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Highly selective synthesis of cyclododecanone over mesostructured VSBA-15 catalysts

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A R T I C L E I N F O

ABSTRACT

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Keywords: VSBA-15 pH-adjusting direct hydrothermal method Hydrothermal stability Catalytic stability Oxidation of CDD Highly ordered VSBA-15 mesoporous catalysts have been synthesized under pH-adjusting direct hydrothermal (pH-aDH) method using vanadyl sulphate hydrate and Pluronic P123 as the sources of vanadium and template, respectively. The mesoporous catalysts characterized by sophisticated instrumental techniques, viz. ICP-AES, XRD, N₂ adsorption, ESR, UV–vis DRS, ⁵¹V MAS NMR, ²⁹Si MAS NMR and TEM show their two-dimensional mesostructures with tetrahedral vanadium species on the silica surface. The well ordered VSBA-15 catalysts have been used in the oxidation of cyclododecane (CDD) with hydrogen peroxide (H₂O₂, 30%) to find their catalytic activities. The regenerated VSBA-15 catalysts have been examined to find their catalytic stabilities. VSBA-15(5) catalyst has been washed with ammonium acetate solution to investigate the leaching of vanadium species in the framework of silica network of SBA-15, and the catalytic activity of washed VSBA-15(5) has also been examined in the catalytic reactions. Moreover, the hydrothermally stable VSBA-15(5) catalyst has also been examined in the catalytic reaction to find the effect of its catalytic activity. Additionally, the influences of various reaction parameters such as temperature, time, ratios of reactant and solvents on the oxidation of CDD have been investigated. Based on the catalytic results, VSBA-15(5) catalyst is found to be a highly active, recyclable and promising heterogeneous catalyst for selective synthesis of cyclododecanone (CDD=O).

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1. Introduction

Vanadium-containing microporous catalysts synthesized using different hydrothermal conditions were used in several oxidation reactions to produce a variety of selective products [1], however, their catalytic activities strongly depend on the syntheses methods [2,3]. The microporous catalysts restrict the accessibility of large substrate molecules due to their smaller pore sizes. The described limitations have been overcome by the discovery of mesoporous M41s materials in 1992 [4]. Since Beck and co-workers reported the mesoporous MCM-41 synthesized using direct hydrothermal method [4], extensive research efforts have focused in the catalytic applications of heteroatoms containing mesoporous silicas [5–8]. Highly ordered mesoporous VMCM-41 materials were successfully synthesized and used in the oxidation of aromatics [6-14], and they gave good catalytic activities with good selective products. In 1998, Zhao et al. reported a new family of mesoporous SBA-15 synthesized under acidic hydrothermal condition [15]. Particularly, all the mesoporous materials (MCM-41 and SBA-15) have received much attention from researchers in the past decade because of their potential applications such as catalysts, adsorbents and guest-host chemical supports for large organic molecules [5-8,16-18]. However, SBA-15 has better hydrothermal stability than MCM-41 due to thicker pore walls [4,15], and it has also larger pore size than MCM-41. But, the pure SBA-15 material is unable to be used directly as a catalyst due to the lack of acidities. Hence, it has reported that the guest species like heteroatoms or organic moieties can be introduced into the framework of SBA-15 to increase the active sites and thus improve the catalytic activity [16,17]. Therefore, it is of great importance to introduce heteroatoms into mesoporous silica materials prepared under strongly acidic conditions. Several research reports are available, as the heteroatoms (M = Al, Fe, V, Ti and Ga) were incorporated in the framework of SBA-15 by direct synthesis or post-synthetic grafting method, for creating the active sites on the silica surface, and the synthesized materials were tested for their catalytic activities for a certain reaction [19–24]. As mentioned in a previous report [25], it is difficult to incorporate the high amounts of heteroatoms into the mesoporous silica walls under the highly acidic conditions, and the introduced metals exist in the cationic form rather than as their corresponding oxo species. Most heteroatoms introduced by post-synthesis procedure may be located with octahedral coordination in the resultant materials [21,24,26]. On the basis of such a serious limitation, the mesoporous MSBA-15 (M=metal species) materials synthesized by different hydrothermal conditions were reported [19,22,23,25]. It was also found that the MSBA-15 mesoporous materials have

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highly active sites on the silica pore walls from the observation of their characterization results. The MSBA-15 materials were widely used as the catalysts in the several catalytic applications [19–24]. Particularly, Selvaraj and his research group successfully reported the mesoporous MSBA-15 materials (M = Cr, Mn, Sn, Ti, Ga, Al and Nb) synthesized using pH-adjusting direct hydrothermal (pH-aDH) method [27–35]. From these characteristic results, one can conclude that MSBA-15 catalysts have higher hydrothermal stabilities than MMCM-41 catalysts. The MSBA-15 catalysts were used in different catalytic reactions to produce the selective fine chemicals [28,30–32,34,35].

In 2004, Hess et al. reported the highly dispersed vanadia on SBA-15 synthesized using organic moiety functionalized vanadium precursor [36]. Recently, Gao et al. reported the VSBA-15 synthesized using ammonium metavanadate as a vanadium source under different pH values [37]. Du et al. reported the VSBA-15 prepared using oxovanadium (V) chloride as a vanadium precursor using atomic layer deposition method [38], and the synthesized VSBA-15 were used in the oxidation of methanol to produce formaldehyde with a good selectivity. Jurado et al. reported the selective epoxidation of alkenes using highly active VSBA-15 catalysts, which were synthesized using vanadium oxytriisopropoxide and ammonium metavanadate as the sources of vanadium [39]. However, to the best of our knowledge, the highly ordered two-dimensional VSBA-15 catalysts synthesized by pH-adjusting direct hydrothermal (pH-aDH) method using vanadyl sulphate hydrate as a vanadium precursor have not been clearly reported with enhanced hydrothermal stabilities and catalytic activities, in the open literature, and the removal of V₂O₅ crystallites on the surface of catalysts is not openly reported.

Herein we report the two-dimensional mesoporous VSBA-15 catalysts synthesized by pH-aDH method. To investigate the mesoporous nature with the environments of vanadium species on the silica network of pore walls, the synthesized VSBA-15 catalysts have been characterized by ICP-AES, XRD, N₂ adsorption, ESR, UV-vis DRS, ⁵¹V MAS NMR, ²⁹Si MAS NMR and TEM. Moreover, the catalytic activities of VSBA-15 catalysts have been also investigated after chemical and hydrothermal treatments. The calcined VSBA-15 catalysts have been used for the synthesis of cyclododecane (CDD=O) by the liquid-phase oxidation of cyclododecane (CDD) with H₂O₂ under different optimal conditions.

2. Experimental

2.1. Chemicals

Triblock copolymer poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) (Pluronic P123, molecular weight = 5800, $EO_{20}PO_{70}EO_{20}$), tetraethylorthosilicate (TEOS), hydrochloric acid (HCl), vanadyl sulphate hydrate (99.999%) were all purchased from Aldrich Chemical Inc. All chemicals were used as received without further purification. Millipore water was used in all experiments. For the oxidation of cyclododecane (CDD), CDD, hydrogen peroxide (30% H_2O_2), acetonitrile (MeCN), diethyl ether and acetone, were all purchased from Aldrich Chemical Inc.

2.2. Synthesis

Mesoporous VSBA-15 catalysts with $n_{Si}/n_V = 5$, 10, 15, 20, 25 and 50 in gel, were synthesized using the pH-adjusting direct hydrothermal (pH-aDH) method. In a typical synthesis of VSBA-15, 4 g of Pluronic P123 was stirred with 25 ml of water for 4 h to get a clear solution. In order to adjust the pH of this solution above 1.8, we added an aqueous HCl solution with n_{H_2O}/n_{HCl} ratio of 295 (75 ml of 0.25 M HCl solution) to the solution, and the mixture solution was again stirred for another 1 h. Then, 9 g of TEOS together with the required amount of vanadyl sulphate solution ($n_{Si}/n_V = 5$, 10, 15, 20, 25 and 50) were added to the solution mixture, yielding a gellike solution with pH > 2. The resulting mixture was again stirred for 24 h at 313 K before it was transferred into an autoclave to be hydrothermally treated at 373 K for 24 h. After the hydrothermal process, the solid products were recovered by filtration, washed several times by water, and dried overnight at 373 K. The molar composition of the gel was 1 TEOS/0.2–0.02 VOSO₄·xH₂O/0.016 P123/0.43 HCl/127 H₂O. Finally, the samples were calcined at 813 K in air for 6 h for complete removal of the template. The calcined samples are denoted as VSBA-15(5), VSBA-15(10), VSBA-15(15), VSBA-15(20), VSBA-15(25) and VSBA-15(50).

For comparison studies, the calcined SiSBA-15 was synthesized according to the published procedure [27], and VMCM- $41(n_{Si}/n_V = 40)$ was also synthesized using a basic direct hydrothermal method [40]. The calcined VMCM-41 catalyst is denoted as VMCM-41(40). The synthesized samples were characterized according to our previous published procedure [27,40].

2.3. Preparation of hydrated VSBA-15

The hydrated VSBA-15 materials were obtained after the calcined samples were exposed to moisture for 2 days under ambient conditions.

2.4. Evaluation of hydrothermal stability

The hydrothermal stabilities of V-containing mesoporous silica catalysts viz. VSBA-15(5) and VSBA-15(50) were investigated using boiling water (373 K) at autogenous pressure for 168 h.

2.5. Characterization

The elemental composition of the resultant solid catalysts was analysed by ICP-AES (Perkin Elmer, Optima 3000) after the samples were dissolved in a HF solution. The small-angle XRD patterns were recorded under ambient conditions on a Shimadzu XRD-6000 with Cu K α radiation (λ = 1.5406 Å). The X-ray tube was operated at 40 kV and 30 mA, while the diffractograms were recorded in the 2θ range of 0.6–10° with a 2θ step size of 0.01 and a step time of 10 s. The *d*-spacing and unit cell parameters were calculated using the corresponding formulas, $n\lambda = 2d \sin \theta$ and $a_0 = 2d_{100}/\sqrt{3}$. Nitrogen adsorption/desorption measurements were conducted using a Quantachrome Autosorb-1 by N₂ physisorption at 77 K. All calcined catalysts were outgassed for 3 h at 250 °C under vacuum $(p < 10^{-5} \text{ mbar})$ in the degas port of the sorption analyzer. The specific surface areas of the catalytic samples were calculated using the BET method. The pore size distributions were calculated from the adsorption branch of the isotherm using the thermodynamicsbased Barrett-Joyner-Halenda (BJH) method. The pore volume was determined from the adsorption branch of the N₂ isotherm. The pore wall thickness (t_w) was also calculated by unit cell parameter (a_0) and pore diameter (d_p) . ESR spectra of the as-synthesized and calcined catalytic samples were recorded at the X-band at 293 K on a Bruker ESP 300 spectrometer. The magnetic field was calibrated with a Varian E-500 gaussmeter and the microwave frequency was measured by a HP 5342A frequency counter. ⁵¹V and ²⁹Si NMR spectra were recorded at 11.75 T on a Varian INOVA 500 NMR spectrometer with a CPIMS probe. ²⁹Si MAS spectra were measured at 99.3 MHz using a SiN rotor at 3 kHz. ⁵¹V NMR spectra were acquired at 131.275 MHz with 5.0 μ s recycle delays using SiN rotors 5 mm in diameter with spinning at 3 kHz. The chemical shifts were estimated in ppm using tetramethylsilane (TMS) and VOCl₃ as reference chemicals for ²⁹Si and ⁵¹V, respectively. All spectra were recorded at room temperature. UV-vis spectra were measured using a Perkin-Elmer 330 spectrophotometer equipped with a 60 mm Hitachi integrating sphere accessory. Powder samples were loaded in a quartz cell with Suprasil windows, and spectra were collected in the 250–800 nm wavelength range against a quartz standard. Transmission electron microscopy (TEM) images were collected on a JEOL 2010 electron microscope operated at an acceleration voltage of 200 kV.

2.6. Catalytic studies

Liquid-phase oxidation of CDD was performed in a 100 ml Parr autoclave reactor at various reaction conditions. In a typical experimental procedure, 1 g of CDD, 15 ml of MeCN, 2 mole ratio of H_2O_2 -to-CDD and 50 mg of VSBA-15(5) were taken for this catalytic reaction, which was performed at 373 K for 24 h. After completion of the reaction, the VSBA-15(5) catalyst was separated, and the products were extracted with diethyl ether and analysed by gas chromatography (GC, Nucon 5700) with a carbowax column using reference samples. Additionally, the products were further confirmed by GC–MS (Hewlett Packard G1800A) equipped with a HP-5 capillary column. This catalytic reaction was also performed with catalysts containing different V concentration. To find an optimal condition in the presence of VSBA-15(5), we repeated the oxidation of CDD with different reaction parameters such as time, temperature, mole ratios of reactants (CDD-to-H₂O₂).

2.7. Experimental procedures for stability of catalyst

The regenerated vanadium-containing mesoporous catalysts viz. VSBA-15(5), VSBA-15(50) and VMCM-41(40) were prepared in the following procedure, and they were reused in the oxidation of CDD to determine their stabilities. In a typical experimental procedure, the VSBA-15(5) catalyst used in a catalytic run was separated from the reaction mixture, washed with acetone several time, and dried at 393 K. Finally, the VSBA-15(5) catalyst was calcined at 773 K for 6 h in air to remove the adsorbed species, and the regenerated VSBA-15(5) catalyst was reused again in further catalytic runs. A similar procedure was used for recycling studies of other catalysts like VSBA-15(50) and VMCM-41(40). After completion of the reaction, the catalyst was filtered and analyzed by ICP-AES to find the percentage of V. The conversion of CDD and the selectivity of the products were calculated using the standard formulas, followed by analyzing results of GC and GC-MS.

In another experiment for finding the catalytic stability of VSBA-15(5), the original catalyst was treated with ammonium acetate solution in order to remove the extra-framework vanadium species. In a typical procedure, about 0.3 g of the calcined VSBA-15(5) catalyst was washed with 1 M ammonium acetate (90 ml) solution under constant stirring for 12 h at ambient temperature. Finally, the VSBA-15(5) catalyst was filtered and calcined at 773 K for 6 h in air to remove the adsorbed species. The treated catalyst is denoted as washed VSBA-15(5) catalyst (W-VSBA-15). The washed catalyst was analyzed by ICP-AES to find the percentage of V, and it was used in the catalytic studies of CDD oxidation. Subsequently the filtrate solution obtained from the treatment of the washing experiment was also used for the oxidation of CDD under similar reaction condition.

The hydrothermally stable VSBA-15(5) catalyst was also used in the catalytic oxidation of CDD.

3. Results and discussion

The mesoporous VSBA-15 materials are synthesized by an impregnation method/organic moiety functionalized method [41–48]. Even though the syntheses methods are good for the preparation of VSBA-15 materials, as already reported [25,36], high

amounts of polymeric vanadium oxide formation (non-framework V_2O_5 crystallites species) are observed with octahedral coordination in the resultant materials, and the uniform pore structures of VSBA-15 materials are sometimes destroyed. The VSBA-15 catalysts synthesized by an impregnation method, however, give good catalytic activities [41–48], but a major decrease of catalytic activities may be observed in the recycle studies due to the leaching of high amounts of non-framework V_2O_5 crystallites species. We thus propose the pH-adjusting direct hydrothermal method to prepare VSBA-15 materials.

Generally, the mesoporous VSBA-15 catalysts synthesized under highly acidic conditions (pH < 1) have low amounts of vanadium on their silica surfaces (Eqs. (1) and (2)) because the V-O-Si bonds are easily dissociated due to increasing hydrolysis rate of vanadyl sulphate hydrate, as the vanadium precursor, with TEOS, as the silicon precursor. However, lowering the acidity of the solution may decrease the hydrolysis rate of the vanadium precursor to match that of the silicon precursor. This might enhance the interaction between the V-OH and Si-OH species in the synthesis gel. However, one more reason may be that the divalent sulphate ion from vanadyl sulphate hydrate creates HSO₄⁻-ions in the synthesis medium. The HSO₄⁻-ions bind weakly with the surfactant. We tried to incorporate high amounts of vanadium on the silica network of SBA-15, as the pH of the synthesis gel was adjusted by a molar ratio of $n_{\rm H_2O}/n_{\rm HCl} = 295$ to reach around 2.2, which is above the zero net charge of silica. Since the pH of the synthesis medium rises above the zero net charge of silica, the negative charge of the silica species automatically forms in the synthesis gel, which might enhance the tendency to interact with the [O=V-OH]⁺ species (Eqs. (3)-(5)). With decreasing H⁺ concentration in the synthesis gel, the concentration of vanadyl hydroxyl species increases (Eqs. (3)-(5)). Hence, under lesser concentration of H⁺ in the synthesis gel at pH around 2.2, not only the partially condensed silica species are able to form V-O-Si bond with [O=V-OH]⁺ species but also the structural and textural order of the mesoporous framework are still maintained. Based on the results, it is remarkably observed that the high amounts of vanadium incorporated into SBA-15 depend upon the concentration of H⁺ ions. The following mechanism is clearly explained for the high amounts of vanadium loaded on the silica surface.

$$\equiv Si-OCH_2CH_3(aq) + H_2O_{(aq)} \xrightarrow{(pH < 2)} \equiv Si-OH_{(aq)} + HOCH_2CH_3(aq)$$
(1)

$$VOSO_{4(aq)} + 2H^{+}_{(aq)} \stackrel{(pH<2)}{\approx} VO^{2+}_{(aq)} + H_2SO_{4(aq)}$$
(2)

$$VO^{2+} + H_2O \xrightarrow{(pH>2)} [HO-V=0]^+ + H^+$$
(3)

$$\equiv \text{Si-OH} + \text{H}_2\text{O} \xrightarrow{(\text{pH}>2)} \equiv \text{Si-O}^- + \text{H}_3\text{O}^+$$
(4)

$$[HO-V=0]^{+} + \equiv Si - O^{-(PH>2)}O = V - O - Si \equiv (-OH)$$
(5)

To prove that the mesoporous structure of the materials was retained after vanadium incorporation, we characterized the calcined VSBA-15 catalysts synthesized using pH-aDH method by ICP-AES, XRD, N₂ adsorption, ESR, UV-vis DRS, ⁵¹V MAS NMR, ²⁹Si MAS NMR and TEM.

3.1. ICP-AES

The calcined VSBA-15 catalysts synthesized with different $n_{\rm Si}/n_{\rm V}$ ratios have been characterized by ICP-AES for the analysis of elemental compositions, and the characteristic results are listed in Table 1. In all cases, the $n_{\rm Si}/n_{\rm V}$ ratios of the calcined catalysts are higher than $n_{\rm Si}/n_{\rm V}$ ratios in the synthesis gel because the vanadium precursors are highly dissociated under acidic conditions. In this

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Physicochemical properties of VSBA-15 catalysts synthesized using different conditions.

Catalysts	$n_{\rm H_2O}/n_{\rm HCl}$	n _{Si} /n _V ratio		<i>a</i> ₀ (Å)	$A_{\rm BET} (m^2/g)$	$d_{\rm p}$ (Å)	$V_{\rm p}~({\rm cm^3/g})$	$t_{\rm w} = a_0 - d_{\rm p}$ (Å)
		Gel	Calcined ^a					
VSBA-15(5)	295	5	14.8	122.9	709	83.4	1.03	39.5
VSBA-15(10)	295	10	18.2	122.6	742	83.6	1.08	39.0
VSBA-15(15)	295	15	31.5	122.2	773	84.1	1.09	38.1
VSBA-15(20)	295	20	42.3	121.3	820	84.7	1.10	36.6
VSBA-15(25)	295	25	53.4	119.7	863	85.1	1.11	34.6
VSBA-15(50)	295	50	87.5	118.8	890	86.3	1.17	32.5
SiSBA-15	40	-	-	118.2	908	87.4	1.07	30.8
VMCM-41(40)	-	40	42.2	45.4	869	27.7	0.72	17.7
W-VSBA-15(5) ^b	-	-	19.5	122.4	710	83.8	1.07	38.6

 a_0 , unit cell parameter; A_{BET} , specific surface area; d_p , pore diameter; V_p , pore volume; pore wall thickness (t_w) = unit cell parameter (a_0) – pore diameter (d_p). ^a The results of n_{S}/n_V ratios in the products are determined by ICP-AES.

^b Washed catalyst.

synthesis method, the $n_{\rm Si}/n_{\rm V}$ ratio decreases from 87.5 to 14.8 due to the higher amount of vanadium incorporated on the pore walls of SBA-15 by the formation of more vanadyl hydroxyl groups because of adjusting the pH values from 1.6 to >2.

3.2. XRD

The as-synthesized VSBA-15 catalysts prepared using different $n_{\rm Si}/n_{\rm V}$ ratios show poorer quality of XRD peaks than SiSBA-15 (not shown). After removal of the polymeric surfactant by calcination process, the XRD patterns of VSBA-15 catalysts become better resolved, as shown in Fig. 1. This may be due to some atomic rearrangement occurring inside the mesoporous catalysts during the calcination. The XRD patterns of all VSBA-15 catalysts exhibit four well-resolved peaks that are indexed to the (100), (110), (200), and (210) reflections of the hexagonal space group p6mm. Due to the higher V species incorporated into SBA-15, the XRD peaks shift to lower angles, and VSBA-15(5) has lesser intensity of (210) peak in the XRD pattern than other VSBA-15 catalysts. Based on this observation, it is interesting to note that VSBA-15(5) has higher thicker hexagonal walls than other VSBA-15, as reported in the literature [49]. Since the XRD peaks shift to lower angle by increasing vanadium-content, an increase of unit cell parameters is observed as compared to those of the purely siliceous SBA-15, as shown in Table 1. This is because the V-O bond length is higher than the Si-O bond length due to the larger ionic radius of V (49.5 pm) than Si (40 pm).



The N₂ adsorption-desorption isotherms of calcined VSBA-15 catalysts synthesized with n_{Si}/n_V ratios are shown in Fig. 2. All isotherms are replicated as IV type isotherms according to the IUPAC classification and all exhibited a H1-type broad hysteresis loop, which is typical of large-pore mesoporous solids [50]. As the relative pressure increases $(p/p_0 > 0.6)$, all isotherms exhibit a sharp step characteristic of capillary condensation of nitrogen within uniform mesopores, where the p/p_0 position of the inflection point is correlated to the diameter of the mesopore. Since SBA-15 has a hexagonal arrangement of mesopores connected by smaller micropores [51,52], the broad hysteresis loop observed in the isotherms of VSBA-15 samples reflects the long mesopores, which limit the emptying and filling of the accessible volume. The textural properties of VSBA-15 catalysts are given in Table 1. With the decrease of $n_{\rm Si}/n_{\rm V}$ ratio up to 14.8, textural properties such as specific surface area, pore diameter and pore volume of VSBA-15 catalysts systematically decrease; as a result, the pore wall thickness increases with the increase of vanadium content in the catalysts (Table 1). This evidence strongly supports the conclusion that the high amounts of vanadium are incorporated on the pore walls of SBA-15. Furthermore, the structural and textural properties of W-VSBA-15(5) are still maintained, as shown in Figs. 1 and 2, such characteristic results are also shown in Table 1.



Fig. 1. XRD powder patterns of calcined VSBA-15 catalysts.



Fig. 2. Nitrogen adsorption isotherms of VSBA-15 catalysts.

3.4. ESR

ESR spectra of as-synthesized VSBA-15 catalysts (Fig. 3) exhibit an axially symmetrical signal of tetravalent vanadium, which originates from the d^1 electron interaction with nuclear spin (⁵¹V, $I_{\rm n}$ = 7/2, natural abundance 99.8%). The ESR intensity of VO²⁺ in the SBA-15 samples increases with the decrease of $n_{\rm Si}/n_{\rm V}$, as a result, the line width systematically increases with increasing the amount of VO²⁺ species. The spectra are characterized by an axially symmetric set of eight lines originating from vanadyl VO²⁺ species coupled to its own nuclear spin. The spin Hamiltonian parameters A tensor and g tensor are g_{\parallel} = 1.945, A_{\parallel} = 191 G and g_{\perp} = 1.981, A_{\perp} = 65 G, where A is the hyperfine coupling constant. The g values and hyperfine coupling constants are typical of vanadyl VO²⁺ species with square pyramidal coordination [10,53]; the similar reports are observed in several mesoporous molecular sieves [53]. Moreover, the well-resolved ESR spectra show that the vanadyl VO²⁺ species assigned in square pyramidal coordination is only observed for the as-synthesized VSBA-15 samples.

ESR peaks of calcined VSBA-15 catalysts completely disappear due to the absence of an unpaired electron on the $3d_{xy}$ orbital of the vanadium, as shown in Fig. 3. These results indicate that the VO²⁺ species become into V⁵⁺ species after calcinations, because no signal attributable to the V⁴⁺ species could be detected in the calcined VSBA-15 sample. From the ESR results, one can observe that the VO²⁺ species assigned in square pyramidal coordination for as-synthesized VSBA-15 catalysts and the V⁵⁺ species in calcined catalysts are incorporated on the silica surface of SBA-15. The ESR results reveal that the "efficiency" of V species being incorporated into silica pore walls increases with decreasing the n_{Si}/n_V ratios from 87.5 to 14.8. These results are in good agreement with the literature [53], where V species are reportedly present, as the V⁵⁺ species in calcined VSBA-15 catalysts is exclusively incorpo-





Fig. 3. ESR spectra of VSBA-15 catalysts.



Fig. 4. ⁵¹V MAS NMR spectra of VSBA-15 catalysts.

rated on the surface of silica pore walls. However, from the ESR results, we could not find whether the V⁵⁺ species only is incorporated in the framework of SBA-15 or the non-framework V₂O₅ crystallites species are dispersed on the surface of VSBA-15 where the high amounts of V species are loaded. Moreover, no information is observed regarding the environmental nature of V⁵⁺ species from the ESR results obtained at 293 K. Thus, the calcined VSBA-15 catalysts have been further characterized by ⁵¹V MAS NMR, ²⁹Si MAS NMR and UV–vis DRS.

3.5. NMR

⁵¹V NMR spectra for calcined VSBA-15 catalysts give useful information to differentiate between the various local coordination environments of V species. The as-synthesized VSBA-15 does not give any NMR active signal, which could be due to the absence of any diamagnetic V species. The ⁵¹V NMR spectra of the calcined VSBA-15 catalysts exhibit a signal around -535 ppm as shown in Fig. 4. The intensities of the spectra increases with the increase of V species incorporated in the framework of silica when the $n_{\rm Si}/n_{\rm V}$ ratios are decreased. For instance, the calcined VSBA-15(5) has a higher intensity than that of calcined VSBA-15(50). The NMR peak around -535 ppm (relative to VOCl₃) is a strong indication of tetrahedral V⁵⁺ species incorporated on the silica surface [54]. However, in the similar spectrum, an addition of a weak peak around -300 ppm shows that small amounts of non-framework V₂O₅ crystallites species are assigned on the silica surface with higher coordination [55]. From the ⁵¹V MAS NMR characteristic results, it is clear that the non-framework V₂O₅ crystallites species are accessible to water molecules. To prove this statement, we have further characterized the W-VSBA-15(5) by ⁵¹V MAS NMR spectroscopy. The ⁵¹V MAS NMR spectrum of W-VSBA-15(5) shows a strong peak around -535 ppm only, which can be assigned to the tetrahedral V⁵⁺ species incorporated into silica surface, as shown in Fig. 4. A weak shoulder around -300 ppm in W-VSBA-15(5) completely disappeared during the washing process, as shown in Fig. 4. This evidence strongly supports the suggestion that a small amount of non-framework V₂O₅ crystallites species are dispersed on the surface of pore walls in rich vanadium-containing SBA-15. It is also observed that the non-framework V₂O₅ crystallites species are completely removed by the washing process (Fig. 4); such a result confirms that the non-framework V₂O₅ crystallites species



Fig. 5. ²⁹Si MAS NMR spectra of SiSBA-15 and VSBA-15(10).

dispersed on the VSBA-15 interact with water molecule easily to become five or six coordination [55]. Furthermore, the results of ²⁹SiMAS NMR spectra show that the intensity of Q₃ peak in VSBA-15(10) is much lesser than that of siliceous SBA-15, as shown in Fig. 5; this observation clearly supports the stabilization of vanadium species via silanol groups (defect sites). However, we were not able to observe from the results of ⁵¹V MAS NMR spectra whether the regular tetrahedral V⁵⁺ species or disordered tetrahedral V⁵⁺ species (central V⁵⁺ with V=O double bond and V–O single bonds) were incorporated in the framework of silica walls. Thus, the fresh calcined and hydrated VSBA-15 catalysts have been further characterized by UV–vis DRS.

3.6. UV-vis DRS

UV-vis DRS spectra of freshly calcined, and hydrated VSBA-15 show the nature and the coordination of V species incorporated into the mesoporous silica (Fig. 6). The strong UV-vis absorption spectra of freshly calcined VSBA-15 appear between 270 and 285 nm (Fig. 6). With the decrease of $n_{\rm Si}/n_{\rm V}$ ratios from 50 to 5, the λ values (wavelength) of absorption peaks shift from 270 to 285 nm, and their intensities increase with the increase of V species incorporation. The absorption band is assigned to the low-energy charge transfer (CT) transition between tetrahedral oxygen ligands (O^{2-}) and central V⁵⁺ species [10-13,56], and the CT band serves as a good indicator for the tetrahedral V5+ species incorporated in the framework of silica walls. However, we were not able to clearly identify whether the regular tetrahedral V⁵⁺ or the disordered tetrahedral V⁵⁺ species are incorporated into the silica pore walls. Then, the hydrated VSBA-15 was analysed using UV-vis DRS. The hydrated VSBA-15 catalysts show two UV absorption peaks at 275 and 375 nm toward lower energy, as shown in Fig. 6. The strong absorption band around 275 nm is attributed to the regular tetrahedral V⁵⁺ species incorporated on the surface of pore walls of SBA-15, and a broad absorption band around 375 nm shows the partially disordered tetrahedral V5+ species incorporated on the silica surface [10-13,56]. The absorption peak around 375 suggests that the disordered tetrahedral V⁵⁺ species attracted by water molecules transform into penta-or-octahedral V5+ species [56]. The



Fig. 6. UV-vis DR spectra of VSBA-15 catalysts.

absorption band around 455 nm shows the non-framework V₂O₅ crystallites species dispersed on the silica surface (Fig. 6). This result is strongly confirmed by ⁵¹V MAS NMR spectra. But the majority of V⁵⁺ species still remain in a tetrahedral coordination upon hydration. We suggest that the isolated tetrahedral V⁵⁺ species are incorporated on the silica surface of SBA-15 [56].

3.7. TEM

Fig. 7 shows the TEM images of the VSBA-15(10) catalyst. The TEM images show well ordered hexagonal arrays of 1D mesoporous channels, further confirming that VSBA-15 catalyst has a 2D *p6mm* hexagonal structure. The distance between two consecutive centres of hexagonal pores estimated from the TEM image is ca. ~11 nm. The average thickness of the wall is ca. ~3.9 nm, which is much larger than that for MCM-41. The pore diameter is around ~8.4 nm, which is in agreement with the N₂ adsorption measurements. The above results show that the VSBA-15 catalysts have well uniformly pore diameters.

The above results of ICP-AES, XRD, N₂ adsorption, ESR, UV-vis DRS, 51 V MAS NMR, 29 Si MAS NMR and TEM suggest the successful incorporation of a larger amount of vanadium species into SBA-15 by a pH-aDH method without affecting the structural and textural order.

3.8. Hydrothermal stability

To investigate the hydrothermal stability, we have treated the calcined V-containing mesoporous catalysts such as VSBA-15(5) and VSBA-15(50) in boiling water at 373 K for 168 h. A study of hydrothermal stability is an important factor to find the distinct structural and textural parameters of VSBA-15, and it can be very helpful to find the catalytic stability because VSBA-15 catalysts can be used for the synthesis of bulk aromatics in chemical industries. After hydrothermal treatment of VSBA-15(50), its structural and textural parameters (Table 2) because it has high numbers of free Si–O–Si bonds due to low amounts of V species being incorporated into the silica pore walls. These results suggest that the hydrothermal treatment for VSBA-15(50) may cause



Fig. 7. TEM micrographs of calcined hexagonal mesoporous VSBA-15(10).

some shrinkage of mesopores and some structural disorder. But the physicochemical properties (structural and textural parameters) of VSBA-15(5) almost remain constant (Table 2) after hydrothermal treatment because it has the high numbers of Si-O-V and V-O-V bonds [14,56], which make thicker pore walls of VSBA-15(5) due to the higher tetrahedral V⁵⁺ species incorporated on the surface of pore walls. However, the VSBA-15(5) catalyst has physicochemical properties lower than that of the freshly calcined VSBA-15(5) (Tables 1 and 2) because the non-framework of V₂O₅ crystallites species dispersed on the VSBA-15(5) are mostly removed during the hydrothermal treatment. The physicochemical results of VSBA-15(5) and W-VSBA-15(5) are almost identical (Tables 1 and 2). This evidence strongly confirms that the non-framework V₂O₅ crystallites species dispersed on the VSBA-15 are completely removed during the hydrothermal treatment, even though the VSBA-15(5) has better hydrothermal stability than VSBA-15(50) due to the thicker pore walls, which are more stable against further attack by boiling water (Table 2). Therefore, the treated VSBA-15(5) is called "hydrothermally stable VSBA-15(5)".

Table 3

Oxidation of CDD with different VSBA-15 catalysts^a.

Catalysts	Conversion of CDD (%)	Selectivity of CDD=O (%)	Selectivity of CDD–OH (%)
VSBA-15(5)	71.4	89.5	10.5
VSBA-15(10)	63.7	82.4	15.1
VSBA-15(15)	55.7	75.8	18.4
VSBA-15(20)	47.6	70.1	21.3
VSBA-15(25)	40.4	58.1	23.4
VSBA-15(50)	27.3	35.3	15.3
VMCM-41(40)	37.3	63.8	16.3

^a Reaction conditions: 50 mg of catalyst; 1 g of CDD; 2 mole ratio of H_2O_2 -to-CDD; 15 ml of MeCN; reaction temperature, 373 K; reaction time, 24 h.

3.9. Oxidation of CDD

The oxidation of CDD has been performed over VSBA-15 catalysts, as shown in Scheme 1. The effects of reaction parameters such as temperature, time and CDD-to- H_2O_2 ratios, have been studied to find optimal values of CDD conversion and CDD=O selectivity. The performance of catalytic stability has been also found through the studies of recycles. After chemical and hydrothermal treatments, the vanadium concentrations and catalytic activities in the VSBA-15(5) catalysts have been also investigated.

The oxidation of CDD was carried out with 2 moles of H₂O₂-to-CDD and 15 ml of MeCN at 373 K for 24 h over mesoporous V-containing mesoporous catalysts viz. VSBA-15(5), VSBA-15(10), VSBA-15(15), VSBA-15(20), VSBA-15(25) and VSBA-15(50), as shown in Table 3. The order of catalytic activity found on the selectivity of CDD=O is as follows: VSBA-15(5)>VSBA-15(10)>VSBA-15(15)>VSBA-15(20)>VMCM-41(40)>VSBA-15(25)>VSBA-15(50). VSBA-15(5) exhibits the best performance with a conversion of CDD (71.4%) and a selectivity of CDD=O (89.5%). As shown in Table 3, the selectivity of cyclododecanol (CDD-OH) increases from VSBA-15(5) to VSBA-15(25) because the active sites on the silica surface are insufficient to convert CDD=O from CDD-OH due to the low amounts of vanadium incorporated in the framework of silica walls. Thus, VSBA-15(5) has higher selectivity of CDD=0 than other VSBA-15 catalysts (Table 3). The higher activity of VSBA-1(5) is presumably ascribed to its two-dimensional space and to the high loadings of tetrahedral V⁵⁺ species on the surface of SBA-15, resulting in a higher number of accessible active sites because the tetrahedral V⁵⁺ species incorporated in the framework of SBA-15 produces high numbers of Lewis acid sites to enhance the catalytic activity in the oxidation of CDD. Moreover, if we compare the catalytic activity for the catalysts with similar vanadium-content as shown in Table 1, the selectivity of CDD=O in VSBA-15(20) is significantly higher as compared to that of VMCM-41(40), as shown in Table 3. It may be concluded from this evidence that the well ordered mesoporosity material with high vanadium loadings plays an important catalytic role in the production of CDD=O with a high selectivity. On the basis of catalytic activities of different

Table 2

Physicochemical properties of VSBA-15 catalysts treated by hydrothermal treatments, and VSBA-15 catalysts reused in three cycles.

Catalysts	Hydrothermal		n _{Si} /n _V i	ratio	<i>a</i> ₀ (Å)	$A_{\rm BET}~(m^2/g)$	$d_{\rm p}$ (Å)	$V_{\rm p}~({\rm cm^3/g})$	$t_{\rm w}$ = $a_0 - d_{\rm p}$ (Å)
	Temperature (K)	Time (h)	Gel	Calcined ^a					
VSBA-15(5)	373	168	5	19.4	122.6	715	83.7	1.03	38.9
VSBA-15(50)	373	168	50	87.6	111.7	610	82.4	0.90	29.3
3rd Run ^b	-	-	-	19.4	122.3	713	83.8	1.07	38.5
3rd Run ^c	-	-	-	87.7	114.5	740	84.1	0.95	30.4

 a_0 , unit cell parameter; A_{BET} , specific surface area; d_p , pore diameter; V_p , pore volume; pore wall thickness (t_w) = unit cell parameter (a_0) – pore diameter (d_p). ^a The results of n_{Si}/n_V ratios in the products are determined by ICP-AES.

^b The regenerated VSBA-15(5) catalyst was reused for recycling reactions.

^c The regenerated VSBA-15(50) was reused for recycling reactions.

Table 4

Oxidation of CDD over the regenerated VSBA-15 catalysts and W-VSBA-15(5)^a.

Catalysts	Conversion of CDD (%)	Selectivity of CDD=0 (%)	Selectivity of CDD–OH (%)
VSBA-15 (5) ^b	63.2	76.3	18.1
VSBA-15 (50) ^b	27.2	35.1	12.1
VMCM-41(40) ^b	32.4	58.4	14.3
W-VSBA-15(5)	62.1	76.4	18.0
VSBA-15(5) ^c	63.2	82.4	17.6
SiSBA-15	5.2	10.3	3.2
Absence of catalyst	4.2	8.3	2.1

^a Reaction conditions: 50 mg of catalyst; 1 g of CDD; 2 mole ratio of H_2O_2 -to-CDD; 15 ml of MeCN; reaction temperature, 373 K; reaction time, 24 h.

^b The results were obtained after three runs.

^c The catalyst was treated with boiling water for the investigation of its hydrothermal stability.

V-containing mesoporous catalysts, VSBA-15(5) is found to be a promising heterogeneous catalyst in the liquid-phase oxidation of CDD for the highly selective synthesis of CDD=O, and its catalytic activity is higher than VMCM-41 [9].

Several vanadium-containing mesoporous catalysts viz. VSBA-15(5) and VSBA-15(50) and VMCM-41(40), have been examined to determine their catalytic stabilities. Initially, the mesoporous catalysts used in the catalytic reaction usually suffer from the loss of catalytic activities, and hence the catalysts need to be regenerated by calcination. The used catalysts were washed four times with acetone and dried at 393 K overnight. Finally, the catalysts were calcined at 773 K for 6 h in air for complete removal of the organics and unreacted CDD molecules. The regenerated catalysts have been reused for this reaction, which was carried out using the similar reaction conditions, as noted in Table 4. The conversion of CDD and selectivity of CDD=O decrease in the first two runs (not shown in Table 4). On the basis of first two runs, one can observe that the non-framework V2O5 crystallites species leach on the catalytic surface (the ranges of $n_{\rm Si}/n_{\rm V}$ ratios obtained by ICP-AES are from 19.4 to 87.7 (Table 2)). The conversion of CDD as well as the selectivity of CDD=O remains constant after three runs, indicating that the vanadium ions cannot be further leached on the mesoporous matrix, which is in good agreement with ICP-AES results of filtrate solutions where no vanadium species is detected. Furthermore, the W-VSBA-15(5) has also been used in this reaction for the investigation of catalytic stability. The effect of this study is nearly identical to that of three runs of VSBA-15(5), as shown in Table 4. However, it is interesting to note that after three runs the catalysts show nearly the same conversion value, indicating that no more leaching of vanadium from the VSBA-15 matrix will be observed by ICP-AES analysis. This reaction was also carried out using SiSBA-15 synthesized by pH-aDH method [27] as well as without catalyst. In both cases, about \sim 5–4% conversion of CDD and \sim 8.3–10% selec-

Table 5

Oxidation of CDD using different reaction conditions over VSBA-15(5)^a.

Catalysts	Conversion	Selectivity of	Selectivity of
	of CDD (%)	CDD=O (%)	CDD–OH (%)
VSBA-15(5) ^b	75.3	84.3	10.4
VSBA-15(5) ^c	60.1	71.2	15.3
VSBA-15(5) ^d	55.3	62.3	10.3
VSBA-15(5) ^e	76.3	83.2	11.1
VSBA-15(5) ^f	55.2	59.3	6.3
VSBA-15(5) ^g	73.2	82.3	10.2

^a Reaction conditions: 50 mg of catalyst; 1 g of CDD; 2 mole ratio of H_2O_2 -to-CDD; 15 ml of MeCN; reaction temperature, 373 K; reaction time, 24 h.

Reaction temperature: 393 K.

Reaction temperature: 353 K.

^d Reaction time: 12 h.

e Reaction time: 48 h.

 $^{\rm f}\,$ 1 mole ratio of H_2O_2-to-CDD.

 $^{\rm g}$ 4 mole ratio of H₂O₂-to-CDD.

tivity of CDD=O have been obtained (Table 4), thus indicating that major activity is only due to vanadium species incorporated in the framework of SBA-15.

The hydrothermally stable VSBA-15(5) was also used in the liquid-phase oxidation of CDD; its catalytic activity is also similar to that of W-VSBA-15, as shown in Table 4. Since the VSBA-15(5) is a promising catalyst in this catalytic oxidation reaction, it has been further used to find the best optimal conditions.

To obtain the highly selective synthesis of CDD=O over VSBA-15(5), the liquid-phase oxidation of CDD was carried out using the different optimal conditions such as reaction temperature, reaction time and ratios of reactant (CDD: TBHP).

The oxidation of CDD was conducted with different reaction temperatures and times using the reaction conditions noted in Table 5, for obtaining a highly selective synthesis of CDD=0. When the reaction temperatures and times are decreased from 373 to 353 K and 24 to 12 h, respectively, the rates of both CDD consumption and CDD=O formation decrease. The feasible CDD conversion decreases with the decrease of temperature and time. This may be due to the formation of fewer Lewis active sites on the surface of the catalyst at low reaction temperature and time, which may not be sufficiently supported to produce CDD=O from CDD-OH. Moreover, the conversion and selectivity have not significantly increased when the reaction temperature and time are increased from 373 to 383 K and 24 to 36 h, respectively. However, at above 390 K and 46 h, the conversion of CDD and the selectivity of CDD=0 decrease due to the formation of overoxidation products such as 1, 2-cyclododecandione and 1, 2-cyclododecandiol, as shown in Scheme 1. This evidence strongly supports the conclusion that a low reaction temperature/time (<353 K/12 h) or high reaction temperature/time (>390 K/46 h) is unsuitable to highly produce



Scheme 1. Catalytic oxidation of CDD with H₂O₂ over vanadium-containing catalysts.

CDD=O with a good selectivity. One can conclude with confidence from the catalytic results obtained with different reaction temperatures/times that the reaction parameters, like temperature of 373 K and reaction time of 24 h, are favourable to produce a high selectivity of CDD=O.

To find the best ratio of CDD-to-H₂O₂ for the highly selective synthesis of CDD=0, we carried out the oxidation of CDD with different ratios of H₂O₂-to-CDD using the reaction conditions noted in Table 5. When this reaction is carried out with 2 mole ratios of H₂O₂-to-CDD, the increase of conversion of CDD as well as selectivity of CDD=O is observed. The selectivity of CDD=O decreases in 1 mole ratio of H₂O₂-to-CDD. We consider that the quantity of reactants is insufficient to react with each other on the catalyst surface while the rate of diffusion may be decreased due to the unreacted organics dispersed on the inner pores of VSBA-15; in 4 moles of H₂O₂ ratio to CDD, the selectivity of CDD=O also decreases. From this result, it is important to note that the overoxidation byproducts (1, 2-cyclododecandione and 1, 2-cyclododecandiol) may be formed with an uneven ratio of reactant, as shown in Scheme 1. On the basis of the effect of the ratios, it is clear that 2 moles ratio of H₂O₂-to-CDD is an optimum ratio for the highly selective synthesis of CDD=0.

4. Conclusions

The highly ordered two-dimensional VSBA-15 catalysts synthesized with high tetrahedral vanadium loadings have been successfully used in the oxidation of CDD to CDD=O with a good selectivity. ICP-AES results of VSBA-15 catalysts show that the amounts of vanadium species are highly incorporated into SBA-15. ²⁹Si MAS NMR results of VSBA-15 catalysts also confirm that high amounts vanadium species are incorporated on the silica surface. The studies of XRD and N₂ adsorption show that the structural and textural properties of VSBA-15 catalysts cannot be affected by the high amounts of vanadium species incorporated in the pore walls of SBA-15. ESR spectra of as-synthesized VSBA-15 show the amounts of square pyramidal V⁴⁺ species located on the silica surface. The results of ⁵¹V MAS NMR spectra show that high numbers of tetrahedral V⁵⁺ species are incorporated in the framework of silica surface and small amounts of non-framework V₂O₅ crystallites species are dispersed on the silica surface. In the hydrated VSBA-15 catalysts, UV-vis DRS results clearly show the distinct of regular and disordered tetrahedral V⁵⁺ species incorporated into silica surface. TEM results confirm the VSBA-15 catalysts synthesized with well ordered hexagonal and uniform pore diameters. From the studies of hydrothermal stability, VSBA-15(5) is found have better hydrothermal stability than VSBA-15(50) due to the thicker pore walls. On the basis of all catalytic studies, it is clearly found that the VSBA-15(5) catalyst is a highly active, recyclable and promising heterogeneous catalyst for the selective synthesis of CDD=O.

References

- [1] B.I. Whitting, J.R. Anderson, J. Phys. Chem. 97 (1993) 1032–1041.
- [2] P.R.H.P. Rao, A.A. Belhekar, S.G. Hegde, A.V. Ramaswamy, P. Ratnasamy, J. Catal. 141 (1993) 595–603.
- [3] T. Sen, P.R. Rajamohanan, S. Ganapathy, S. Sivasanker, J. Catal. 163 (1996) 354–364.
- [4] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Nature 359 (1992) 710–712.

- [5] D. Trong On, D. Desplantier-Giscard, C. Danumah, S. Kaliaguine, Appl. Catal. A: Gen. 253 (2003) 545–602.
- [6] A. Corma, H. Garcia, Chem. Rev. 103 (2003) 4307–4366.
- [7] C. Baleizão, H. Garcia, Chem. Rev. 106 (2006) 3987-4043.
- [8] J.A. Melero, R. van Grieken, G. Morales, Chem. Rev. 106 (2006) 3790-3812.
- [9] K.M. Reddy, I. Moudrakovski, A. Sayari, J. Chem. Soc., Chem. Commun. (1994) 1059–1060.
- [10] Z. Luan, J. Xu, H. He, J. Klinowski, L. Kevan, J. Phys. Chem. 100 (1996) 19595–19602.
- [11] D.H. Park, C.-F. Cheng, H. He, J. Klinowski, J. Mater. Chem. 7 (1997) 159-162.
- [12] S. Lim, G.L. Haller, J. Phys. Chem. 106 (2002) 8437-8448.
- [13] P. Selvam, S.E. Dapurkar, J. Catal. 229 (2005) 64-71.
- [14] M. Selvaraj, T.G. Lee, Micropor. Mesopor. Mater. 85 (2005) 39-51.
- [15] D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky, Science 279 (1998) 548–552.
- [16] F.-S. Xiao, Top. Catal. 35 (2005) 9-24.
- [17] F. Hoffmann, M. Cornelius, J. Morell, M. Fröba, Angew. Chem., Int. Ed. 45 (2007) 3216–3251.
- [18] M. Vallet-Regi, F. Balas, D. Arcos, Angew. Chem., Int. Ed. 46 (2007) 7548–7558.
 [19] Y. Yue, A. Gideon, J.-L. Bonardet, N. Melosh, J.-B. D'Espinose, J. Fraissard, Chem.
- Commun. (1999) 1967–1968. [20] C. Nozaki, C.G. Lugmair, A.T. Bell, T.D. Tilley, J. Am. Chem. Soc. 124 (2002) 13194–13203.
- [21] Z. Luan, J.Y. Bae, L. Kevan, Chem. Mater. 12 (2000) 3202-3207.
- [22] W.-H. Zhang, J. Lu, B. Han, M. Li, J. Xiu, P. Ying, C. Li, Chem. Mater. 14 (2002) 3413–3421.
- [23] Z.E. Berrichi, L. Cherif, O. Orsen, J. Fraissard, J.-P. Tessonnier, E. Vanhaecke, B. Louis, M.-J. Ledoux, C.P. Huu, Appl. Catal. A: Gen. 298 (2006) 194–202.
- [24] M. Morey, S. O'Brien, S. Schwarz, G.D. Stucky, Chem. Mater. 12 (2000) 898–911.
- [25] S. Wu, Y. Han, Y.-C. Zou, J.-W. Song, L. Zhao, Y. Di, S.-Z. Liu, F.-S. Xiao, Chem. Mater. 16 (2004) 486–492.
- [26] S. Sumiya, Y. Oumi, T. Uozumi, T. Sano, J. Mater. Chem. 11 (2001) 1111–1115.
- [27] M. Selvaraj, S. Kawi, Chem. Mater. 19 (2007) 509-519.
- [28] M. Selvaraj, T.G. Lee, J. Phys. Chem. B 110 (2006) 21793-21802.
- [29] M. Selvaraj, S. Kawi, J. Mater. Chem. 17 (2007) 3610-3621.
- [30] M. Selvaraj, Y. Choe, Appl. Catal., A: Gen. 373 (2010) 186.
- [31] M. Selvaraj, M. Kandaswamy, D.W. Park, C.S. Ha, Catal. Today (in press) doi:10.1016/j.cattod.2010.04.041.
- [32] M. Selvaraj, S. Kawi, Catal. Today 131 (2008) 82-89.
- [33] M. Selvaraj, S. Kawi, D.-W. Park, C.S. Ha, Micropor. Mesopor. Mater. 117 (2009) 586-595.
- [34] M. Selvaraj, S. Kawi, Stud. Surf. Sci. Catal. 165 (2007) 219-222.
- [35] M. Selvaraj, S. Kawi, D.-W. Park, C.S. Ha, J. Phys. Chem. C 113 (2009) 7743-7749.
- [36] C. Hess, J.D. Hoefelmeyer, T.D. Tilley, J. Phys. Chem. 108 (2004) 9703–9709.
- [37] F. Gao, Y. Zhang, H. Wan, Y. Kong, X. Wu, L. Dong, B. Li, Y. Chen, Micropor. Mesopor. Mater. 110 (2008) 508–516.
- [38] G. Du, S. Lim, M. Pinault, C. Wang, F. Fang, L. Pfefferle, G.L. Haller, J. Catal. 253 (2008) 74–90.
- [39] M.J. Jurado, M.D. Gracia, J.M. Campelo, R. Luque, J.M. Marinas, A.A. Romero, J. Mater. Chem. 19 (2009) 8603–8609.
- [40] M. Selvaraj, B.H. Kim, T.G. Lee, Chem. Lett. 34 (2005) 1290-1291.
- [41] Y. Segura, P. Cool, P. Kustrowski, L. Chmielarz, R. Dziembaj, E.F. Vansant, J. Phys. Chem. B 109 (2005) 12071–12079.
- [42] V. Fornés, C. López, H.H. López, A. Martínez, Appl. Catal. A: Gen. 249 (2003) 345–354.
- [43] Y.-M. Liu, Y. Cao, N. Yi, W.-L. Feng, W.-L. Dai, S.-R. Yan, H.-Y. He, K.-N. Fan, J. Catal. 224 (2004) 417–428.
- [44] Y.-M. Liu, W.-L. Feng, T.-C. Li, H.-Y. He, W.-L. Dai, W. Huang, Y. Cao, K.-N. Fan, J. Catal. 239 (2006) 125–136.
- [45] Y.-M. Liu, Y. Cao, K.-K. Zhu, S.-R. Yan, W.-L. Dai, H.-Y. He, K.-N. Fan, Chem. Commun. (2002) 2832–2833.
- [46] Y.-M. Liu, Y. Cao, S.-R. Yan, W.-.L. Dai, K.-N. Fan, Catal. Lett. 88 (2003) 61–67.
- [47] B.M. Lin, X.X. Wang, Q. Guo, W. Yang, Q.H. Zhang, Y. Wang, Chem. Lett. 32 (2003) 860–861.
- [48] S. Shylesh, A.P. Singh, J. Catal. 244 (2006) 52-64.
- [49] B.P. Feuston, J.B. Higgins, J. Phys. Chem. 98 (1994) 4459-4462.
- [50] A. Sayari, P. Liu, M. Kruk, M. Jaroniec, Chem. Mater. 9 (1997) 2499-2506.
- [51] M. Imperor-Clerc, P. Davidson, A. Davidson, J. Am. Chem. Soc. 122 (2000)
- 11925–11933.
- [52] M. Kruk, M. Jaroniec, Chem. Mater. 13 (2001) 3169-3183.
- [53] M. Chatterjee, T. Iwasaki, H. Hayashi, Y. Onodera, T. Ebina, T. Nagase, Chem. Mater. 11 (1999) 1368–1375.
- [54] G. Centi, S. Perathoner, F. Trifiro, A. Aboukais, C.F. Aissi, M. Guelton, J. Phys. Chem. 96 (1992) 2617–2629.
- [55] M.D. Curran, T.E. Gedris, A.E. Stiegman, Chem. Mater. 11 (1999) 1120-1127.
- [56] J.S. Reddy, P. Liu, A. Sayari, Appl. Catal. A: Gen. 148 (1996) 7-21.