Direct incorporation of vanadium into three-dimensional KIT-6: 2. Reactivity test for styrene oxidation

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Abstract−The direct incorporation of vanadium into the three-dimensional (3-D) cubic Ia3d mesostructure designated as V-KIT-6 was prepared, and the material obtained therein showed a very high specific surface area of ~1,000 m^2/g with tunable pore diameters in a narrow distribution of sizes, ~5.7 to 6.0 nm. The coordination and nature of the V sites in V-KIT-6 were characterized by ^{51}V-spin-echo NMR analysis. It shows that after calcination, the V^{4+} species are totally oxidized to the V^{5+} state with 4- and 6-coordinated V-O environments in a highly dispersed state with much less crystalline V_2O_5 formation. The calcined V-KIT-6 materials showed excellent catalytic activity in the direct oxidation of styrene using tert-butyl hydroperoxide (TBHP) as an oxidant.

Key words: KIT-6, Vanadium, Styrene, Oxidation

INTRODUCTION

Vanadium-substituted zeolites have attracted a great deal of attention in the past few decades because of their excellent catalytic properties in selective oxidation reactions [1,2]. However, most of them were microporous solids, and their applications were restricted to relatively small molecules, owing to the pore-size limitation [3]. This led to the discovery of a series of ordered mesoporous molecular sieves by the researchers at Mobil Corporation in 1992 [4]. As the direct synthesis method often requires specialized synthesis conditions depending on the respective structures of the materials, only a few reports have appeared on the direct incorporation of V in M41S materials. Reddy et al. [5] studied vanadium incorporated MCM-41 materials by ^{51}V NMR and concluded that vanadium was atomically dispersed in tetrahedral positions with a unit cell parameter a_0 of 37 Å. A more detailed characterization of the coordination of vanadium containing mesoporous molecular MCM-41 sieves was accomplished by Gontier and Tuel [6].

In the past few years, the optimization of the synthesis of the hexagonal SBA-15 has received a great deal of attention [7]. Although of great potential use in catalytic applications, there have been only a few reports on the V incorporated SBA-15 materials because of the difficulty in introducing the metal ions into SBA-15 under strong acidic hydrothermal conditions due to the easy dissociation of metal-O-Si bonds. Hence, several studies have dealt with incorporation of metal ions into SBA-15 through post synthetic grafting methods. Nevertheless, preparation of the materials by these methods always leads to the extra-framework species and irregularly distributed active sites [8]. Large-pore three-dimensional (3D) mesoporous silicas such as SBA-1 and SBA-16 are among the most interesting mesoporous materials discovered in recent years, and they have attracted much attention for potential applications requiring easily accessible,

uniform large pores [9]. However, all of these surfactant directed cubic mesoporous materials lack an efficient synthesis condition for tuning the structural and textural properties with uncertain degree of ordering and phase purity. For instance, when vanadium was incorporated into SBA-1 a transformation of phase from cubic into hexagonal phase occurred when high metal was incorporated [10]. Moreover, the successful syntheses of vanadium incorporated three-dimensional materials reported by several groups were either done at relatively longer synthesis times or with very low amount of vanadium really substituted [11-15]. Very recently, large-pore mesoporous silica (KIT-6), with a cubic *Ia3d* structure synthesized by using triblock copolymer as structure-directing agent under various synthesis conditions, was found to be a most interesting material as it consists of two interpenetrating continuous networks of chiral channels [16]. Its unique 3-D channel network is thought to provide a highly opened porous host with easy and direct access for guest species, thus facilitating inclusion or diffusion throughout the pore channels without pore blockage.

The selective oxidation of styrene with an oxidant to produce non-chlorine benzaldehyde was considered to be a green process. But most catalysts used in this reaction are homogeneous noble metal-organic compounds [17,18]. Therefore, research on heterogeneous catalysts becomes important and significant, but so far most of the studies have focused upon the one-dimensional hexagonal molecular sieves [6,19]. In our previous work [20], we reported the optimization of synthesis conditions for V-KIT-6. To study the catalytic performance of V-KIT-6, the selective oxidation of styrene was chosen as a model reaction. In the present study, we investigated the effects of Si/V ratio of V-KIT-6 and reaction parameters on the selective oxidation of styrene with TBHP.

EXPERIMENTAL

1. Materials

The mesostructured vanadium incorporated KIT-6 materials were

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prepared under various synthetic conditions using a mixture of poly (alkylene oxide)-based triblock copolymer Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, MW=5,800, Aldrich), *n*-butanol (Aldrich, 99.4%) as a structure-directing mixture, TEOS (Aldrich, 98%) as a silica source and NH_4VO_3 (Aldrich, 99.9%) as a vanadium source.

2. Preparation and Characterization of Catalysts

The V-KIT-6 materials were prepared by using a molar composition in the range of 0.017 P123/0.08-2.4 V/1.3 TEOS/1.31 BuOH/3.00 HCl/195 H_2O. 4.0 g of P123, along with 7.4 g of 37 wt%. HCl was dissolved in 144 g of distilled water, and after forming a complete dissolution, 4.0 g of BuOH was added. Then, 8.6 g of TEOS with the required amount of vanadium was added at once to the homogeneous clear solution. This mixture was left under vigorous and constant stirring at 100 °C for 48 h. The precipitated product was filtered, washed thoroughly, and dried for 24 h. The obtained material was calcined in a programmable oven (25-550 °C; heating rate 1 °C/min) for 8 h in N_2 and 8 h in an air atmosphere.

X-ray diffraction measurement was performed by XRD (Philips X′ pert PRO MRD system) by using nickel filtered CuKα radiation (λ=1.5406 Å). The metal content in the KIT-6 was measured with an ICP optical emission spectrometer (JOBIN YVON) and an X-ray Fluorescence Spectrometer (Philips PW 2400). Surface area, pore volume, and pore size distribution were measured by nitrogen adsorption at 77 K with a BET apparatus (ASAP-2010, Micromeritics). ^{51}V spin-echo NMR study was performed by a Bruker DSX 400 spectrometer in a magnetic field of 9.4 T. FT-Raman spectra and diffuse reflectance UV-Vis spectra of samples were reported in our previous work [15].

3. Oxidation of Styrene

The catalytic oxidation of styrene (2.6 mmol) was carried out in the presence of 2.6 mmol oxidant TBHP (70% in water) with 10 mL of acetonitrile as a solvent. 50 mg of catalyst was used at the temperature range from ambient temperature (AT) to 80 °C for 24 h under atmospheric pressure. After the reaction, the catalyst was separated and the products were analyzed by GC with a capillary column. The products were identified with authentic samples.

RESULTS AND DISCUSSION

1. Characterization of V-KIT-6

The vanadium-incorporated mesoporous molecular sieves were generally synthesized over relatively longer synthesis times with very low amount of vanadium really substituted [11-15]. An effort was made to incorporate a high V content into the silica cubic Ia3d mesophase of KIT-6 at the shortest period. Table 1 shows physicochemical properties of V-KIT-6 synthesized with different Si/V ratios.
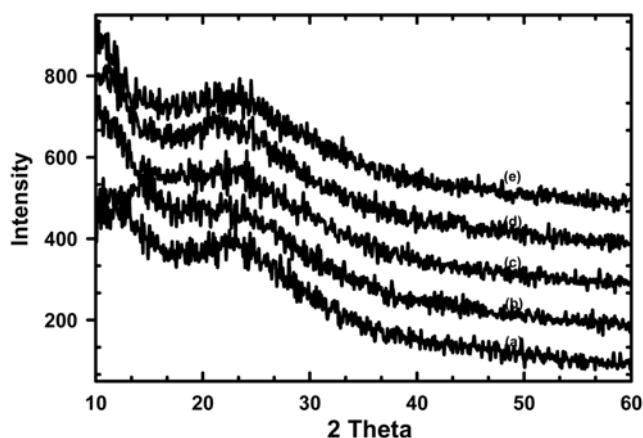

Fig. 1. High angle X-ray diffraction spectra of V-KIT-6 samples in hydrated condition [(a) Si/V=11, (b) Si/V=49, (c) Si/V=65, (d) Si/V=212, (e) Si/V=305].

The unit cell parameter calculated by the formula $a_o=6^{1/2}d_{211}$ was around 21.8-23.1 nm. The enlargement of the unit cell indicates heteroatom insertion and thickening of the pore wall by a transition metal promoted cross-linking of the amorphous silica walls [21]. The combination of the pore wall thickening and the enlargement of the unit cell is a good indication for an actual incorporation of the V centers. The optimization yielded the incorporation of a vanadium metal content range from 0.37 to 4.95 wt%. The Si/V ratios measured by XRF showed that comparable amounts of vanadium taken in the initial gel mixture were incorporated into the framework. To confirm the uniform distribution of vanadium species at the external surface and internal pores, high angle XRD diffraction patterns for V-KIT-6 were obtained and shown in Fig. 1. It can be seen that the catalysts had no distinct peak around 15.4, 20.2, and 26.1° corresponding to crystalline V_2O_5 [22]. This confirms the highly dispersed vanadium oxide species even at 4.95 wt% vanadium incorporation.

The spectra of ^{51}V spin echo NMR for V-KIT-6 materials under calcined and hydrated conditions are shown in Figs. 2 and 3, respectively. It is well-known that the line shape of the vanadium compound determines the symmetry of oxygen environments [23]. The more inequivalance between bond length and angles in a VO_x unit, the more anisotropy observed in the spectra. In our case, the presence of a narrow symmetrical line centered around −590 ppm can be interpreted as due to the presence of V^{5+} sites in a nearly symmetrical tetrahedral environment. The result is similar to those observed with zeolite around −500 to −600 ppm, which are attributed

Table 1. Textural properties of V-KIT-6 synthesized with various Si/V ratios with a gel composition of 0.017 P123/0.08-2.4 V/1.3 TEOS/1.31 BuOH/3.0 HCl/195 H_2O at 100 °C

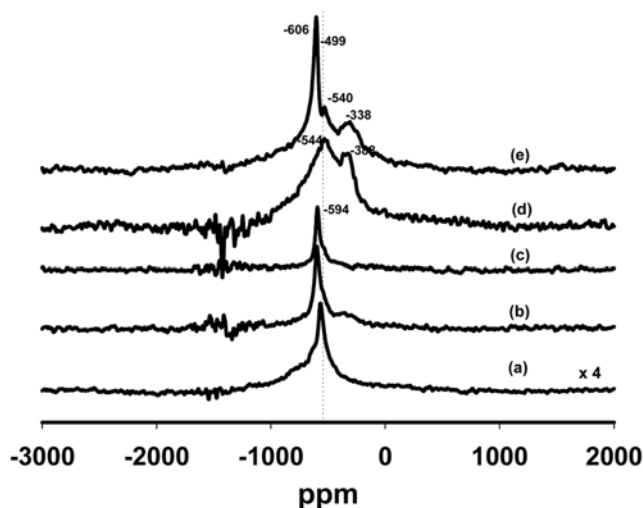| Catalyst	Si/V in gel	V (wt%)	d_{211} (Å)	a_o (nm)	Surface area (m²/g)	Pore size BJH$_{adsorp}$ (nm)	Pore volume BJH$_{adsorp}$ (cm³/g)	d (nm)	NH_3 (mmol/g)
V-KIT-6 (11)	10	4.95	93.0	22.7	712	6.0	1.17	5.3	5.92
V-KIT-6 (49)	40	1.89	91.1	22.3	691	6.0	1.10	5.1	2.50
V-KIT-6 (65)	60	1.74	94.6	23.1	916	5.7	1.19	5.8	4.56
V-KIT-6 (212)	200	0.46	90.2	22.0	1036	5.8	1.37	5.2	1.90
V-KIT-6 (305)	300	0.32	89.3	21.8	837	5.7	1.24	5.2	1.54

Fig. 2. ^{51}V-NMR spectra of V-KIT-6 with various Si/V ratios in dehydrated condition [(a) Si/V=305, (b) Si/V=212, (c) Si/V=65, (d) Si/V=49, (e) Si/V=11].

Fig. 3. ^{51}V-NMR spectra of V-KIT-6 with various Si/V ratios in hydrated condition [(a) Si/V=305, (b) Si/V=212, (c) Si/V=65, (d) Si/V=49, (e) Si/V=11].

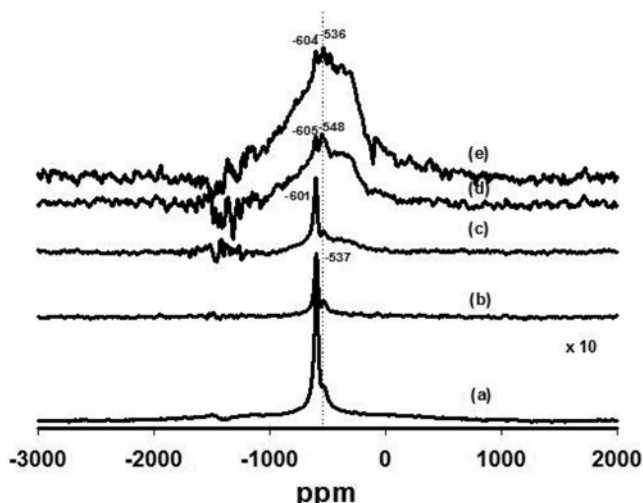to V^{5+} ions in a tetrahedral coordination [24]. The absence of a chemical shift at −350 ppm for V-KIT-6 upto Si/V=65 (Fig. 2(a)-(c)) in dehydrated conditions shows the reduced accessibility of vanadium to water molecules. As the metal content increased (Si/V≥49), the peak around −350 ppm increased proportionally (Fig. 2(d) and (e)). As reported earlier, the appearance of this chemical shift was attributed to hexa-coordinated vanadium. It shows that at this Si/V ratio, vanadium tends to bond with silanol groups, thereby increasing the accessibility of vanadium to water molecules and leading to the partial hydrolysis of the vanadium species. The study was extended by investigating the effect of water coordination in hydrated conditions (Fig. 3(a)-(e)). The samples were kept open in atmospheric condition for 6 days. Unlike other materials [23], there was a shift in the peak observed for KIT-6 even at a very low amount of vanadium, by $\delta=-330\pm100$ ppm and $\delta=-540\pm10$ ppm. The observed shift

Table 2. The activity of V-KIT-6 with various Si/V ratios (11, 49, 65, 212 and 305) at various temperatures for the oxidation of styrene using TBHP as an oxidant

Catalysts	Temp (°C)	Conversion (%)	BZ[b] (%)	SO[c] (%)	PhA[d] (%)	Others (%)
V-KIT-6 (305)	80	62.7	31.3	48.6	11.7	7.9
	60	41.3	51.2	25.4	15.9	7.2
	40	21.1	82.2	17.7	-	-
	AT[a]	26.4	83.9	16.0	-	-
V-KIT-6 (212)	80	75.1	40.6	8.0	21.8	32.0
	60	71.8	64.3	13.7	21.9	-
	40	73.9	70.1	13.1	5.1	2.2
	AT	60.3	69.5	12.5	7.4	10.2
V-KIT-6 (65)	80	72.1	40.9	9.5	23.6	20.4
	60	78.0	32.3	6.7	28.6	32.1
	40	55.3	65.7	17.6	4.6	12.0
	AT	60.5	76.1	15.2	8.7	-
V-KIT-6 (49)	80	38.2	68.9	10.31	20.9	-
	60	49.4	69.5	18.7	11.7	-
	40	51.0	51.1	20.4	30.4	-
	AT	49.6	73.0	21.7	-	5.1
V-KIT-6 (11)	80	42.8	47.8	20.1	27.2	4.6
	60	74.1	46.2	9.2	21.6	32.0
	40	72.3	66.1	18.4	9.5	15.2
	AT	65.3	69.3	22.8	7.6	-

[a]Reaction performed at ambient temperature, [b]Benzaldehyde, [c]Styrene oxide, [d]Phenyl acetaldehyde

Reaction condition: Styrene : TBHP ratio=1 : 1, Catalyst amount= 0.1 g, Time=24 h

indicates that the hydrolysis of the vanadium species not only occurs at the surface but also inside the pores, proving the easy accessibility of active sites by the water molecules.

2. Oxidation of Styrene with V-KIT-6

2-1. Effect of Si/V Ratio

To study the influence of Si/V ratio of V-KIT-6 on its catalytic activity, styrene was oxidized in a liquid phase setup by using tert-butyl hydroperoxide (TBHP) as an oxidant for 24 h at ambient to 80 °C. The catalytic results are presented in Table 2. The main products were benzaldehyde (BZ), and styrene epoxide (SO), with considerable amount of phenyl acetaldehyde (PhA). The activity of V-KIT-6 materials in general showed higher activity at lower reaction temperatures (≤40 °C). The styrene conversion and epoxidation selectivity were found to be strongly dependent upon the V content in the KIT-6 materials, where the styrene conversion as well as the selectivity for BZ increased with decreasing V content. For example, V-KIT-6 (212) with a low vanadium content (0.46 wt%) showed the highest styrene conversion of 73.9% with the BZ selectivity of 70.1% at 40 °C. For the V-KIT-6 with Si/V ratio 11 having 4.95 wt% vanadium content, though it seemed to show high styrene conversion (~70%), the by-product selectivity (SO and PhA) was found to be considerably high (Table 2). The observed different catalytic activities for the studied materials could be attributed to different acidity. In the case of V-KIT-6 (212), though the total acidity was less as shown in Table 1, the high activity could be attributed to the pres-
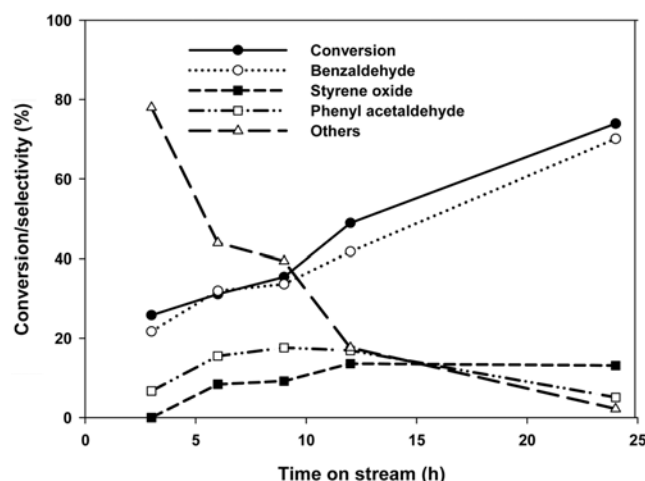
Fig. 4. Time variant conversion of styrene and selectivities of products for V-KIT-6 (212) catalyst (styrene : TBHP=1 : 1, catalysts amount=0.05 g, temperature=40 °C).

ence of medium Brønsted acid sites due to the tetrahedrally coordinated vanadium ion in the framework.

2-2. Effect of Time on Stream

The effects of reaction time on the styrene oxidation over V-KIT-6 (212) with a styrene to TBHP mole ratio of (2 : 1) at 40 °C are shown in Fig. 4. The conversion of styrene increased gradually from 25.8% at 3 h to 71.8% for 24 h. The selectivity of BZ also increased with increasing the reaction time, from 21.7% at 3 h to 64.3% for 24 h. The selectivity with respect to SO, and PhA increased slightly to 13.7% and 21.9%, respectively. The formation of the by-product with a long run could be attributed to secondary oxidation of the epoxide [25].

2-3. Effect of Mole Ratio of Styrene/TBHP

The effect of styrene to TBHP mole ratios (1 : 1, 1 : 2, 1 : 4, 2 : 1, 3 : 1 and 4 : 1) over V-KIT-6 (212), at 40 °C for 24 h is shown in Fig. 5. With an increase in the mole ratio of TBHP from 1 : 1 to 1 : 2, the conversion of styrene increased steeply to 100%, while the se-
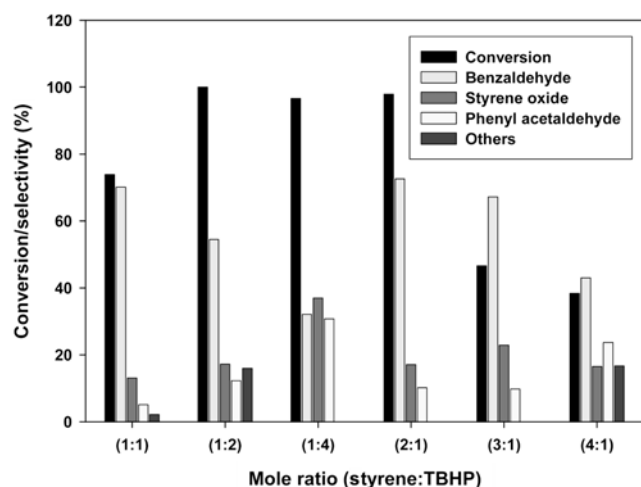

Fig. 5. Effect of styrene:TBHP mole ratio on the conversion of styrene and selectivities of products for V-KIT-6 (212) catalyst (catalysts amount=0.05 g, temperature=40 °C, time=24 h).

lectivity with respect to BZ was significantly lowered to 54.5%, which then decreased to 32.1% when the TBHP mole ratio was 1 : 4. The selectivity with respect to SO and PhA increased proportionately. On the other hand, with the increase in the styrene mole ratio to 2 : 1 both the conversion and selectivity of BZ increased. The obtained conversion was 97.9% with a high BZ selectivity of 72.6%. Hence, it was considered as the optimum mole ratio for further studies. Increasing the mole ratio of styrene to 3 : 1 and 4 : 1 only decreased the conversion of styrene with poor epoxidation selectivity.

2-4. Recycle Test

The activity of a recycled catalyst was tested by filtering the used V-KIT-6 (212) catalyst from the reaction mixture, washing it with acetone and drying it overnight followed by drying overnight in an oven at 100 °C. The catalyst was subsequently activated at 500 °C for 3 h under an air flow and reused in the above reaction under the optimized conditions. The activity was found to be similar to that with the fresh catalysts. The conversion of styrene remained high at 96.4%. The selectivity with respect to BZ, SO, and PhA was 72.0%, 17.3%, and 10.6%, respectively. The vanadium content of the used V-KIT-6 (212) was 0.44 wt%.

CONCLUSION

Vanadium incorporated three-dimensional KIT-6 with Si/V ratios as low as 11 was successfully synthesized and the obtained material therein showed a high surface area ~1,000 m^2/g. The pore size distribution varied between 5.7 to 6.0 nm with the wall thickness of about 5.8 nm at the maximum. In styrene oxidation, V-KIT-6 catalysts showed high conversion of styrene with good selectivity for benzaldehyde. The conversion of styrene and selectivity to BZ increased with increased reaction time up to 24 h. The optimum mole ratio of styrene to TBHP was 2 : 1.

ACKNOWLEDGMENT

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