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Radius of curvature effect of V-MCM-41 probed by methanol oxidation

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Abstract

A series of V-MCM-41 samples was prepared with very long-range ordered structure, different pore sizes, and constant composition by applying a recently developed quantitative model [Y.H. Yang, S.Y. Lim, C. Wang, D. Harding, G.L. Haller, Micropor. Mesopor. Mater. 67 (2–3) (2004) 245–257]. Oxygen titration of catalysts pre-reduced with methanol vapor at the reaction temperature showed a constant active site density regardless of the pore diameter at lower temperature. A pore wall radius of curvature effect on the catalytic reaction existed when the methanol oxidation was used as a probe reaction over a 100-K temperature range (573–673 K). The effect was represented by a "volcano curve" in which the turnover frequency increases with increasing pore diameter to a maximum and then decreases. The effect of pore size on active site density at temperatures above the reaction temperature was observed, a result associated with the pore size effect on stability of Si–O–V units in the pore wall. Based on previous research, there were no surface vanadium compounds in our catalysts, a fact confirmed by Raman spectroscopy for both fresh and used catalysts. Several different characterization techniques, including nitrogen physisorption, X-ray diffraction, and ultraviolet–visible spectroscopy, were used to demonstrate that the structural stability of catalysts determines the activity and how vanadium incorporation into the framework controls the selectivity of reactions. Hydrogen temperature-programmed reduction experiments over the same series of V-MCM-41 catalysts demonstrated that reduction stability was influenced by the radius of curvature, and that there was a strong correlation between the reducibility and selectivity of formaldehyde and dimethyl ether.

Keywords: Radius of curvature effect; V-MCM-41; Methanol oxidation; N_2 Physisorption; X-Ray diffraction; Ultraviolet–visible spectroscopy; Raman spectroscopy; H_2 Temperature-programmed reduction

1. Introduction

Methanol oxidation is an important chemical reaction that produces valuable intermediates used in chemical industry. Methanol, as the major starting reactant, can be used for the synthesis of various useful products, including hydrocarbons and mild oxidation products. Among these oxidation processes, the production of formaldehyde for the synthesis of phenolic resins is largely preferred [2]. Methyl formate and dimethyl ether may be produced with high selectivity and yield directly by catalytic methanol oxidation on vanadium oxide catalysts [3,4]. These versatile products are of great interest for industry, because they can be transformed into N–N dimethyl formamide or acetic acid [5]. Methanol oxidation was chosen to be a good probe reaction and to characterize the surface properties of some oxide catalysts because this reaction is sensitive to the structure of the catalyst surface, which allows a meaningful comparison among the catalysts tested. Compared with other oxidation reactions, methanol oxidation has a wide selectivity pattern and set of reaction mechanisms [2].

Among the silica-supported metal oxide catalysts, V_2O_5/SiO_2 catalysts have been identified as some of the most selective catalysts for methanol oxidation to formaldehyde [6,7]. Wachs et al. [8] summarized extensive studies and various techniques, grouped by experimental conditions, that have been conducted to identify the molecular structures of dispersed surface vanadium oxide species on silica supports, in an effort to better understand their physicochemical and catalytic properties.

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Porous materials are of great utility as catalysts for industrial applications; their large surface areas (>1000^2/g for MCM-41) can enhance the efficiency of catalysis and sorption [9]. The idea of introducing foreign atoms into solids to change their catalytic properties, such as activity and selectivity, is one of the main themes of heterogeneous catalysis research. The isomorphous substitution of certain transition metals into the zeolite lattice produces catalysts with remarkable catalytic activity for partial oxidation of hydrocarbons. However, these materials are restricted to structures with pore diameters <1.3 nm. Large organic molecules are severely hindered in zeolites [10]. A new mesoporous molecular sieve, designated MCM-41, was patented by Mobil scientists in 1992 [11,12]. MCM-41 has a regular array of hexagonal, uniform, and one-dimensional mesopores that can be systematically changed in size from 1.6 to 10 nm. It bridges the gap between crystalline zeolites and amorphous silica in terms of pore size and pore size distribution. The MCM-41 catalysts present an opportunity for the constitution of catalytically active sites inside uniform channels with controllable nano-order pore diameter.

The original goal of this research was to test the hypothesis that the activity and selectivity of a catalytic site might be varied by changing the radius of curvature of the pore wall in terms of pore diameter on which the catalytic site was located. Derouane et al. [13] discussed the radius of curvature effect for the case of reaction in a zeolite. They hypothesized that the surface curvature effect allows one to coherently rationalize various isolated observations in physisorption and catalysis by zeolites. Namely, the dependence of sorption heats on pore size is now accounted for in a continuous range of surface curvatures. More recently, researchers have demonstrated the effect of radius of curvature on cracking and disproportionation reactions [14,15], but in these microporous catalysts the catalytic effect was not directly associated with the radius of curvature. In fact, the direct chemical effect on the catalytic activity could not be determined, because there are no known zeolites in which pore size can be varied without also varying both the composition and structure [16].

Even though the radius of curvature changes in the mesoporous MCM-41 is small compared with the microporous zeolites (1.9–2.9 nm for MCM-41 used here, compared with about 0.4–1.3 nm for zeolites), very small changes in local geometry might have significant effects on atomic properties that could affect catalytic activity. Feng et al. [17] observed a radius of curvature effect on catalytic activity using an acid-catalyzed isomerization of 2-methyl-2-pentene as a probe reaction on Al-MCM-41. They found an apparent variation in acid strength of about a factor of 5 as the pore size was decreased by about a factor of 2. A more prominent effect of pore size on reaction, mediated by a Pt cluster, was reported by Chueh et al. [18]. Here the support appears to become more basic, and the metal cluster senses this change as the pore size becomes smaller. Most recently, the pore size of Co-MCM-41 catalyst was observed to have a dramatic influence on Co cation reducibility and the resulting Co cluster size, which is a very crucial factor in controlling the diameter of single-wall carbon nanotubes synthesized on Co-MCM-41 with different but uniform diameter pores [19].

A convincing example of radius of curvature effect on catalytic activity has been observed for methanol oxidation with vanadium-containing MCM-41 (V-MCM-41), which has received particular attention because many oxidation catalysts contain vanadium as an active component [10]. The reaction rate changes about one order of magnitude and reaches a maximum at a certain pore diameter of V-MCM-41 catalysts. For the work reported in this paper, we prepared highly ordered (relative to the previous V-MCM-41 preparation [10]) V-MCM-41 as catalysts to systematically investigate the radius of curvature effect on catalytic behavior of these materials in the gas phase methanol oxidation reaction using molecular oxygen. We used various characterization techniques, including nitrogen physisorption, X-ray diffraction (XRD), Raman spectroscopy, and ultraviolet–visible (UV–vis) spectroscopy, to characterize the fresh and used catalysts.

2. Experimental

2.1. Synthesis

Our goal was to quantitatively determine the association between pore size and catalytic activity and selectivity. To do this, we needed to synthesize V-MCM-41 with a very high degree of structural order, constant composition, and different pore sizes. Based on previous research experience, we knew that these three variables would interact. That is, ideally we wished to change the pore diameter at constant composition (V loading) and structure (e.g., degree of long-range order, defects); however, changing the radius of curvature affects the stability of Si–O–V units in the pore wall, so that, all other variables held constant, the amount of V incorporated also varies. Most recently, our laboratory developed quantitative models that correlate these three variables with the synthesis parameters (e.g., alkyl chain length of surfactant, metal concentration in the synthesis suspension, water content). Results demonstrate that models are reasonably good at predicting the structure, pore diameter of V-MCM-41 samples, and vanadium loading. Based on these modeling functions, synthesis conditions were determined to prepare samples with predicted highly ordered structure and different pore diameter but the same vanadium loading. Properties of the catalyst samples used in these experiments are given in Table 1. The synthesis procedure was as described previously [1].

2.2. Characterization

2.2.1. N_2 physical adsorption

Adsorption–desorption isotherms of N_2 at 77 K were measured with a Quantachrome Autosorb-1C static volu-

Table 1
The V-MCM-41 catalysts used in methanol oxidation

ID	Slope of capillary condensation (a.u.)	Diameter (nm)	V loading (wt%)
C16	3667	2.87	0.39
C14	2949	2.54	0.35
C12	1324	2.28	0.33
C10	844	1.89	0.34

metric instrument. Pore size and pore size distribution were calculated by the BJH method using the desorption branch of the isotherm.

2.2.2. XRD

XRD using a SCINTAG X-ray diffractometer (Cu$K\alpha$, wavelength $\lambda = 1.542$ Å) was done to determine whether the prepared V-MCM-41 has the characteristic hexagonal pore structure after calcination.

2.2.3. Diffuse reflectance UV–vis spectroscopy

Diffuse reflectance spectra were recorded in the UV–vis region on a Hewlett–Packard 8452A diode array spectrometer. The spectra were recorded in air at room temperature.

2.2.4. Raman spectroscopy

Raman spectra were recorded using an excitation wavelength of 532 nm on a LabRam instrument from Jobin Yvon Horiba equipped with an Olympus confocal microscope. Samples were pressed into wafers and dehydrated at 393 K for 1 h before each scan, to remove surface moisture. Spectra were collected over different wafer locations and averaged to obtain the final spectrum.

2.2.5. Temperature-programmed reduction (TPR)

The reducibility and the stability of C10–C16 V-MCM-41 samples prepared were investigated by a TPR technique using a thermal conductivity detector (TCD) of a gas chromatograph (6890 Plus; Agilent). Approximately 200 mg of each sample was loaded into a quartz cell. Before each TPR run, the sample cell was purged with ultra zero-grade air at room temperature, and then the temperature was increased to 773 K at a rate of 5 K/min. The sample was soaked for 1 h at that temperature, then cooled to room temperature. This procedure was performed to oxidize adsorbed hydrocarbon species before running the TPR. The gas flow was switched to 5 vol% hydrogen in argon balance, and the baseline was monitored until stable. After baseline stabilization, the sample cell was heated at 5 K/min and held for 1 h at 1173 K to ensure complete vanadium reduction. An acetone trap was installed between the sample cell and the TCD to condense any water produced by sample reduction.

2.2.6. Inductively coupled plasma (ICP) analysis

Because the preparation process may result in some loss of vanadium and silica in the byproducts, the vanadium content of each sample was measured by the inductively coupled plasma (ICP) technique at Galbraith Laboratories.

2.2.7. Methanol oxidation

In this work we used gas phase partial oxidation of methanol to formaldehyde (CH_2O) and dimethyl ether (CH_3OCH_3) as a probe reaction to test the effect of radius of curvature on the catalytic activity of the V-MCM-41 catalysts. The methanol oxidation was carried out in a computer-controlled reaction system. The reaction was performed in an isothermal fixed-bed downflow 10-mm i.d. quartz reactor operating at atmospheric pressure; 150 mg of catalyst was held in the middle of the reactor. The helium was bubbled through a methanol saturator to maintain a constant flow rate of the liquid vapor. The oxygen and another helium stream, both mass-flow controlled, were then combined with the methanol vapor to give a flow rate of 109 sccm with the reactant mixture of O_2 ($\sim$3 vol%), methanol ($\sim$3 vol%), and helium (balance). The outlet of the reactor to the gas chromatograph was heated at 393 K, to avoid product condensation. The products were analyzed by an on-line gas chromatograph (HP 6890) equipped with a TCD and a Hayesep T column (100/120 mesh, 6 ft. long). Blank runs were performed on the empty quartz reactor without any detectable conversions of methanol. Samples were pretreated at 773 K for 60 min in an air stream before each run. The oxidative dehydrogenation was then carried out over a 100-K temperature range (573–673 K) to obtain the conversion, selectivity, and activation energy data. The conversion was controlled at around 20%. The activities for different catalysts were converted to turnover frequency, the moles of methanol converted per mole of surface active site density per second.

2.2.8. Oxygen titration

The oxygen uptake was evaluated to obtain the surface active site density in a computer-controlled automatic flow system equipped with an online TCD. Samples (50 mg) were loaded into a quartz tube cell, and a four-way valve allowed switching between the pretreatment gas and carrier gas without the need to disconnect the sample cell. The oxygen chemisorption on V-MCM-41 samples was measured after reduction under reaction conditions by dosing very small amounts of oxygen over the catalyst samples. The catalysts were recalcined at 773 K for 1 h in flowing air, then the reduction was performed at each actual methanol oxidation condition in 3 vol% flowing methanol vapor, the helium balance needed to reach 1 atm pressure. After reduction, a large flow of UHP helium was applied at reaction temperature to remove the physisorbed methanol and further clean the catalyst surface. The catalysts were then exposed to a sequence of 0.0125-ml oxygen pulses at 5-min intervals under the reaction conditions. The oxygen taken up was measured with the aid of the TCD after product separation using the Hayesep T column.

3. Results and discussion

3.1. Active site density

Knowledge of the density of surface active sites allows one to calculate the catalytic turnover frequency during the methanol oxidation. To obtain the actual density of active sites at reaction conditions, we performed titration at the same temperature as reaction, and found that the uptake of oxygen was normalized by vanadium concentration, as shown in Fig. 1. At a temperature of 573 K, the active site density (reducible V^{+5}) is quite low compared with the vanadium loading: 0.05 mol oxygen/1 mol vanadium. The catalyst adsorbs only 0.1 mol of oxygen per 1 mol of vanadium even when the temperature is increased to 623 K. This suggests that most of the vanadium species are incorporated in the silica framework instead of on the surface, and thus are not easily reduced at 573 K. Oxygen uptake by surfaces of pre-reduced catalyst samples demonstrates an apparent effect of pore size on active site density at 673 K. The catalysts have a higher active site density in large and small pores, but this density is still quite low (<0.2 mol O/1 mol V adsorption) in intermediate pores, even at 673 K. The Si–O–V bond angle may vary with changes in pore diameter, and the stability of Si–O–V units in the pore wall may be changed, resulting in altered catalytic behavior of this active site. This trend is not clear at low temperature, which is consistent with the findings of previous work in our laboratory [10].

A challenge still exists regarding the different approaches used to quantify the surface active site density on metal oxide catalysts. Some authors have suggested that methanol reduction pretreatment leads to unreliable oxygen titration results because of formation of the $V–OCH_3$ group, which is quite volatile and will migrate quickly to agglomerate into large-surface vanadium species [20]. But our samples were prepared hydrothermally with extremely low vanadium loading (~0.02 V atoms/nm^2), and previous work using different characterization techniques confirmed that no surface vanadium compounds could be detected [1]. In this study the dispersion of vanadium was studied by Raman spectroscopy. Fig. 2 shows the spectra of fresh and used V-MCM-41 samples used for the methanol reactions compared with the impregnated samples with higher vanadium content, with impregnated samples prepared as described elsewhere [8]. A strong Raman band at 994 cm^{-1} due to surface V_2O_5 crystallites exists with 5 wt% vanadium impregnated onto the silica support Cab-O-Sil. However, only the 1032 cm^{-1} band, which is assigned to the V=O stretching vibration of isolated VO_4 species, shows when the same amount of vanadium was impregnated into the Si-MCM-41 support. This finding is probably due to the greater surface area of Si-MCM-41 (>1200 m^2/g). The strength of this Raman band decreases with decreasing vanadium content. The same Raman band profile as observed in results published elsewhere was observed when 1.0 wt% vanadium was impregnated with Cab-O-Sil silica source [8]. But once the

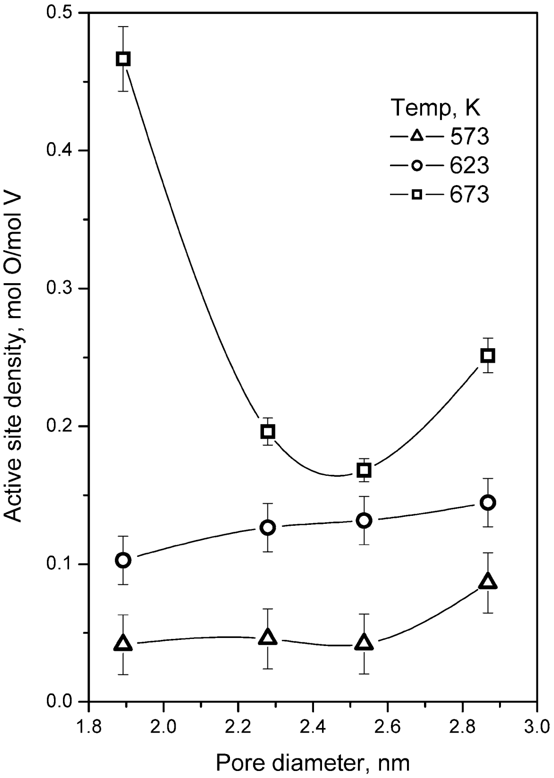

Fig. 1. Profile of active site density as function of temperature and pore diameter.

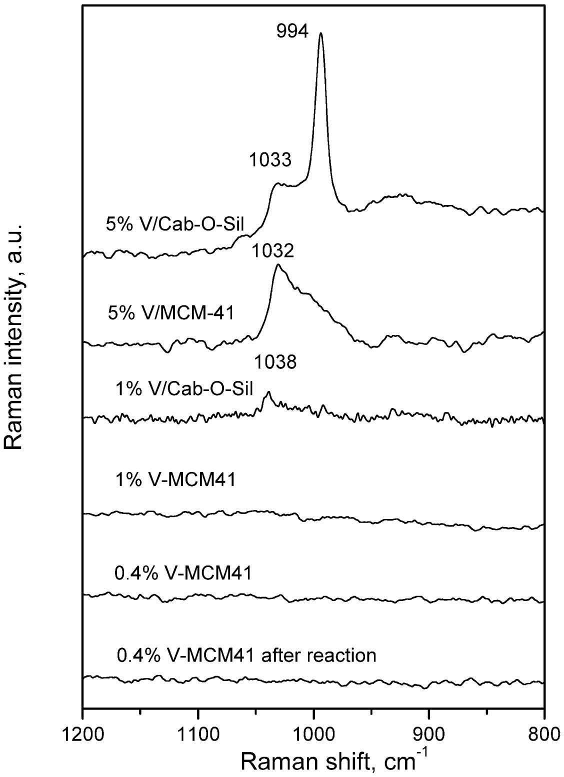

Fig. 2. Raman spectrums of dehydrated V-MCM-41 samples before and after methanol oxidation.

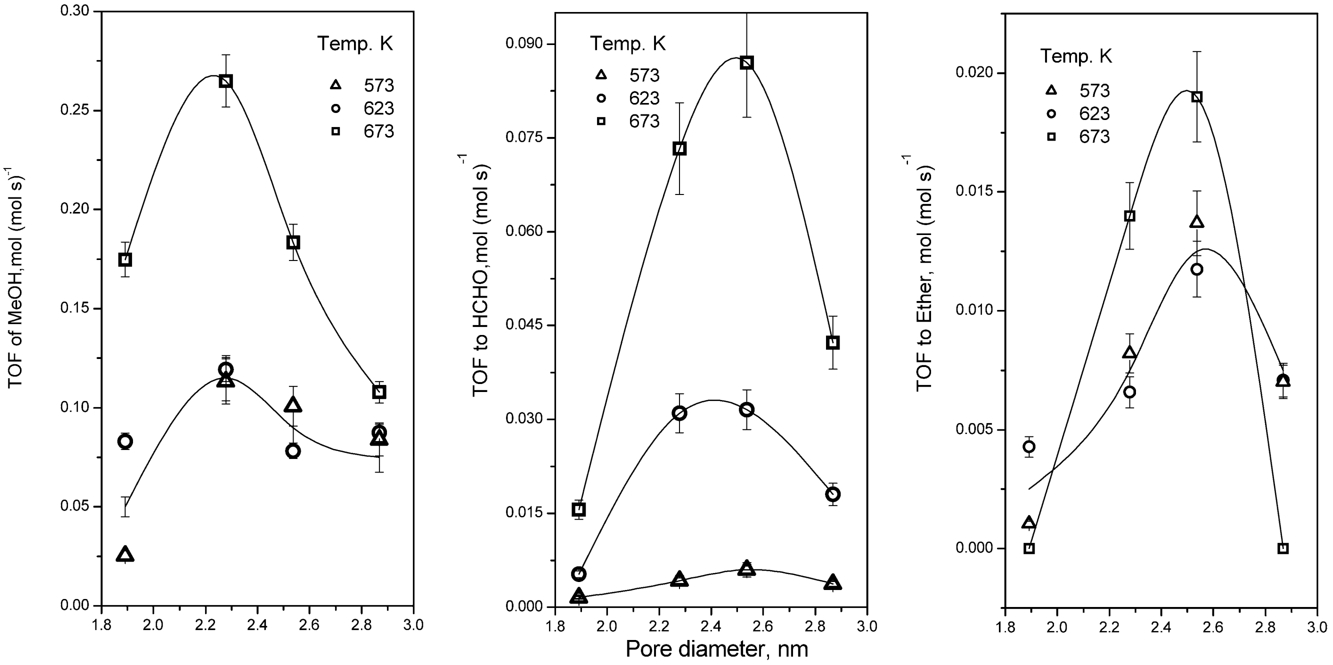

Fig. 3. Effect of pore size on the turnover frequency to methanol, formaldehyde and dimethyl ether.

samples are prepared hydrothermally with low vanadium loading (∼0.4 wt%), a Raman band for V is no longer detected in the MCM-41 matrix, because of the atomic-level dispersion of vanadium species. Even after methanol oxidation, there is no evidence of vanadium migration on the surface to form V_2O_5 crystallites.

Based on these Raman results and previous studies [1], all of the vanadium species was atomically incorporated into the framework of MCM-41. They will not migrate on the surface under the condition of methanol oxidation, even though the $V–OCH_3$ intermediates are quite volatile. Thus the active site density calculated by oxygen titration should be reliable.

3.2. *Gas phase methanol oxidation*

Di Wei et al. [10] observed a strong effect of pore diameter when they plotted the rate of methanol conversion and formaldehyde production as a function of pore size (varied by the template chain length used in the synthesis). They sought to interpret the phenomena by means of XANES and to attribute this effect of pore size to the increasing rate of V ion reduction with increasing pore size (as the radius of curvature increases and bond angles relax); however, in their work the catalyst structure was not very good, and the concentration of vanadium loaded in the silica framework was not constant.

In the present research, improvements in the synthesis procedure [1] allow us to prepare catalysts with highly ordered structure and maintain the chemical composition based on the quantitative model for predicting the synthesis of V-MCM-41 catalysts that we developed. We carried out gas phase oxidative dehydrogenation of methanol over a 100-K temperature range (573–673 K) on these samples. During the reaction we detected formaldehyde, dimethyl ether, CO, CO_2, and trace amounts of methyl formate; however, we consider only the main products formaldehyde and dimethyl ether in this discussion.

We observed a strong effect of pore size on catalytic reactivity and selectivity in this series of V-MCM-41 samples. Interestingly, this effect is represented by a "volcano curve" in which the turnover frequency increases with increasing pore diameter to a maximum and then decreases. The highest value of the turnover frequency is four times larger than the lowest value at the same temperature. Higher reaction temperature not only increases the reaction rate in terms of turnover frequency, but also has a significant influence on this volcano profile. All turnover frequencies here are normalized to the oxygen uptake at the same temperature for reaction. Our results show significantly greater TOF compared with results published elsewhere with comparable low vanadium loading [7]. This is probably due to the strong effect of the support. The MCM-41 materials used in this study have highly ordered structure and enormous surface area.

Because all of the catalyst samples have a constant vanadium concentration and active site density (low temperature), but different pore diameters, we can attribute this phenomenon to the pure effect of the radius of curvature, as shown in Fig. 3. The maximum reaction rate occurs at different pore diameters for the conversion of methanol and the synthesis of formaldehyde and ether, which makes interpretation of the experimental results very difficult. One possible explanation for these findings might be that the conversions of methanol to formaldehyde and methanol to ether are controlled by different mechanisms, as would be expected. The radius of curvature has the largest influence on the formation of dimethyl ether, which is the largest molecule among these

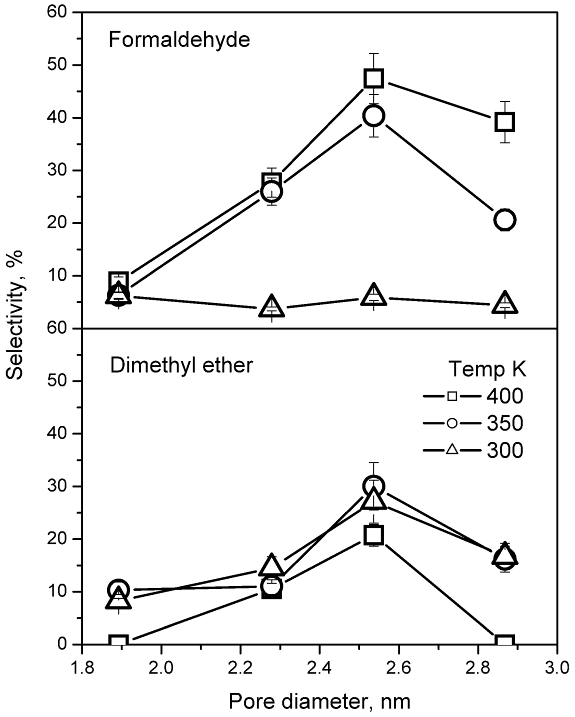

Fig. 4. Radius of curvature effect on the selectivity of formaldehyde and dimethyl ether.

three species; the turnover frequency changes about one order of magnitude. A possible rationalization for this may be that the relatively larger the molecule, the more restriction that the pore imposes on the molecular mobility. The T–O–T bond angle is the most important structural factor in zeolites; for example, varying the T–O–T angle will change the acidity of the proton on the bridging hydroxyl of Si–OH–Al in most zeolites [21]. The fundamental chemical variable is the change in the relative participation of *s* and *p* orbitals in the bonding. A similar proposal can be assumed here, and this phenomenon might be related to the change in stability and/or reducibility of Si–O–V unit in terms of the local bond angles of Si–O–V in the V-MCM-41 catalyst samples with changes in the degree of curvature of the pore wall. In the case of V-MCM-41, which has acidity due to impurities, the acidity (i.e., selectivity to dimethyl ether) is also affected by the Si–O–V bond angles. This result is a very good example demonstrating how methanol oxidation can lead to various products by varying the catalyst structure and the reaction conditions.

Fig. 4 shows the selectivity of formaldehyde and dimethyl ether as functions of temperature and pore diameter of the V-MCM-41 catalysts. Different reaction conditions (in terms of temperature here) lead to various selectivities of formaldehyde and dimethyl ether. Interestingly, the radius of curvature also affects the selectivity of both formaldehyde and dimethyl ether. They also exhibit the volcano curvel, which is quite similar to the turnover frequency profile. The larger-pore catalysts have roughly three- to five-fold greater selectivity than the smaller-pore catalysts. With increasing temperature, selectivity to formaldehyde increases for the larger-pore catalysts, reaching a maximum around 50% for the catalyst with a pore size of ∼2.6 nm at a temperature of 673 K. For the small-pore catalyst (pore diameter ∼1.9 nm), selectivity is very low (∼10%) and independent of temperature. Dimethyl ether shows a negative trend of selectivity as a function of temperature. Considering possible reaction schemes, dimethyl ether can be obtained directly through bimolecular dehydration of methanol, and formaldehyde formation requires one oxidation step. Therefore, dimethyl ether selectivity may describe a catalyst's pure dehydration capacity, which is generally related to its acidic character. If strong acid sites and very weak basic centers are present, then only dimethyl ether is formed; formaldehyde formation prefers both weak acid and basic sites [22]. According to earlier results in our laboratory, only the weak Lewis acid site was found on the surface of the V-MCM-41 samples, yielding formaldehyde as the main product for the current reaction [29]. The acid strength of active sites probably decreases with increasing temperature, because formaldehyde formation increases at higher temperatures.

The silica source used to prepare the V-MCM-41 samples was HiSil 233 (Pittsburgh Plate Glass), containing 2.5 wt% NaCl impurity, which produces strong acidic sites on these catalysts. As described earlier, the production of dimethyl ether is associated with the acidic impurities; complementary experiments were conducted to verify the correlation between acidic impurities and dimethyl ether formation. Ultra-high-purity silica (Cab-O-Sil; Cabot Co.) was used as the silica source to prepare the V-MCM-41 samples with different pore diameters but the same vanadium content, as described previously [1]. Methanol oxidation and oxygen titration were carried out to quantify the reaction activity and active site surface density. The reaction shows formaldehyde and CO_2 only (and almost 100% selectivity to formaldehyde with C14-V-MCM-41 with a pore size of about 2.6 nm), with no detectable dimethyl ether. Clearly, there are no strong acidic sites on the surface of V-MCM-41 that can catalyze the methanol oxidation to dimethyl ether. Fig. 5 shows clear volcano profiles of methanol TOF and illustrates the selectivity of formaldehyde maximum at a pore size of about 2.6 nm using Cab-O-Sil as the silica source. These results are consistent with those obtained for the V-MCM-41 samples prepared with HiSil 233 as the silica source.

Lim et al. [23] studied higher loading of vanadium and found that methanol oxidation is not significantly affected by the pore size of V-MCM-41. That is, there is no obvious direct effect of the radius of curvature on methanol oxidation at higher loading. However, activity is indirectly affected by pore size, because the amount of incorporated vanadium content changes with pore size. In Lim et al., the vanadium loading was rather high (>1 wt%, up to 1.77 wt%). This high vanadium loading likely overwhelms the effect of the change in pore diameter. Also, the active site density in his case was extremely high for some of the experiments (O_2:V molar ratio of 1.45). Excess vanadium was exposed

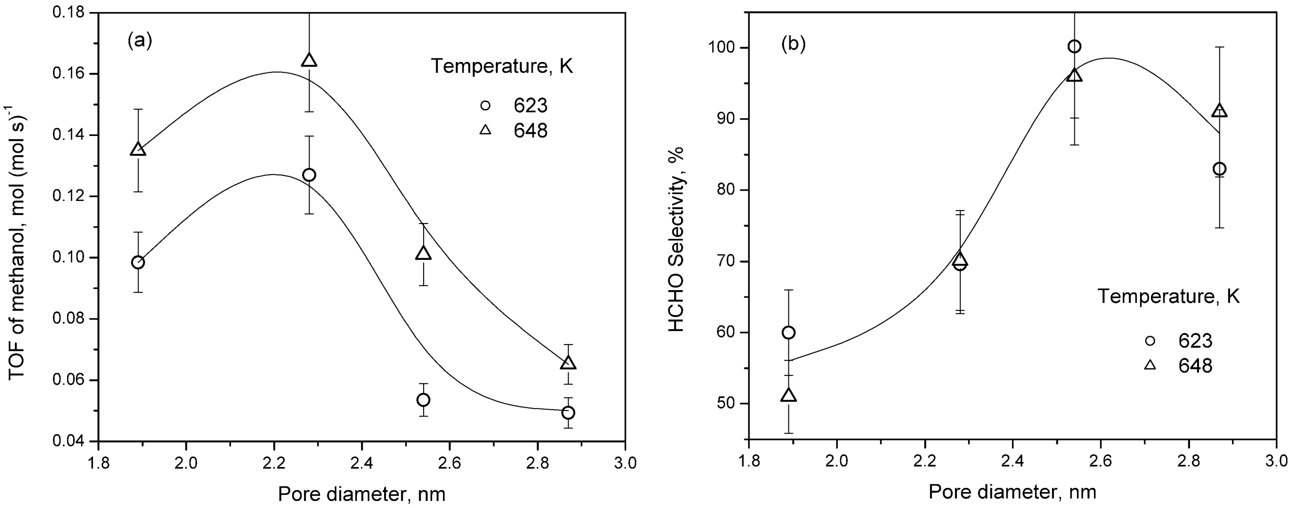

Fig. 5. Radius of curvature effect on the turnover frequency to methanol and the selectivity of formaldehyde by using high purity silica source to prepare V-MCM-41.

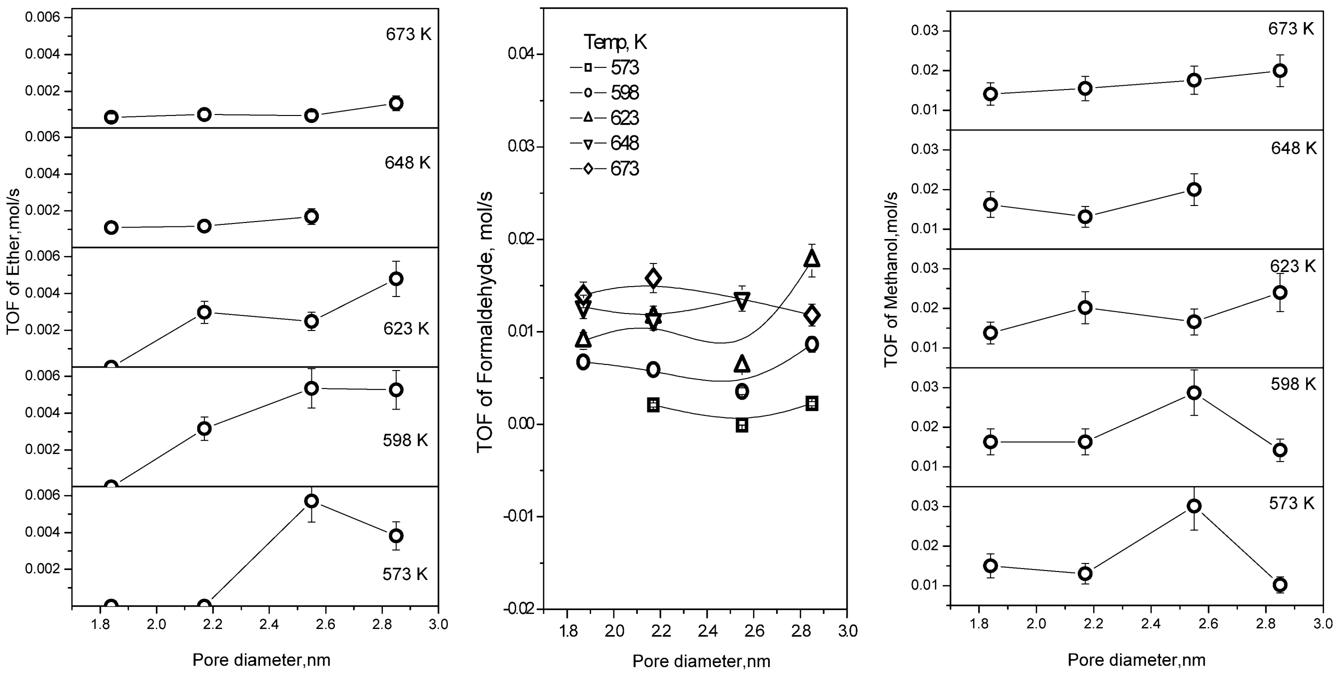

Fig. 6. Effect of pore size on the turnover frequency to methanol, formaldehyde and dimethyl ether on V-MCM-41 with medium vanadium loading (∼0.8 wt%).

on the surface, which results in retention of intermediate species when reduced by methanol, causing consumption of more oxygen during the reoxidation of reduced catalysts, a problem noted by Wachs [8]. Recently, to confirm the influence of vanadium loading on reactivity and selectivity, we reproduced methanol oxidation using the catalysts with medium vanadium loading (around 0.8 wt%). Fig. 6 shows the TOFs of methanol, formaldehyde, and dimethyl ether. From the profile of TOF as a function of pore diameter, we can deduce a competition among the pore diameter of the V-MCM-41 catalysts, the reaction temperature, and the vanadium composition. At low temperatures (573–598 K), pore diameter has a significant effect on the TOF of methanol and ether. The effect also approximates a volcano curve, except that the volcano curve maximum appeared at ∼2.3 nm pore diameter with the lower vanadium-loading samples and at ∼2.6 nm or greater with the medium vanadium-loading samples. In contrast, at relatively higher temperatures (623–673 K), the pore size of V-MCM-41 has no obvious effect on TOF, which is in accord with Lim's results. In particular, this effect disappears gradually as the temperature increases from 623 to 673 K, and the radius of curvature effect is totally gone when the temperature exceeds 623 K. Pore diameter has no influence on formaldehyde formation with these medium vanadium-loading catalysts.

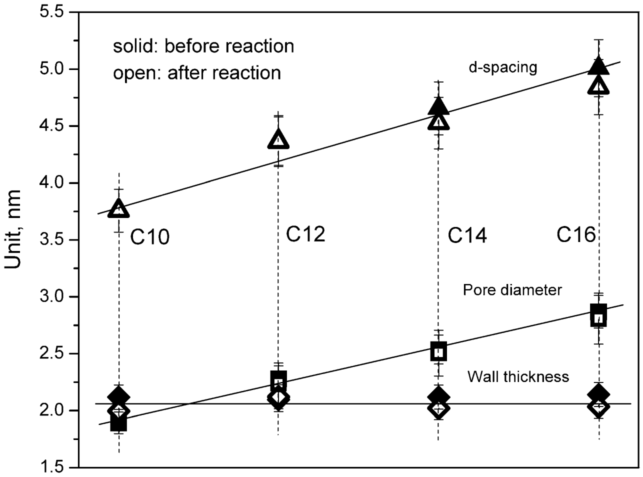

Fig. 7. Structure of V-MCM-41 catalysts during the methanol oxidation.

Summarizing the results that we have obtained for methanol oxidation on V-MCM-41 catalysts, we can draw the following conclusions. The radius of curvature effect is dramatic when the vanadium concentration is quite low (say, <0.4 wt%), no matter how high the reaction temperature. With vanadium loading >1 wt%, the effect of pore diameter is completely overwhelmed by the catalytic active site density, perhaps on, but not in, the pore wall and probably resulting from surface vanadium compounds. At medium vanadium concentrations, the competition among temperature, metal loading, and pore diameter effect is intense. The radius of curvature shows a modest effect at low reaction temperatures. With increasing temperature, the changing nature of the catalytic active sites plays a more important role during the reaction, even when the pore diameters are varied.

3.3. Characterization of catalysts

Nitrogen physisorption and XRD studies have shown that the structure of V-MCM-41 catalysts is very stable, changing only slightly after methanol oxidation in terms of pore diameter, d-spacing, and wall thickness, as shown in Fig. 7. To obtain a sense of how the physical structure of catalysts may influence reactivity, we define the concept of "stability" here as the structural factor [slope of the capillary condensation in physisorption and the peak area ratio of (110) to (100) diffraction peaks in XRD] of used catalysts divided by the structural factor of the fresh catalysts. By plotting the stability of the catalyst samples versus different pore diameters, we can find a volcano curve that is consistent with the profile of conversion of methanol as shown in Fig. 8. This may explain how the stable structure of V-MCM-41 catalysts contributes to the activity in the methanol oxidation reaction, or may simply mean that structural stability of V-MCM-41 and methanol oxidation activity correlate with the same local, not-yet identified V structure property.

UV–vis spectroscopy experiments were performed to provide information on the local environment of vanadium ions; the results are illustrated in Fig. 9. The assignment of UV–vis bands was based on reports in the literature [24–26]. Compared with other samples, the C14-V-MCM-41 catalyst had more vanadium species tetrahedrally incorporated into the silica framework after calcination, and this catalyst did not change dramatically after the methanol oxidation reaction. This finding probably provides a rationalization for why the C14 sample has the highest selectivity to formaldehyde and ether.

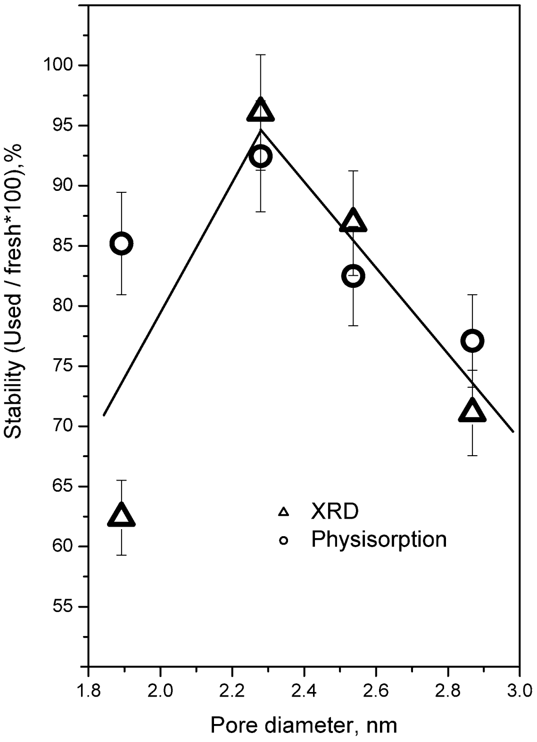

Fig. 8. Stability of V-MCM-41 catalysts in methanol oxidation, XRD: peak area ratio of (110) to (100); Physisorption: slope of capillary condensation [1].

3.4. Radius of curvature effect on reduction stability

The reducibility of vanadium species has been related to the activity and selectivity of catalysts for oxidative dehydrogenation reactions. Thus understanding the reduction behavior is essential to developing the catalysts for these reactions [27]. TPR is a very convenient technique for studying the reduction behavior of supported oxide catalysts, qualitatively.

Hydrogen TPR experiments were carried out several times on the same sample; the results are shown in Fig. 10. The second and the third runs show reduction patterns similar to that of the first run, which means the metal component is quite stable, so that the tetrahedrally coordinated vanadium in the silica framework is not completely reduced to metal even after reduction at 1173 K for 2 h. The temperature of the maximum reduction rate is shifted to a higher temperature after the first run. This may be due to the pore size decrease resulting from thermal contraction, which is related to the reduction stability of smaller pores, as explained

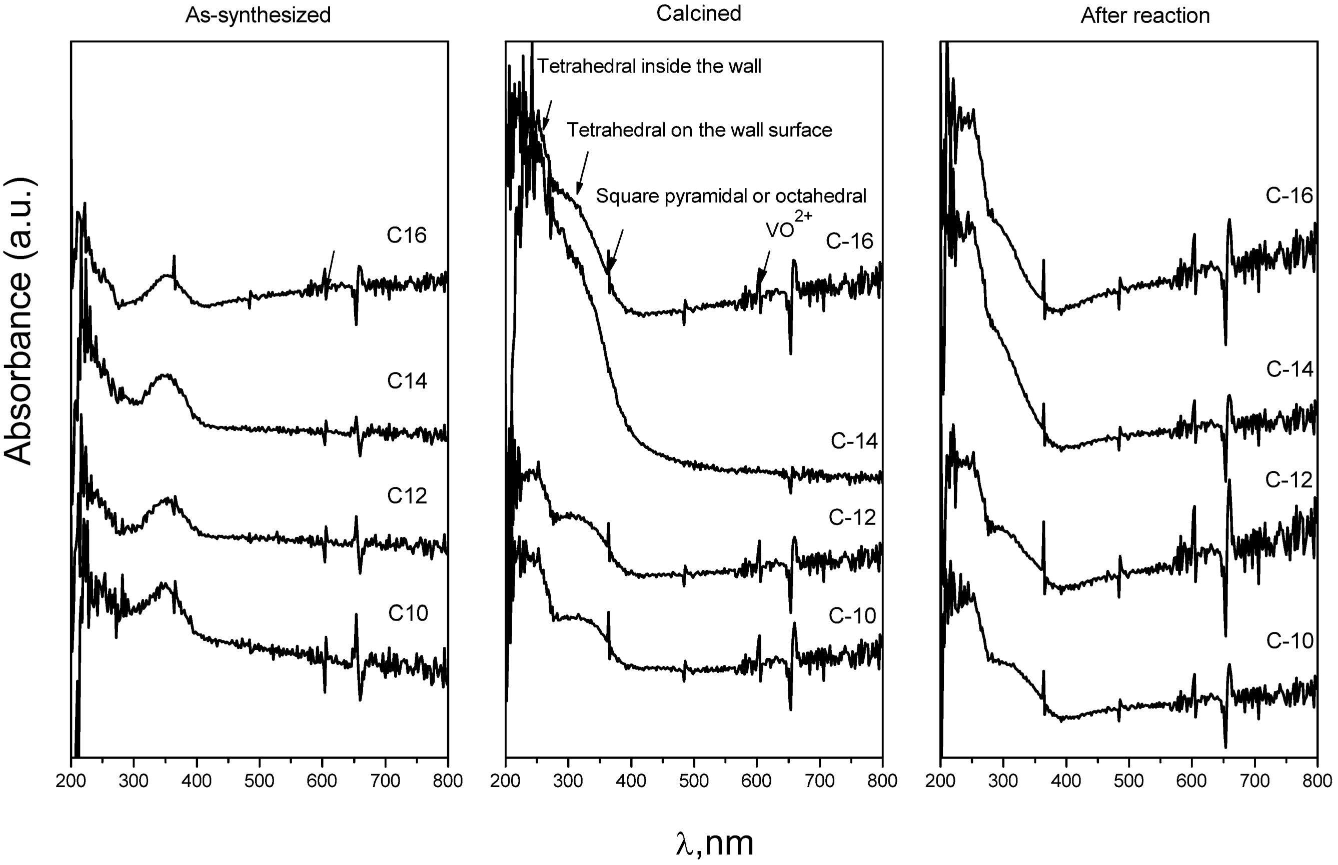

Fig. 9. UV–vis spectrum of V-MCM-41 catalyst.

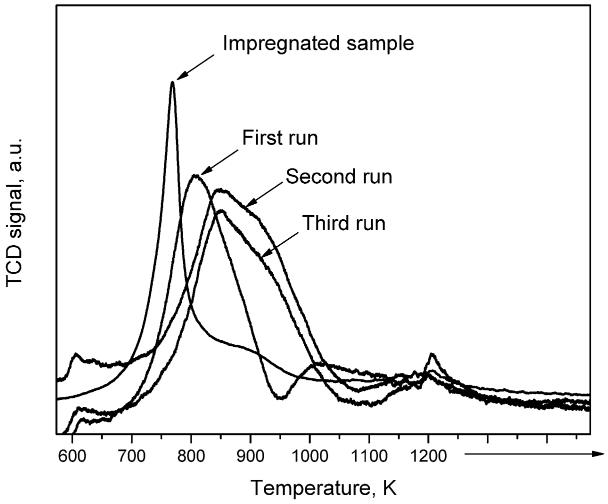

Fig. 10. Profile of multiple hydrogen reduction of V-MCM-41 catalyst.

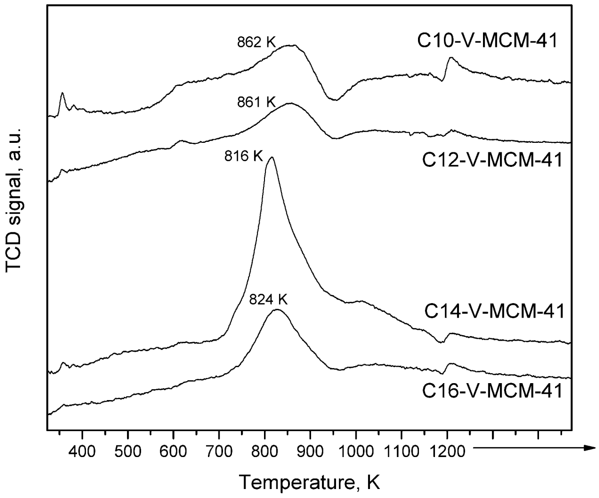

Fig. 11. Effect of pore diameter on the hydrogen reduction of V-MCM-41 catalysts.

elsewhere [28]. A hydrogen TPR experiment of an impregnated vanadium MCM-41 sample was also carried out, and demonstrated a lower reduction temperature (around 763 K) compared with the hydrothermally prepared V-MCM-41 samples. Therefore, the V-MCM-41 samples that we prepared hydrothermally had no surface oxide detected by TPR, even after repeated redox cycles at high temperature.

To test the effect of pore diameter on the reduction behavior of V-MCM-41 catalysts, a series of TPR experiments was performed on several samples with the same vanadium loading (0.36 ± 0.03 wt%) but different radii of curvature. Experimental results showed a significant influence of pore size on the reduction pattern of V-MCM-41 catalysts (Fig. 11; Table 2). The impregnated sample had the lowest reduction

Table 2
Reducibility of V-MCM-41 samples measured by temperature-programmed reduction

Catalysts	Temperature at maximum reduction rate (K)	Reduction activation energy (kJ/mol)	Initial oxidation state	Final average oxidation state[a]
Imp C16-V/MCM-41	768	–	5+	3.02+
C10-V-MCM-41	862	183.3	5+	3.94+
C12-V-MCM-41	861	136.3	5+	3.95+
C14-V-MCM-41	816	108.4	5+	3.15+
C16-V-MCM-41	824	124.0	5+	3.75+

[a] Measured by hydrogen consumption in the TPR.

temperature relative to the incorporated samples, indicating that it is reduced easily because most vanadium species are on the surface. Of all of the incorporated samples, C14-V-MCM-41 (2.54-nm pore diameter) had the narrowest reduction peak with the lowest activation energy, final reduction state, and temperature for the maximum rate of reduction (816 K); this is the catalyst with the highest selectivity for both formaldehyde and dimethyl ether (see Fig. 4). The TPR peak for C14-V-MCM-41 indicates a more uniform structure and suggests that selectivity correlates with this uniformity and ease of reduction. However, the most active (i.e., having the highest TOF of methanol oxidation; see Fig. 1) occurs on the C12-V-MCM-41 (2.28-nm pore size), and although it is less reducible (maximum rate at 861 K), this catalyst has the greatest stability against loss of structural order during reaction (see Fig. 6). Note also that the highest reaction temperature (673 K) is well below the temperature of the peak reduction rate in the TPR, implying only minor reduction under steady-state methanol oxidation. In fact, the most active catalyst (C12-V-MCM-41) and the most selective catalyst (C14-V-MCM-41) are both the least reduced at the highest reaction temperature (see Fig. 1), suggesting that perhaps the association between pore size and the reducibility of isolated vanadium in the MCM-41 silica matrix is the reason for the radius of curvature effect.

4. Conclusion

We prepared highly ordered V-MCM-41 samples with different pore sizes and reasonably constant composition by applying a quantitative model that we recently developed [1]. A strong effect of radius of curvature on the catalytic reaction and reduction stability exists when the methanol oxidation and hydrogen TPR were used as probes. The radius of curvature effect on catalytic behavior is represented by a “volcano curve” in which the turnover frequency increases with increasing pore diameter to a maximum and then decreases. Oxygen uptake by surfaces of pre-reduced catalyst samples shows an apparent association between pore size and active site density at higher temperature. Various characterization techniques have shown how the structural stability of catalysts affects activity and how the incorporation of vanadium into the framework affects the selectivity of methanol oxidation, but confirm that it is the effect of the radius of curvature on vanadium reducibility that likely controls reactivity and selectivity overall.

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