R: 11.5 H_2O: 1.25 Act	No precipitate	–	–

Synthesis conditions: duration = 2 h, temperature = 298 K, rotation = 650 rpm. TEA: triethylamine, ODTCS: octadecyltrichloro silane, Act: acetone, R: octadecyltrimethoxy silane, methyltrimethoxy silane, octyltrimethoxy silane

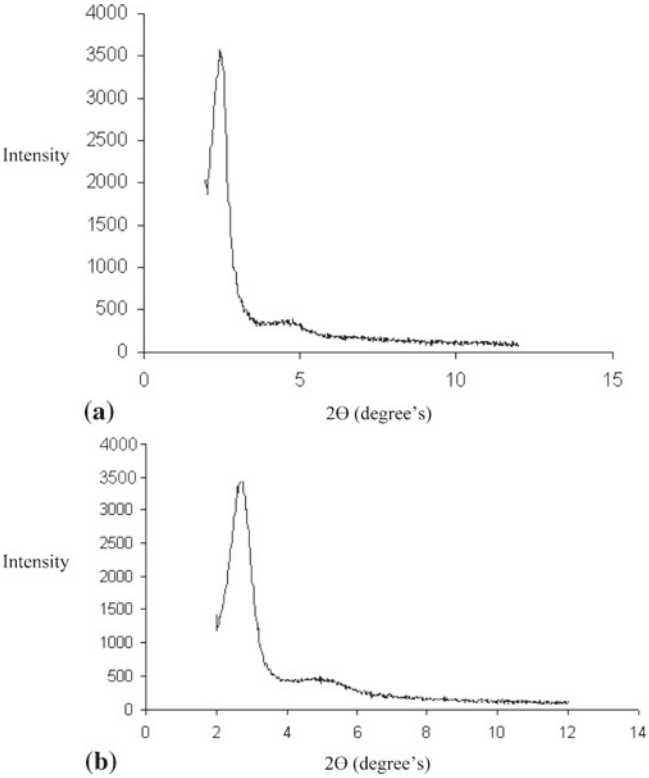

Figure 1. The low angle X-ray diffraction patterns of vanadium containing solid core mesoporous silica shell (Si/V = 100) catalyst in (**a**) as-synthesized and (**b**) calcined form.

micrograph of vanadium containing solid core mesoporous silica shell shows the morphology. The pure solid core mesoporous silica shell, vanadium containing solid core mesoporous silica shell and vanadium containing nano silica are spherical, and the particle sizes are 400, 500 nm and 500 nm. E-DAX analysis (table 1) of the as-synthesized samples shows the presence of larger extent of octadecyltrichlorosilane and triethylamine in solid core mesoporous silica shell surface. The samples prepared only with triethylamine has the amine on surface to considerable extent. The Transmission electron micrograph of the calcined samples shows the particle sizes of 400 nm (shell size 45 nm), 500 nm (shell size 50 nm), 500 nm for vanadium-free and vanadium containing solid core mesoporous silica shell and vanadium containing nanosilica samples (figure 2). The presence of large extent of octadecyltrichlorosilane is available not only on surface, but also in the bulk is observed from the thermogravimetry/differential thermal analysis. It shows about 60% exothermic weight loss on calination in the presence of air from room temperature to 900°C. But vanadium containing nanosilica losses only 25%.

The Typical nitrogen adsorption isotherms of vanadium containing solid core mesoporous silica shell at 77 K (figure 3) show a linear increase of the amount of adsorbed nitrogen at low pressures (P/Po = 0.0–0.2).

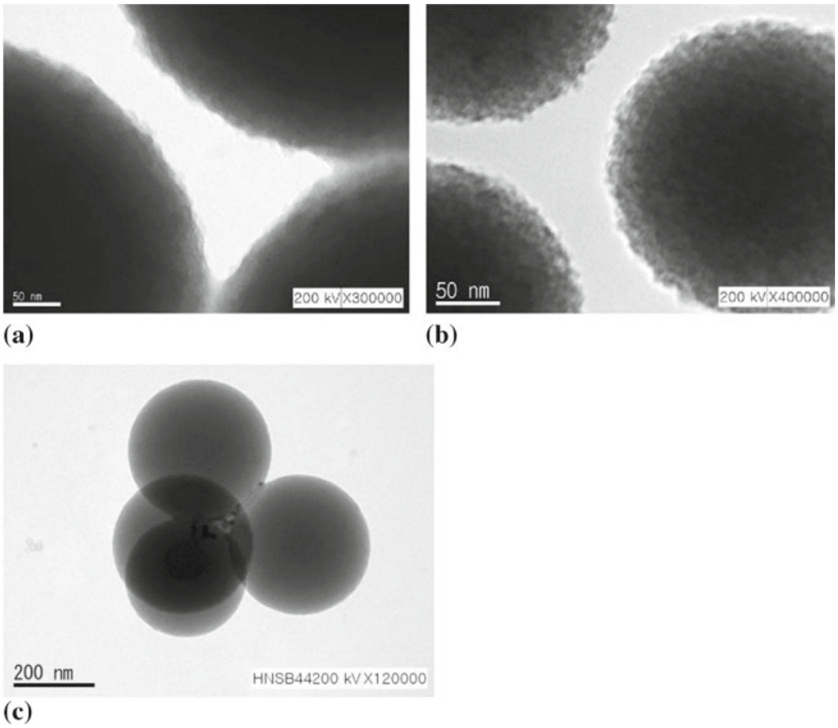

Figure 2. Transmission electron micrograph of calcined (**a**) Solid core mesoporous silica shell, (**b**) vanadium containing solid core mesoporous silica shell (Si/V = 100) catalyst and (**c**) vanadium containing nanosilica (Si/V = 100).

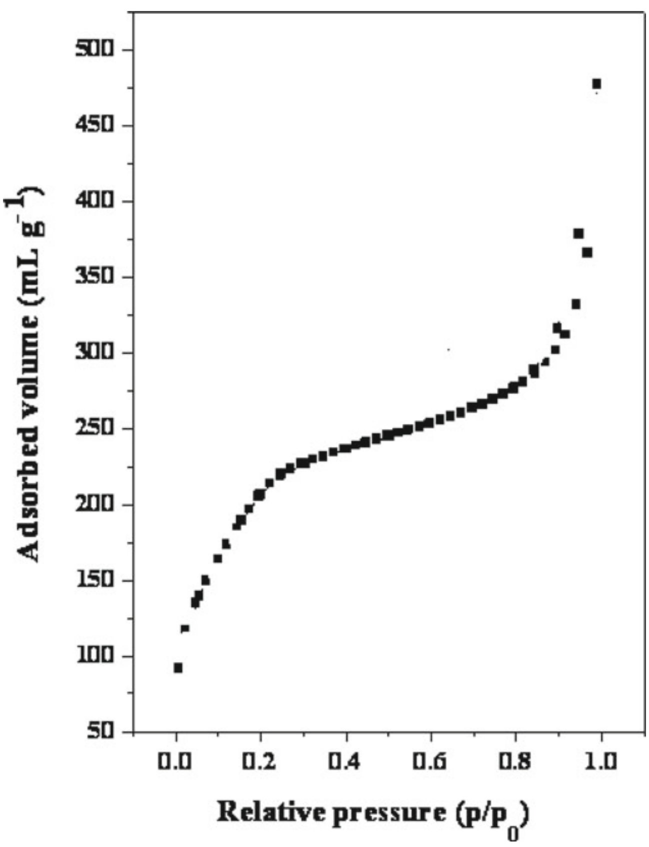

Figure 3. N_2 adsorption – desorption isotherms of calcined vanadium containing solid core mesoporous silica shell (Si/V = 100) catalyst.

The resulting isotherm can be classified as a type II isotherm according to the IUPAC nomenclature.[10] The steep increase in nitrogen uptake at relative pressures at around P/Po = 0.9 shows that the presence of a narrow pore size distribution. Thus, the variation of template in the solution during the growth process enables one to adjust and to control pore structural parameters such as the specific surface area, 550 m^2/g (mesoporous area = 350 m^2/g and microporous area = 202 m^2/g), specific pore volume (mesopore = 1.29 cm^3/g and micropore = 0.25 cm^3/g), average pore diameter (mesoporous = 239 Å and micoroporous = 6.2 Å) and medium pore width, 302 Å. Surface area of V – nano silica is 207 m^2/g. It is deduced that from the above analysis that a larger surface area of the calcined materials are due to the vacant sites created by the loss of octadecyl trichlorsilane and or triethylamine species.

Fourier transform infrared spectrum of vanadium containing solid core mesoporous silica shell as-synthesized sample shows that peaks around 1700 and 3430 cm^{-1} corresponding to the carboxyl and hydroxyl groups, respectively.[11] The adsorption peak belonging to the Si–O stretching vibration of Si–O$^-$M$^+$ bond appears at 960 cm^{-1}.[12] The weak peaks at 2855 and 2920 cm^{-1} belong to the stretching vibrations of C–H bonds, which show a few organic groups that are adsorbed on the spheres. The strong peaks near 1100, 802 and 467 cm^{-1} agree to the Si–O–Si bond which implies the condensation of silicon alkoxide.[12]

Diffuse reflectance Ultraviolet-Visible spectra of the as-synthesized vanadium containing solid core mesoporous silica shell and vanadium containing nanosilica samples show (figure 4) peaks at 350, 280 and 220 nm and 370, 270 and 220 nm, respectively. The peak at 220 nm is due to Si–O$^-$ species and peak at around 280 nm is due to tetrahedrally coordinated V^{4+} species and peak at around 350 nm is due to blue shifted square pyramidal vanadium species.[13,14] Calcined sample shows a single broad peak at around 460 nm corresponds to V^{5+} in square pyramidal environments.[15,16] Pure solid core mesoporous silica shell sample shows a peak around 280 nm alone due to free Si–O$^-$ species.

The electron spin resonance spectra (figure 5) of vanadium containing solid core mesoporous silica shell/vanadium containing nanosilica as-synthesized samples show a eight line hyperfine splitting with $A_{\parallel} = 198$, $g_{\parallel} = 1.9293$, $A_{\perp} = 78$ and $g_{\perp} = 1.9814$ parameters correspond to VO^{2+} in a distorted octahedral or square pyramidal environment.[17,18] On calcinations most of the vanadium is oxidized to V^{5+} ions and the eight-line hyperfine splitting intensity reduced to one fifth of the original peak intensity. Thermal reduction with hydrogen gave ESR spectrum similar to that of the as-synthesized sample, but the intensity was one third of that of the as-synthesized form. This clearly demonstrates the redox behaviour of the vanadium present in the samples.

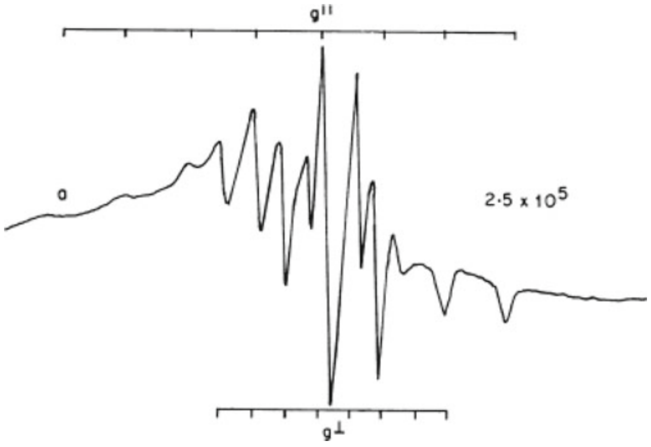

Figure 4. Electron spin resonance spectrum of as-synthesized vanadium containing solid core mesoporous silica shell (Si/V = 100) catalyst.

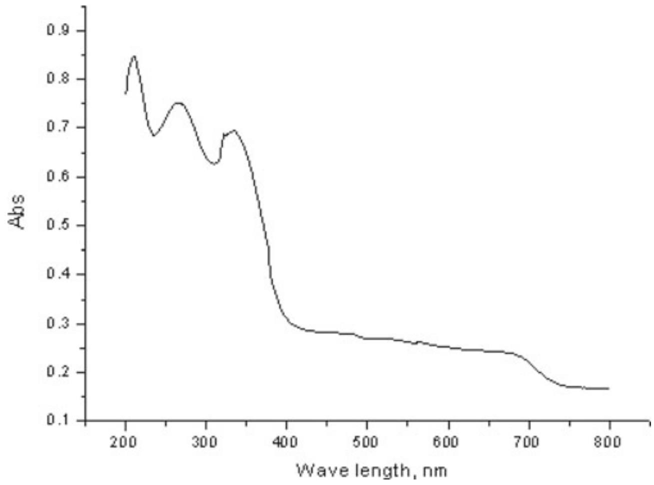

Figure 5. Diffuse reflectance ultraviolet – visible spectrum of as-synthesized vanadium containing solid core mesoporous silica shell (Si/V = 100) catalyst.

Raman spectra show (figure 6) a peak at 940 cm^{-1} for vanadium in tetrahedral silica framework[19] in solid core mesoporous silica shell and also show two peaks at 2800–3000 cm^{-1} region for C-H freqeuencies in as-synthesized sample.

Figure 7 shows the ^{29}Si Magic angle spinning nuclear magnetic resonance spectrum of vanadium containing solid core mesoporous silica shell, which contains four distinct lines at −107, −93 and −60 and −53 ppm in as-synthesized sample and on calcination the peaks at −60 and −53 ppm intensities are disappeared. Vanadium containing nanosilica did not give the last two peaks. Solid core mesoporous silica gave single peak at around −110 ppm. The four peaks present in as-synthesized vanadium containing solid core mesoporous silica shell samples are due to Si: 4Si, Si: 2V: 2Si and Si: 3C: Si and Si: 2C: Si species, respectively.[20]

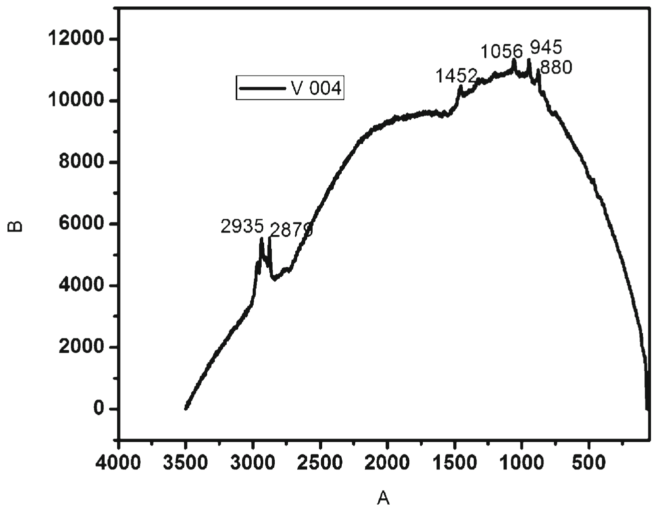

Figure 6. Raman spectra (A = wave number (cm^{-1}) and B = intensity (cps)) of as-synthesized vanadium containing solid core mesoporous silica shell (Si/V = 100) catalyst.

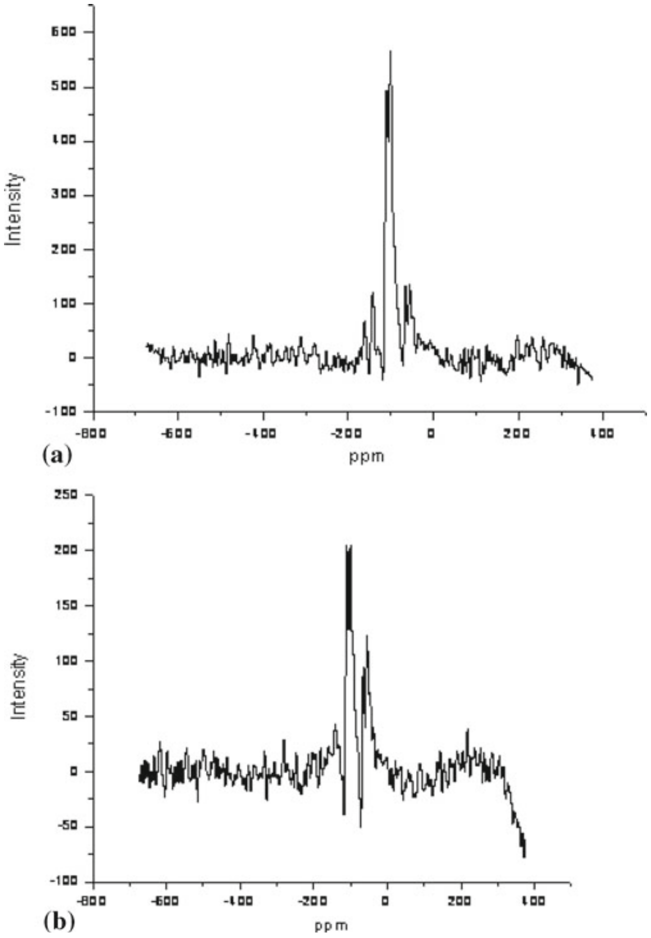

Figure 7. ^{29}Si Magic angle spinning nuclear magnetic resonance spectra of (**a**) as-synthesized and (**b**) calcined vanadium containing solid core mesoporous silica shell (Si/V = 100) catalyst.

The effect of vanadium content (table 2) on vanadium containing solid core mesoporous silica shell catalysts for diphenylmethane to benzophenone conversion and selectivity was carried out at optimized reaction conditions. The feed ratio of diphenylmethane to molecular oxygen from air was set at 1:4 (molar ratio) and that of WHSV as 4 h^{-1}. Typically, the diphenylmethane conversion was increased with decreasing Si/V ratios from 200 to 100. The conversion and selectivity increase with vanadium content. Vanadium containing nanosilica and pure solid core mesoporous silica shell gave least conversion.

The vapour phase oxidation of diphenylmethane using CO_2-free air as oxidant was carried out on fixed

Table 2. Diphenyl methane to benzophenone conversion with respect to vanadium content of vanadium containing solid core mesoporous shell silica.

Catalysts	Vanadium content (Wt.%)	Diphenyl methane conversion (%)	Benzophenone selectivity (%)
V-SMS (100)	3.1	53	90
V-SMS (125)	2.1	41	89
V-SMS (150)	2.0	33	87
V-SMS (200)	1.6	29	88
V-NS (100)	3.2	5	70
SMS	–	2	50

Conditions: Weight of the catalyst: 0.5 g; Temperature: 593 K; WHSV: 4 h^{-1}; Flow rate of DPM to air 1:4 (mol ratio); V-SMS = vanadium containing solid core mesoporous shell silica; V-NS = vanadium containing nanosilica; SMS = solid core mesoporous shell silica

bed down flow reactor operating at atmospheric pressure at different temperature ranging from 563 to 713 K over Si/V = 100 ratio vanadium containing solid core mesoporous silica shell catalyst for 2 h. The molar feed ratio of diphenylmethane to molecular oxygen (from air) was set as 1:4 with WHSV (weight hourly space velocity) of diphenylmethane as 4 h^{-1}. It could be seen from figure 8 that as the temperature increased from 563 to 713 K the conversion of diphenylmethane gradually increased and benzophenone selectivity was drastically reduced due to by-products. This observation was further verified by mass balance calculation. The optimum temperature for better conversion and selectivity was found to be 593 K.

The effect of time on the conversion and selectivity over Si/V = 100 catalyst was studied at 593 K, diphenylmethane to molecular oxygen (from air) molar ratio is 1:4 and WHSV of diphenylmethane is 4 h^{-1}. The observed results are illustrated in figure 9. The conversion and selectivity remain same without significant change. The results also demonstrate that there was no coke blocked the pores. The conversion and selectivity was almost similar with regenerated catalysts.

The influence of contact time on conversion and selectivity was studied at optimum conditions and 0.05 to 0.25 h^{-1}. The conversion is increased linearly with increasing the contact time from 0.05 to 0.25. The selectivity remains same even at lower contact time.

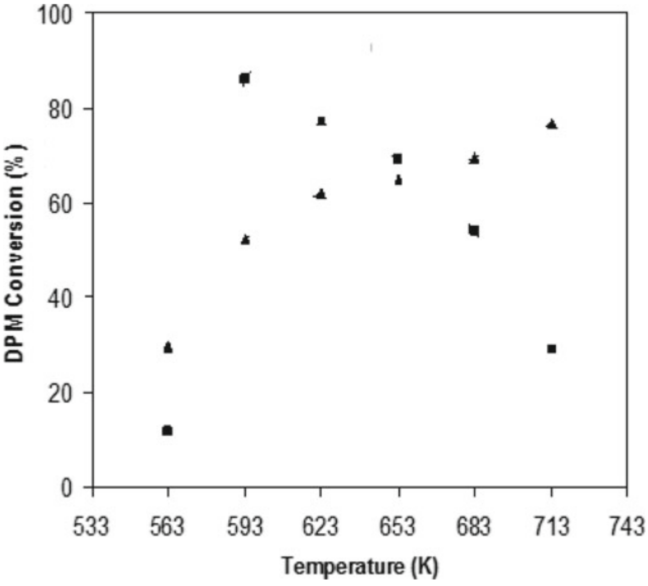

Figure 8. Effect of temperature on the conversion (▲) and selectivity (■) of diphenylmethane, reaction conditions: weight of the catalyst 0.5 g; WHSV; 4 h^{-1}; flow rate of DPM to air 1:4 (mol ratio); reaction time; 2 h. Catalyst: Vanadium containing solid core mesoporous silica shell (Si/V = 100) catalyst.

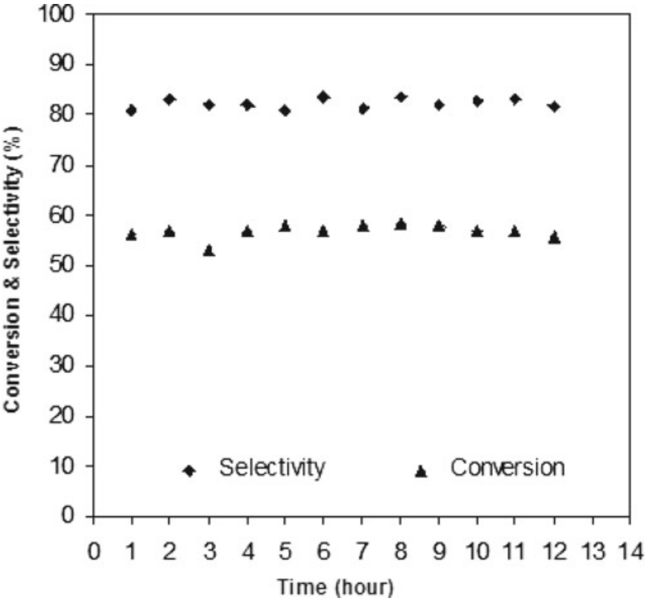

Figure 9. Effect of reaction time on diphenylmethane conversion and benzophenone selectivity, reaction conditions: weight of the catalyst: 0.5 g; temperature: 593 K; WHSV: 4 h^{-1}; flow rate of DPM to air 1:4 (mole ratio); catalyst: vanadium containing solid core mesoporous silica shell (Si/V = 100) catalyst.

4. Conclusions

A novel vanadium containing solid core mesoporous silica shell catalysts for diphenyl methane gas phase oxidation was synthesized and characterized. It is found to be nanocrystalline. The presence of mesoporosity along with microporosity was deducted from the catalyst. Vanadium is present as V^{4+} in as-synthesized from and V^{5+} in calcined form. Most of the vanadium is present in tetrahedral or square pyramidal species. Vanadium incorporation in silica framework is also conformed by ^{29}Si MAS NMR analysis. The activity profiles are clearly shown that the conversion increases with increasing vanadium content. The isolated tetrahedral vanadium species are found to be responsible for the catalytic activity. It is proposed that the diphenyl methane is oxidized by peroxide radical mechanism.

Acknowledgements

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