Structural and Catalytic Properties of a Novel Vanadium Containing Solid Core Mesoporous Shell Silica Catalysts for Gas Phase Oxidation Reaction

N. Venkatathri[*,1], K. Vijayamohanan Pillai[2], A. Rajini[1], M. Nooka Raju[1] and I.A.K. Reddy[1]

[1]*Department of Chemistry, National Institute of Technology, Warangal 506 004, Andhra Pradesh, India*

[2]*Physical and Materials Chemistry Division, National Chemical Laboratory, Pune 411 008, Maharastra, India*

Abstract: A novel Vanadium containing Solid core Mesoporous shell Silica catalyst was synthesized with different Si/V ratios by co-precipitation method under neutral conditions. The synthesized materials were characterized by various techniques and Gas phase Diphenyl methane oxidation reaction. The characterization reveals that a large amount of vanadium is mainly incorporated in isolated tetrahedral environment with terminal V=O bond. Among the various Vanadium containing solid core mesoporous shell silica catalysts, the Si/V=100 ratio exhibited maximum efficiency towards Diphenyl methane to Benzophenone gas phase reaction.

Keywords: Gas phase oxidation, vanadium containing solid core mesoporous shell silica, 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 $K_2Cr_2O_7$ [2, 3].

An alternative route for the production of Benzophenone is Friedel-Crafts acylation reaction of aromatics by acid halide/anhydride, using stoichiometric amounts of corrosive $AlCl_3$ catalysts. In the above two processes, a large amount of waste is produced, and the usage of stoichiometric amount of catalysts makes the process unacceptable. The current issue is to replace the homogeneous catalysts by heterogeneous catalysts e.g. by incorporation of transition metal ions or complexes into the framework or cavities of zeolites [4], AlPOs [5], and xero or aerogels etc. [6-9]. 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, new Solid core Mesoporous shell silica is recently synthesized with combined micro- and mesoporous material with uniform mesopores [10]. This remarkable interest stems from many desirable features of this mesoporous silica, including tailored pore size, high degree of structural ordering, larger pore size, thicker pore walls, ease of synthesis, and higher hydrothermal/ thermal stability in comparison to MCM-41, MCM-48, SBA-15 and HMS mesoporous materials. In addition to that the porogen employed to obtain this Solid core Mesoporous shell silica, Octadecyltrimethoxy silane is cheaper than the surfactants used initially in the synthesis of MCM-41 and SBA-15 [11-14].

In the recent past, Vanadium-substituted molecular sieves have been found to be excellent catalysts for many selective oxidation reactions [15-18]. The catalytic activity and selectivity of vanadium-substituted molecular sieves are directly related to the co-ordination structures of the vanadium species in the molecular sieves. Since, research had taken great effort to synthesis of vanadium containing mesoporous molecular sieves for bulkier molecule transformation. In this regard, attempts have been taken to synthesize vanadium containing mesoporous molecular sieves by adopting different methods. These methods include ion grafting [19], direct hydrothermal synthesis [20], impregnation [21], and molecular designed dispersion [22]. Despite its potential, there are no reports on the direct synthesis of Vanadium containing Solid core mesoporous shell silica.

For many oxidation reactions, it is always desirable to choose air as oxidant due to its availability in the nature and there by carrying out the reaction in gas phase, it is possible to avoid the leaching of metal from the framework with the solvent free condition [23]. Therefore, the gas-phase oxidation of organic compounds over heterogeneous catalysts is environmentally benign from the viewpoint of "green chemistry" [24, 25].

In the present investigation, synthesis of novel Vanadium containing Solid core Mesoporous shell silica by co-precipitation method is established and its application towards vapor phase oxidation of Diphenylmethane using CO_2 free air as oxidant. In order to achieve the better activity

*Address correspondence to this author at the Department of Chemistry, National Institute of Technology, Warangal 506 004, Andhra Pradesh, India; Tel: +91-9491319976; E-mail: venkatathrin@yahoo.co

and selectivity, effect of temperature, time on stream, and vanadium content were studied.

2. EXPERIMENTAL

The Vanadium containing Solid core mesoporous shell silica was synthesized by co-precipitation method using the following procedure. 74 ml of Acetone (99.5 %, s.d.fine, India) was mixed with 11 ml of Tetraethylortho silicate (98 %, Aldrich, USA). 3.3 ml of Triethylamine (98 %, s.d.fine, India) and 2 ml of Octadecyltrichlorosilane (98 %, Aldrich, USA) were mixed with the above gel. 0.102 g V_2O_5 (98 %, Aldrich, USA) was mixed well with the above mixture. Finally 10 ml distilled water was mixed and stirred well for 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 physico-chemical 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 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 and particle size and shape were analyzed 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 in 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 shell silica 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. X-ray Photoelectron spectroscopic analysis carried out using ESCA-3000 (VG Scientific, UK) instrument. Cyclic voltammetric analysis was carried out using Solaratron S1 1287 Electrochemica interface and Solaratron 1255B Frequency Response analyzer. Solid State Nuclear Magnetic Resonance spectrum is 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 (Scheme **1**). Prior to the reaction, the reactor was charged with 0.5 g of the catalyst and preheated 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 analyzed 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.
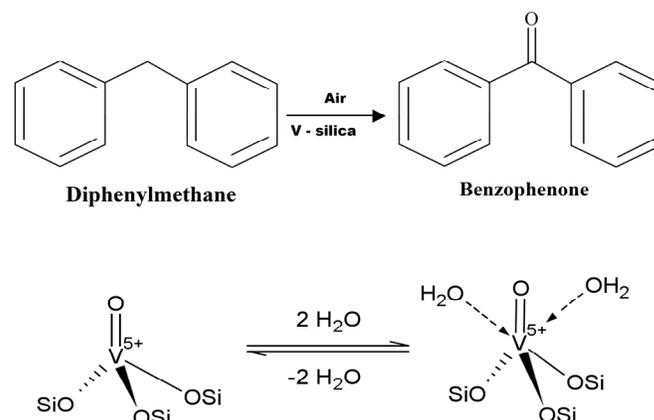
Scheme 1. Vapour phase oxidation of Diphenylmethane.

3. RESULTS AND DISCUSSION

Presence and absence of Octadecyltrichlorosilane and Triethylamine along with other ingredients give solid precipitate (Table **1**). However use of Methyltrimethoxysilane and Octyltrimethoxy silane instead of Octadecyltrichlorosilane did not give precipitate. The reason is probably due to the enhanced hydrolyzing rate in Octadecyltrichlorosilane. The small angle X-ray diffraction pattern (Fig. **1**) of the as-synthesized Vanadium containing Solid core mesoporous shell silica show that they are probably mesoporous. On calcinations the pattern does not change considerably, however a small line broadening is observed. Scanning electron micrograph of Vanadium containing Solid core mesoporous shell shows the morphology of pure solid core Mesoporous shell silica and Vanadium containing solid core mesoporous shell silica are spherical, however the particle size are 400 and 500 nm. The Transmission electron micrograph of the calcined samples shows 400 nm (shell size 45 nm) and 500 nm (shell size 50 nm) for Vanadium free and Vanadium containing solid core mesoporous silica shell samples (Fig. **2**). E-DAX analysis (Table **1**) of the as-synthesized samples shows the presence of larger extent of Octadecyltrichlorosilane and Triethylamine in surface of the Solid core Mesoporous shell silica. It is deduced that from the above analysis, the larger surface area of the calcined materials are due to the vacant sites created by the loss of these species. The presence of large extent of Octadecyltrichlorosilane is available not only in surface, but also in bulk is observed from the Thermogravimetry/Differential thermal analysis. It shows about 60 % exothermic weight loss on calination in presence of air from room temperature to 900 °C.

Typical nitrogen adsorption isotherms at 77 K (Fig. **3**) show a linear increase in the amount of adsorbed nitrogen at low pressures (P/Po = 0.5). The resulting isotherm can be classified as a type II isotherm with a type H2 hysteresis, according to the IUPAC nomenclature [26-29]. The steep increase in nitrogen uptake at relative pressures in the range between P/Po = 0.40 and 0.60 is reflected in a narrow pore size distribution. Thus, the variation of the catalyst in the

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 = 2h, Temperature = 298 K, Rotation = 650 rpm.TEA : Triethylamine, ODTCS : Octadecyltrichloro silane, Act : Acetone, R : Octadecyltrimethoxy silane, Methyltrimethoxy silane, Octyltrimethoxy silane.
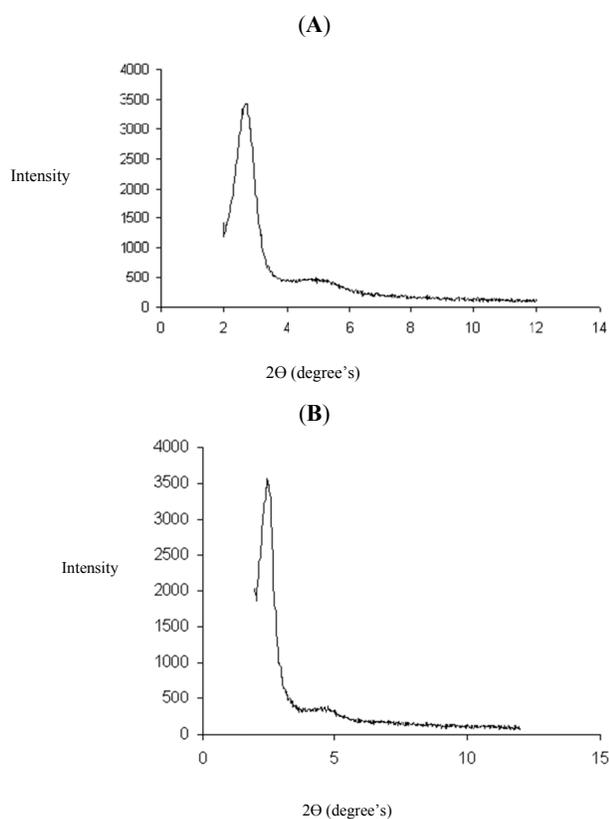
(A)

(B)

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

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, specific pore volume 1.29 cm^3/g, average pore diameter, 239 Å and medium pore width, 302 Å.

Fourier transform Infrared spectrum of the as-synthesized sample shows that peaks around 1700 and 3430 cm^{-1} corresponding to the carboxyl and hydroxyl groups [30] respectively. The adsorption peak belonging to the Si-O stretching vibration of Si-O⁻M⁺ bond appears at 960 cm^{-1} [31]. The weak peaks at 2855 and 2920 cm^{-1} belong to the stretching vibrations of C-H bonds, which show a few organic groups 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 [31].

Diffuse reflectance Ultra violet - visible spectra of as synthesized sample shows (Fig. **4**) peaks at 350, 280 & 220 nm. The peak at 220 nm is due to Si-O⁻ species and peak at 280 nm is due to tetrahedrally coordinated V^{5+} species and peak at 350 nm is due to blue shifted square pyramidal Vanadium species [32,33]. Calcined sample shows a single broad peak at 460 nm corresponds to V^{5+} in square pyramidal environments [34,35].

The electron spin resonance spectra (Fig. **5**) of the Vanadium containing as-synthesized sample shows a eight line hyperfine splitting with A_{ll} = 198, g_{ll} = 1.9293, $A_{\perp}$ = 78 and $g_{\perp}$ = 1.9814 parameters correspond to VO^{2+} in a distorted octahedral or square pyramidal environment [36-41]. On calcinations most of the vanadium is oxidized to V^{5+} ions and the eight-line hyperfine splitting intensity reduced to one
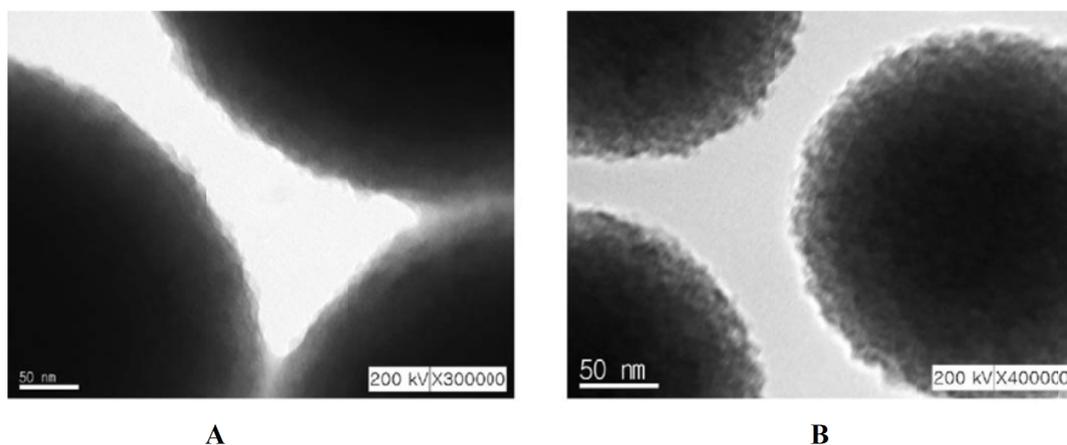

A

B

Fig. (2). Transmission electron micrograph of calcined (**A**) Solid core mesoporous shell silica and (**B**) Vanadium containing solid core mesoporous shell silica (Si/V = 100) catalyst.

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 behavior of the vanadium present in the samples.
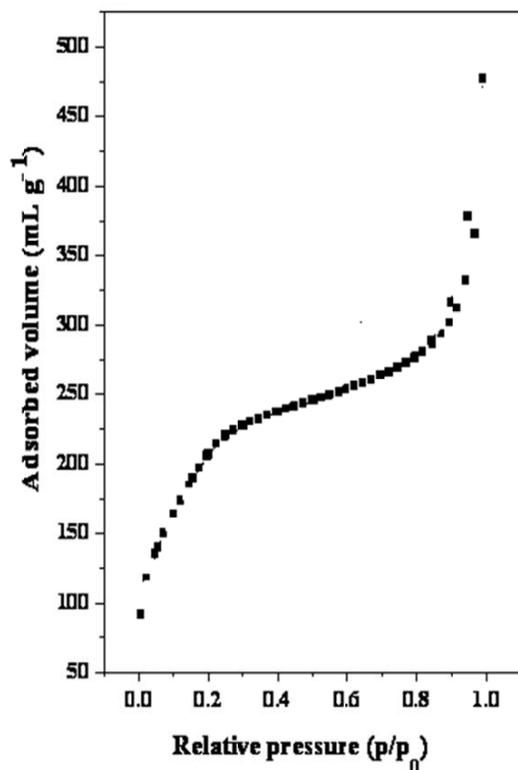

Fig. (3). N_2 adsorption - desorption isotherms of calcined Vanadium containing solid core mesoporous shell silica (Si/V = 100) catalyst.
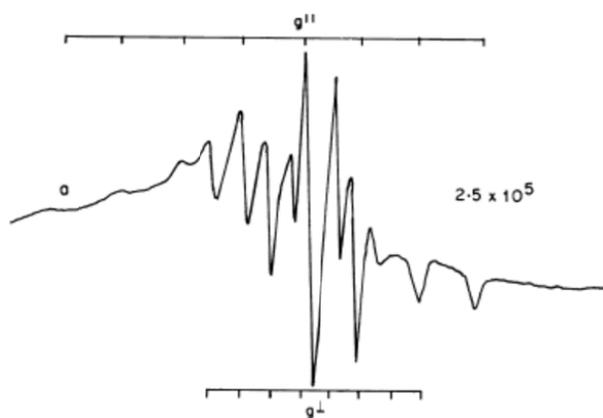

Fig. (4). Electron spin resonance spectrum of as-synthesized Vanadium containing solid core mesoporous shell silica (Si/V = 100) catalyst.

The X-ray Photoelectron spectra of as-synthesized sample in V_{2p} region (528-540 eV) are shown in Fig. **(6)** shows two peaks, one is corresponding to V^{4+} at 528 eV shows d other one corresponding to V^{5+} at 539 eV [42]. This

shows that as-synthesized sample contains both V^{4+} and V^{5+} species, among them V^{5+} content is more.
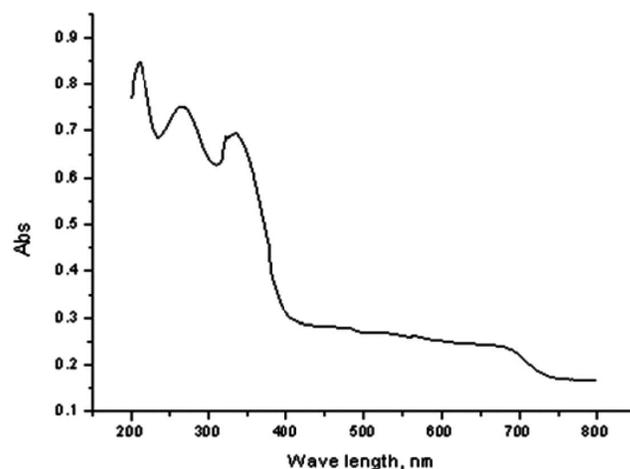

Fig. (5). Diffuse reflectance Ultraviolet - visible spectrum of as-synthesized Vanadium containing solid core mesoporous shell silica (Si/V = 100) catalyst.
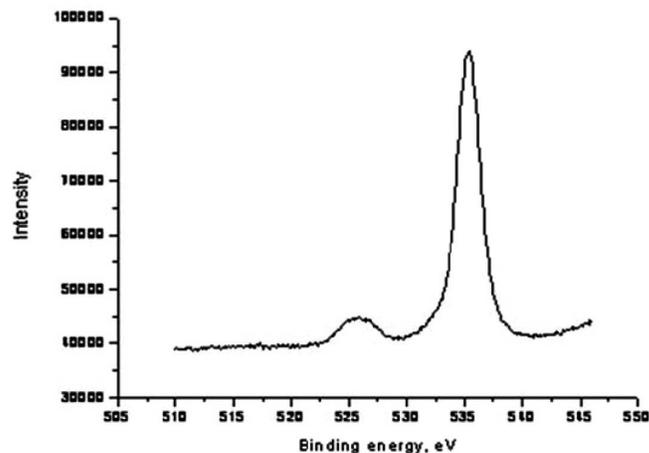

Fig. (6). X-ray photoelectron spectrum of as-synthesized Vanadium containing solid core mesoporous shell silica (Si/V = 100) catalyst.

Castro-Martins *et al*. [43,44] have used cyclic voltammetric techniques to prove the presence of Ti^{4+} ions in the frameworks of TS-1 and TS-2. Venkatathri and co-workers have extensively investigated VS-1. VS-2, VAPO-5 and V-Al-β [44,45]. The cyclic voltammetry of Vanadium containing solid core mesoporous shell silica shows one redox couple of peaks between +0.6 V to -0.2 V. It was suggested earlier that the redox couple were due to V^{5+}/V^{4+} redox couple originated from V^{5+} present in as-synthesized samples [45,46] with distorted tetrahedral symmetry.

Fig. (**7**) shows the ^{29}Si Magic angle spinning Nuclear magnetic resonance spectrum of Vanadium containing solid core mesoporous shell silica, which contains four distinct lines at -107, -93 and -60 & -53 ppm in as-synthesized sample and on calcination the peaks at - 60 and -53 ppm intensities are disappeared. The four peaks present in as-synthesized samples are due to Si: 4Si, Si: 2V: 2Si and Si: 3C: Si and Si: 2C: Si species [47-51].
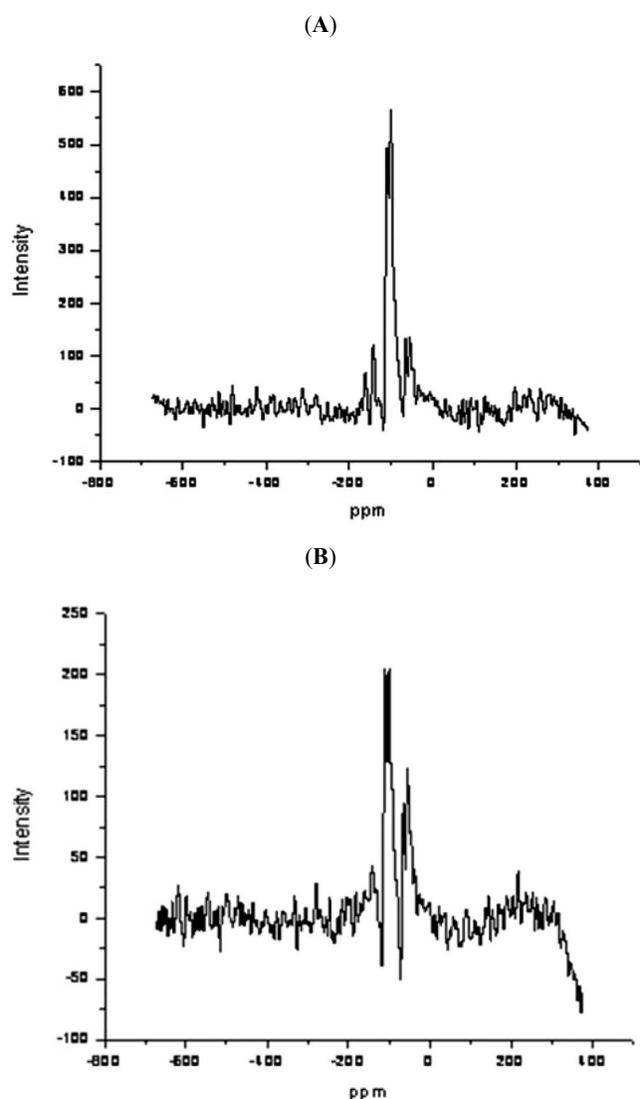
(A)

(B)

Fig. (7). ^{29}Si Magic angle spinning Nuclear Magnetic Resonance spectra of **A**) as-synthesized, **B**) calcined Vanadium containing solid core mesoporous shell silica (Si/V = 100) catalyst.

The effect of vanadium content on Vanadium containing solid core mesoporous shell silica 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 vapor phase oxidation of Diphenylmethane using CO$_2$ free air as oxidant was carried out on fixed bed down flow reactor operating at atmospheric pressure at different temperature ranging from 563 to 713K over Si/V= 100 ratio Vanadium containing solid core mesoporous shell silica catalyst for 2h. 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 Fig. (**8**) that as the temperature increased from 563 to 713K 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.
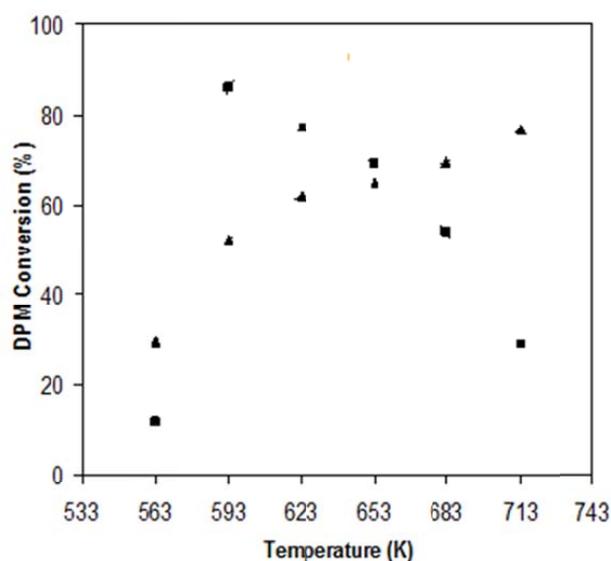

Fig. (8). Effect of temperature on the conversion (Δ) and selectivity (□) of diphenylmethane, Reaction conditions: Weight of the catalyst 0.5g; WHSV;4h^{-1}; Flow rate of DPM to Air 1:4 (mole ratio); Reaction time; 2h. Catalyst: Vanadium containing solid core mesoporous shell silica (Si/V = 100) catalyst.

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 Fig. (**9**). The conversion and selectivity are remains same without significant change. It also demonstrate that there was no coke blocked the pores. The conversion and selectivity was almost similar with regenerated catalysts.
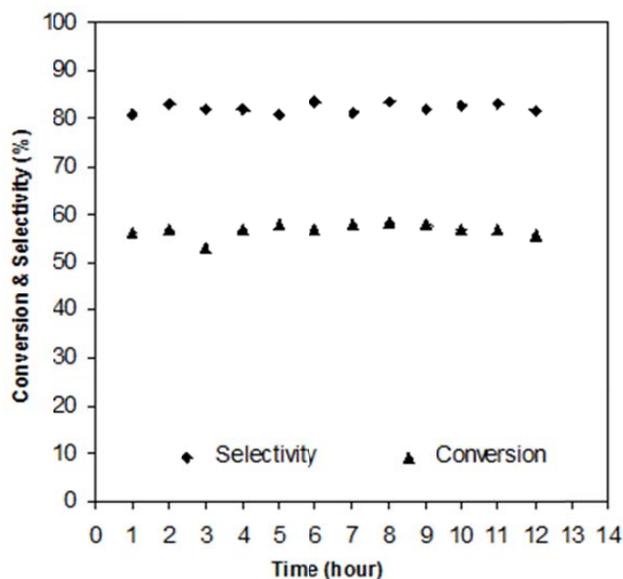

Fig. (9). Effect of reaction time on Diphenylmethane conversion and Benzophenone selectivity, Reaction conditions: Weight of the catalyst: 0.5g; Temperature: 593K; WHSV: 4h^{-1}; Flow rate of DPM to Air 1:4 (mole ratio); Catalyst: Vanadium containing solid core mesoporous shell silica (Si/V = 100) catalyst.

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.

CONCLUSIONS

In summary, novel Vanadium containing solid core mesoporous shell silica catalysts for Diphenyl methane gas phase oxidation were synthesized and characterized. The activity profiles are clearly shown that the conversion increases with increasing vanadium content. The isolated tetrahedral vanadium species (Scheme **1**) are found to be responsible for the catalytic activity. It is proposed that the Diphenyl methane is oxidized by peroxide radical mechanism. Such a species will be formed easily, only when the Vanadium is in tetrahedral co-ordination as given in the scheme.

ACKNOWLEDGEMENTS

CONFLICT OF INTEREST

Declared done.

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