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Synthesis of Aromatic Ketones from Aromatic Compounds Using Vanadium-Containing Mesoporous Silicates

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Aromatic ketones were synthesized from aromatic compounds via liquid-phase oxidation at 60 °C and 1 atm over vanadium-containing MCM-41 catalysts using a batch reactor. The catalysts were prepared by direct hydrothermal (4V-MCM-41) and wet impregnation (9V/MCM-41) methods. Their physico-chemical properties were determined with various characterization techniques. For the oxidations of all substrates in this work, 4 V-MCM-41 exhibits superior catalytic performance than 9 V/MCM-41 due to its larger values of unit cell parameter, BET surface area, and vanadium dispersion as well as stronger oxidation ability of vanadium-oxygen species. Apparently, the single site, isolated vanadium centers in 4V-MCM-41 possess much higher activity (based on the turnover number) than those containing more vanadium atoms in 9V/MCM-41. In addition, the substrate activities decrease in the order of diphenylmethane > fluorene > 9,10-dihydroanthracene > ethylbenzene ≥ 4-nitroethylbenzene, which are attributed to their distinct molecular structures.

Keywords: Oxidation; (V) MCM-41; Diphenylmethane; Ethylbenzene; 4-Nitroethylbenzene; Fluorene; 9,10-Dihydroanthracene.

INTRODUCTION

Aromatic ketones are important organic intermediates in the industries of flavors, perfumes, pharmaceuticals, and agrochemicals. Traditionally, these ketones were produced by Friedel-Crafts acylation of aromatic compounds using Lewis acids or strong protonic acids as catalysts. Another different route utilized $KMnO_4$, $K_2Cr_2O_7$, or SeO_2 as oxidants to oxidize the aromatics. However, both processes exhibited many disadvantages including highly corrosive wastes, environmental hazards, and separation difficulty of catalyst from the reaction mixture.[1] As a consequence, for the past decade much efforts have been made to develop more economic and clean processes for the synthesis of aromatic ketones by the oxidation of aromatics over a variety of heterogeneous catalysts. Up to now, the majority of studies reported the oxidation of diphenylmethane to benzophenone[2-12] and ethylbenzene to acetophenone.[3-6,12-19] Other aromatics like 4-nitroethylbenzene[3,6] and fluorene[12,20-22] have received much less attention. To our knowledge, so far there is no report on the oxidation of 9,10-dihydroanthracene over solid catalyst.

MCMs type materials possess characteristic mesoporous structure, large surface area, and high thermal stability, which allow their potential applications in catalysis, adsorbants, and energy conversion.[23,24] Recently, M-MCM-41 (M = Ti, V, Cr),[5] cobalt containing MCM-41,[8,11] Mn-MCM-41,[10,18,19] and Cr-MCM-41[12,13] were prepared and applied to the liquid-phase oxidation of diphenylmethane, ethylbenzene, or 4-nitroethylbenzene with low to moderate catalytic activities. Although vanadium-containing MCM-41 materials have been applied to the oxidation of light alkanes,[25] benzene,[26,27] and styrene,[27] only few studies have been reported for other aromatics so far. In the oxidation of diphenylmethane over V-MCM-41, low conversion (<16%) and benzophenone selectivity (48%) were observed.[5]

In this study, the vanadium-containing MCM-41 catalysts ((V)MCM-41) were synthesized by direct hydrothermal (4 V-MCM-41) and wet impregnation (9 V/MCM-41) methods. These two materials were characterized with various techniques and were utilized for the liquid-phase oxidation of aromatics such as diphenylmethane, ethylbenzene, 4-nitroethylbenzene, fluorene, and 9,10-dihydroanthracene. The catalytic performance was compared between the two catalysts and correlated to their properties. Furthermore, different catalytic activities were observed for various aromatic compounds due to the variation of their molecular structures.

EXPERIMENTAL

Chemical reagents

Fluorene (99%), benzophenone (99%), and anthracene (99%) were purchased from Fluka Corp. tert-Butyl-

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hydroperoxide (70% in H_2O) and 4-nitroethylbenzene (99%) were supplied by Lancaster and Avocado Corp., respectively. Ethylbenzene (99%) and acetophenone (98%) were obtained from Riedel-de Haen Corp. Diphenylmethane (99%), 9,10-dihydroanthracene (97%), 9-fluorenone (98%), anthrone (97%), anthraquinone (97%) and other chemicals were purchased from Aldrich Corp.

Catalyst preparation

4 V-MCM-41 was prepared by direct hydrothermal synthesis from vanadyl sulfate hydrate ($VOSO_4 \cdot 5H_2O$, 99%), sodium silicate, n-hexadecyltrimethylammonium bromide (95%), and sulfuric acid, following the procedures described in the literature.[28] The Si/V mol ratio in the gel was 12.5 while such ratio was 16.0 and the vanadium content was 4 wt.% in the calcined sample. Si-MCM-41 was synthesized similarly except no vanadyl sulfate hydrate was added into the starting mixture. To prepare 9 V/MCM-41, 4 g Si-MCM-41 was added into a solution containing 1.704 g vanadyl sulfate dissolved in 20 mL deionized water. The mixture was stirred, dried at 110 °C for 12 h, and finally calcined at 540 °C for 6 h. The vanadium content in this sample is 9.1 wt.%.

Catalyst characterization

The vanadium content of 4 V-MCM-41 was analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Tobin Yvon JY 38 Plus). The powder X-ray diffraction was determined by a diffractometer (Shimadzu XRD-6000) using Ni filtered CuK_α radiation ($\lambda = 0.154$ nm) with 2θ in the range of 2-10° at a scanning speed of 1°/min. The BET surface area was measured with a N_2 sorption analyzer (Quantasorb). The IR spectra of catalyst samples were recorded at room temperature on a FT-IR spectrometer (Perkin-Elmer 2000) with resolution of 2 cm^{-1}.

The catalyst acidity was evaluated by temperature-programmed desorption (TPD) of ammonia with a self designed apparatus.[29] The catalyst reducibility was determined by the temperature-programmed reduction (TPR) of H_2 gas. During the run the H_2 uptake was monitored as described elsewhere.[30] The amount of chemisorbed oxygen and the vanadium dispersion were determined with the chemisorption apparatus (Micromeretics Pulse ChemiSorb 2705) as reported in the literature.[31] The temperature was kept the same at 370 °C for both sample reduction by hydrogen gas and subsequent oxygen chemisorption on the sample. The vanadium dispersion was estimated as follows: Dispersion (%) = (2x mol of O_2 adsorbed/mol of vanadium in the sample) × 100%, where the value of 2 was the adsorption coefficient of O_2 gas on vanadium.[31]

Catalytic oxidation

Liquid-phase oxidation of aromatics with tert-butylhydroperoxide as oxidant was performed in a stirred, batch reactor (250 mL) connected with a condenser at 1 atm and 60 °C. Typically, 0.6 mL of ethylbenzene (5 mmol), 2.8 mL of tert-butylhydroperoxide (20 mmol), and 50 mL of acetonitrile (1000 mmol) were added into the glass reactor which was immersed in a water-bath. After the reaction temperature was reached, 0.05 g of catalyst was added into the reactor to start the reaction. The products were collected periodically and analyzed on a gas chromatograph (China G. C. 9800) equipped with a HP 5 column (30 m × 0.32 mm × 0.25 μm) and a flame-ionization detector. Further, they were confirmed with authentic samples as well as a combined gas chromatograph-mass spectrometer (Micromass Trio 2000).

RESULTS AND DISCUSSION

Catalyst properties

The low angle XRD patterns of various calcined samples are shown in Fig. 1. All samples exhibit four distinct peaks, corresponding to (100), (110), (200), and (210) reflections. This clearly indicates that these samples possess highly ordered mesoporous structure.[32] Apparently, both vanadium-containing MCM-41 samples display smaller 2θ angles than Si-MCM-41. Furthermore, the (100) peak intensity of 4 V-MCM-41 is lower than that of 9 V/MCM-41, which reveals the diminished crystallinity for the 4 V-MCM-41 sample prepared by direct hydrothermal method.

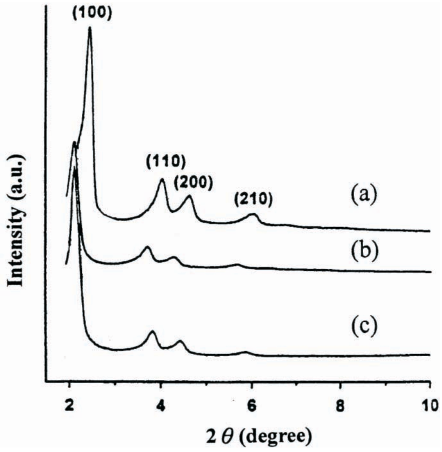


Fig. 1. The low angle XRD patterns of various calcined samples. (a) Si-MCM-41; (b) 4 V-MCM-41; (c) 9 V/MCM-41.

Table 1. Physicochemical properties of various samples

Sample	d_{100} (nm)	a_o[a] (nm)	A_{BET} (m^2/g)	Acid amount (mmol/g)	H_2 uptake (mmol/g)	O_2 adsorbed (μmol/g)	Dispersion (%)
Si-MCM-41	3.59	4.15	900	0.10	—	—	—
4 V-MCM-41	4.11	4.75	785	0.24	1.92	280	71.4
9 V/MCM-41	3.92	4.53	613	0.31	4.13	493	55.2

[a] Unit-cell length $a_0 = 2d_{100}/\sqrt{3}$

Table 1 lists physico-chemical properties of various calcined samples. Both 4 V-MCM-41 and 9 V/MCM-41 have larger d_{100} basal spacing and unit cell parameter a_o than Si-MCM-41, which is attributed to the incorporation of vanadium atoms in the MCM-41 framework. As the V-O bond distance is longer than the Si-O bond distance, the crystal lattices of vanadium-containing MCM-41 samples are thus expanded. In addition, the 9 V/MCM-41 sample has smaller a_o value in spite of its larger vanadium content as compared to 4 V-MCM-41, which implies only a certain degree of vanadium insertion in the framework of 9 V/MCM-41.[27]

It is clear that the BET surface area is reduced after vanadium introduction into Si-MCM-41 due to surface coverage by vanadium species. Fig. 2 shows the FT-IR spectra of different calcined samples. The broad band at 1076 cm^{-1} with a shoulder at 1237 cm^{-1} and the band at 806 cm^{-1} are ascribed to Si-O stretching and Si-O-Si bending, respectively.[33,34] A slight decrease in the wavenumber of these bands is observed in both samples (Fig. 2b & 2c), showing the substitution of Si by V in the MCM-41 framework. Moreover, Si-MCM-41 exhibits a band at 960 cm^{-1}, which is attributed to Si-O stretching vibration of Si-OH group.[28,35] Although the assignment of this band is still controversial, the enhanced intensity of this band in both 4 V-MCM-41 and 9 V/MCM-41 samples is generally attributed to the presence of V-O-Si linkage.[36,37] The above results of vanadium incorporation in the MCM-41 framework are in agreement with the XRD studies.

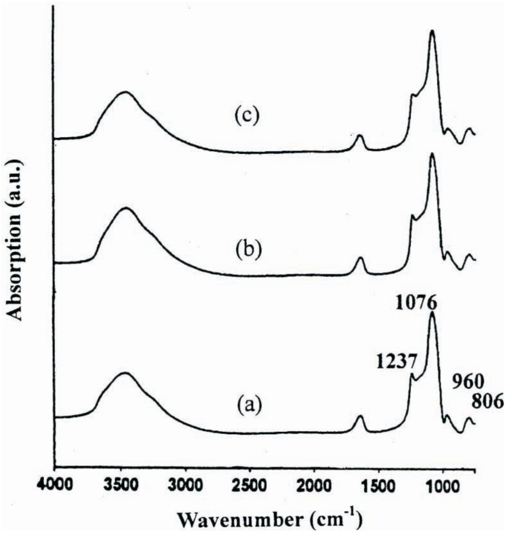


Fig. 2. FT-IR spectra of various calcined samples. (a) Si-MCM-41; (b) 4 V-MCM-41; (c) 9 V/MCM-41.

The TPD of ammonia profiles from various samples are depicted in Fig. 3. A very broad and small peak is found for Si-MCM-41, showing the location of lesser weak acid sites in this sample.[38] Introduction of vanadium in the samples causes the appearance of a major peak centered at about 168 °C. Consequently, both vanadium-containing samples own weak acidity and their acid amounts are larger than that of Si-MCM-41 (Table 1). Such result demonstrates that the vanadium sites in the structure should be the main sources for the acidity of vanadium-containing MCM-41 catalysts.[34]

In general, the availability and reactivity of active species in the oxidation catalyst are characterized by the TPR technique. Fig. 4 shows the TPR of hydrogen profiles

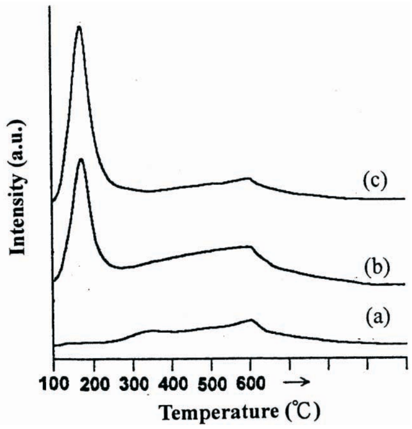


Fig. 3. TPD of ammonia profiles from various calcined samples. (a) Si-MCM-41; (b) 4 V-MCM-41; (c) 9 V/MCM-41.

from the two calcined vanadium-containing samples. A broad peak centered at 540 °C and 562 °C is observed for 4 V-MCM-41 and 9 V/MCM-41, respectively. 4 V-MCM-41 reveals lower reduction temperature than 9 V/MCM-41 since it has better vanadium dispersion (see below). As a result, the vanadium-oxygen species in 4 V-MCM-41 can be reduced more easily and thus have higher oxidation ability than those in 9 V/MCM-41. It is noted that the hydrogen uptake is proportional to the vanadium content, indicating complete reduction of all vanadium-oxygen species in the samples during the TPR run.

The metal dispersion of supported V_2O_5 after reduction in hydrogen has been determined by oxygen chemisorption.[31,39] It is important to control the same temperature of 367 °C for both the reduction and subsequent oxygen chemisorption of catalyst surface without involving the bulk phase.[31] The same operating temperature of 370 °C was applied in this study. Table 1 indicates the amount of chemisorbed oxygen per gram of catalyst and the calculated vanadium dispersion. 4 V-MCM-41 has markedly higher dispersion than 9 V/MCM-41 in accordance with its lower reduction temperature in the H_2-TPR diagram (Fig. 4 and Table 1).

Catalytic oxidation

To compare the effect of different substrates on catalytic activity, two types of aromatics were chosen. One was alkylaromatic compounds including diphenylmethane, ethylbenzene, and 4-nitroethylbenzene. The other was benzylic cyclics such as fluorene and 9,10-dihydroanthracene. The products in the liquid-phase oxidation of these aromatics with tert-butylhydroperoxide over vanadium-containing MCM-41 catalysts are illustrated in Scheme I. The solvent of acetonitrile was selected because it has been shown as an effective solvent in the related oxidation reactions.[9,32] In case of 9,10-dihydroanthracene, a combination of acetonitrile and benzene was used as solvents to increase the mutual solubility among different constituents in the reaction mixture. The reaction temperature of 60 °C was chosen to avoid faster decomposition of tert-butylhydroperoxide at higher temperatures. The conversion and product selectivity are calculated with respect to the moles of aromatic substrate converted. According to preliminary runs at variant stirring speeds of 50, 100, 200, and 300 rpm, it was found that the reaction system was free of diffusional limitation at a speed of 200 rpm. Consequently, this stirring speed was utilized for all further reaction runs.

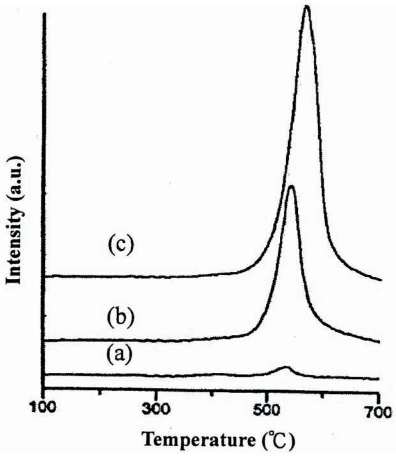
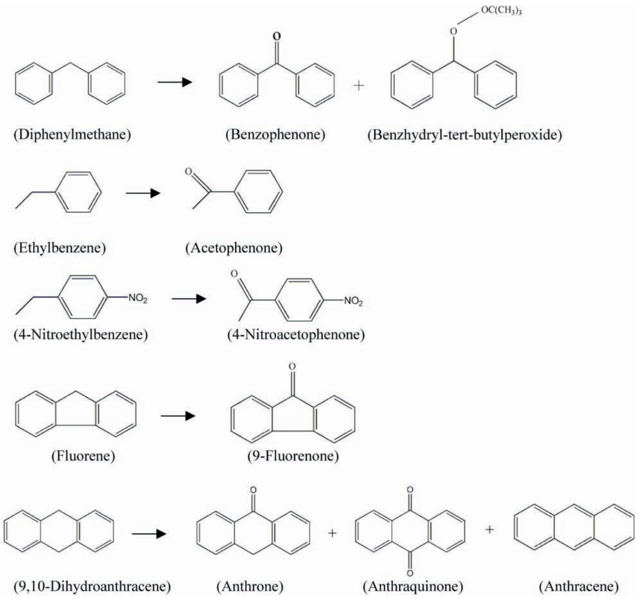


Fig. 4. TPR of hydrogen profiles from various calcined samples. (a) Si-MCM-41; (b) 4 V-MCM-41; (c) 9V/MCM-41.

Scheme I



In the oxidation of diphenylmethane, the main and side products are benzophenone and benzhydryl-tert-butylperoxide, respectively. With ethylbenzene and 4-nitroethylbenzene, complete selectivity to acetophenone and 4-nitroacetophenone are observed, respectively. For fluorene oxidation, 9-fluorenone is the only product. In case of 9,10-dihydroanthracene, the product anthracene is formed via oxidative dehydrogenation whereas anthrone and anthraquinone are produced by successive oxidation on the methylene groups of the substrate. Fig. 5 shows the conversion and product yields as a function of reaction time in the oxidation of 9,10-dihydroanthracene over 4 V-MCM-41.

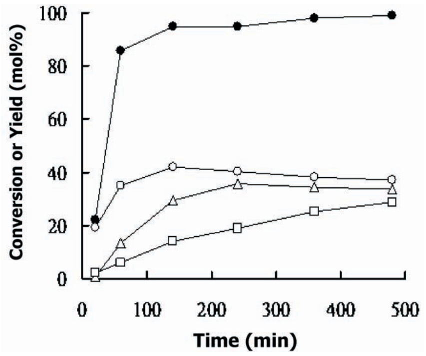


Fig. 5. The influence of reaction time on the conversion and product yields in the oxidation of 9,10-dihydroanthracene over 4 V-MCM-41. (●) conversion; yield: (○) anthrone; (Δ) anthraqinuone; (□) anthracene.

Clearly, anthrone is the reaction intermediate and anthraquinone is the final product. Table 2 presents the catalytic results for the oxidation of these aromatics over vanadium-containing MCM-41 catalysts. It is noticeable that for all substrates except ethylbenzene and 4-nitroethylbenzene both catalysts exhibit good catalytic performance due to their characteristic mesoporous structure, large specific surface area and accessible vanadium-oxygen species (Fig. 1 and Table 1). Further, 4 V-MCM-41 shows superior activity than 9 V/MCM-41, which is attributed mainly to the better dispersion and higher oxidation ability of vanadium-oxygen species as active sites in the MCM-41 framework. The role of catalyst acidity should cause little effect on catalytic activity because the catalytic activity does not correlate with the catalyst acid amount (Table 1 & 2). It is noteworthy that the single-site, isolated vanadium centers in 4 V-MCM-41 show much higher activity (based on the turnover number, TON) than those containing more vanadium atoms in 9 V/MCM-41. Similar results were reported in the oxidation of benzene[26,27] and styrene.[27]

As indicated in Table 2, the ratios of catalyst (g) : substrate (mmol) : oxidant (mmol) : solvent (mmol) are not the same for all substrates. However, it is known that the substrate conversion enhances with the ratio of catalyst/substrate as well as oxidant/substrate. Hence, the conversions of diphenylmethane and 9,10-dihydroanthracene should become larger and smaller, respectively, under the same ratio as that for ethylbenzene, 4-nitroethylbenzene, or fluorene. As a result, the activity based on the turnover number decreases in the order of diphenylmethane > fluorene > 9,10-dihydroanthracene > ethylbenzene ≥ 4-nitroethylbenzene. This activity difference can be attributed to the dissimilarity of molecular structures of various substrates. A comparison of the oxidation of diphenylmethane and that of ethylbenzene reveals that the reactivity of the -CH_2- group attached to the benzene ring depends strongly on the other group like phenyl and methyl. Electronic resonance is supposed to occur in phenyl group of diphenylmethane, resulting in favorable activity whereas the electron donating methyl group of ethylbenzene exhibits adverse effect on the oxidation activity. Therefore, diphenylmethane shows remarkably higher activity than ethylbenzene. It is interesting to note that the presence of the electron withdrawing -NO_2 group on the 4-postion of benzene ring in ethylbenzene decreases only slightly the reactivity.[3,6] For the oxidation of fluorene, the fused penta carbon cyclic between two benzene rings diminishes the electronic resonance on these rings, which lowers the oxidation reactivity of the methylene group. This effect is even more pronounced for the ox-

Table 2. Catalytic results in the oxidation of various aromatics

Substrate	Ketone product	Catalyst	Conversion (%) 1 h/3 h	Selectivity (%) 1 h/3 h	TON 1 h/3 h
Diphenylmethane	Benzophenone	4 V-MCM-41	43.0/58.0	84.7/80.7	91.2/123
		9 V/MCM-41	37.7/55.3	74.6/71.0	35.2/51.6
Ethylbenzene	Acetophenone	4 V-MCM-41	7.8/18.0	100/100	9.7/22.4
		9 V/MCM-41	8.7/16.7	100/100	4.8/9.2
4-Nitroethylbenzene	4-Nitroacetophenone	4 V-MCM-41	6.8/14.1	100/100	8.7/18.0
		9 V/MCM-41	6.1/13.7	100/100	3.4/7.6
Fluorene	9-Fluorenone	4 V-MCM-41	52.9/97.3	100/100	67.4/124
		9 V/MCM-41	22.9/83.8	100/100	12.8/46.9
9,10-Dihydroanthracene	Anthrone + Anthraquinone	4 V-MCM-41	54.6/89.2	35.5/53.5	34.8/56.8
		9 V/MCM-41	28.1/54.6	50.4/63.6	7.9/15.3

Reaction conditions: temperature = 60 °C, catalyst (g): substrate (mmol): oxidant (mmol): solvent (mmol) = 0.3: 50: 100: 800 for diphenylmethane; 0.05: 2.5: 10: 770 (acetonitrile) + 560 (benzene) for 9,10-dihydroanthracene; 0.05: 5: 20: 1000 for all other substrates.

idation of 9,10-dihydroanthracene with two methylene groups. Hence, the activity order of various substrates is interpreted according to the above discussion.

CONCLUSIONS

Aromatic compounds were selectively oxidized to their corresponding ketones at 1 atm and 60 °C under mild reaction conditions using vanadium-containing MCM-41 catalysts prepared by direct hydrothermal synthesis (4 V-MCM-41) and wet impregnation methods (9 V/MCM-41). Both catalysts are effective for the liquid-phase oxidation of aromatics with tert-butylhydroperoxide due to highly ordered mesoporous structure, large specific surface area, and easily accessible active sites of vanadium-oxygen species. Further, the 4 V-MCM-41 material possesses larger values of unit cell parameter a_o, BET surface area, vanadium dispersion as well as stronger oxidation ability as compared to the 9 V/MCM-41 material. As a result, 4 V-MCM-41 shows remarkably better catalytic performance in the oxidation reaction. A comparison of catalytic activity of various aromatics based on the turnover number follows the order of diphenylmethane > fluorene > 9,10-dihydroanthracene > ethylbenzene ≥ 4-nitroethylbenzene. This activity difference is attributed to the electronic effect of the group attached to methylene group in aromatics due to their distinct molecular structures.

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