

Catalytic performance of vanadium incorporated MCM-41 catalysts for the partial oxidation of methane to formaldehyde

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Abstract

The catalytic performance of incorporated V-MCM-41 catalysts for the partial direct oxidation of methane to formaldehyde with molecular oxygen has been investigated. V-MCM-41 catalysts containing 0.56–1.86 wt.% V have been prepared by incorporating the vanadium ions into the framework of mesoporous siliceous MCM-41, resulting in a highly ordered structure with large BET surface area and high surface density of isolated vanadium atoms. The structure of the V-MCM-41 catalysts was studied by N₂ physisorption. The influence of the main reaction parameters, i.e. reaction temperature, reaction pressure, CH₄:O₂ ratio, gas hourly space velocity (GHSV) and vanadium content, on the selectivity and space time yield (STY) of formaldehyde were studied. A formaldehyde selectivity of 59.4% using a 0.56 wt.% vanadium loading V-MCM-41 catalyst was achieved at a temperature of 873 K, pressure of 12 psi, CH₄:O₂ molar ratio of 13:1, GHSV of 2.0×10^3 l kg⁻¹ h⁻¹. The highest STY_{HCHO} of 2103 g kg⁻¹ h⁻¹ with a high HCHO selectivity of 53.2% was obtained with the V-MCM-41 catalyst containing 1.86 wt.% vanadium loading at 933 K, CH₄:O₂ ratio of 13:1, GHSV of 1.3×10^6 l kg⁻¹ h⁻¹. The improved catalytic performance of the V-MCM-41 catalysts is related to the highly dispersed vanadium oxide species forming a high concentration of isolated active sites, which are crucial to minimize the consecutive oxidation of formaldehyde to carbon oxides.

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1. Introduction

The world's known reserves of gas are large enough to be comparable to those of liquid fuels [1,2] and the reserves are increasing much faster than that of oil. Methane, as the principle component of the natural gas and by product of oil refining and chemical processing, has been considered as an important sustainable feedstock for the chemical industry. The effective single-step catalytic conversion of methane into useful oxygenated products, such as formaldehyde and methanol in sufficient yield remains as a great challenge for catalysis in the new century [2–4].

Industrially, formaldehyde is produced from methane by a three-step process including: (i) high temperature steam reforming of methane to syngas (CO and H₂), (ii) high pressure conversion to methanol and (iii) oxidative dehydrogenation of methanol to formaldehyde. The conventional three-step process

clearly has some disadvantages, e.g. the energy requirements of the endothermic steam reforming of the first step, the high pressure operation of the second step and the elimination of the energy of the strongly exothermic oxidation of the last step [5]. Consequently, the direct conversion of methane to formaldehyde via partial oxidation would be highly attractive, and has been the subject of extensive research. However, in spite of the various efforts made, the low selectivities and yields obtained by all of these works have prevented the direct application for commercial consideration [5–7].

Since Blair and Wheeler first demonstrated the catalytic partial oxidation of methane [8], intensive efforts have been made to develop a heterogeneous catalyst system for the partial oxidation of methane, and many reviews have been published outlining the issues for commercial processes [3,4,6,7,9–17]. Many catalyst systems have been investigated for the direct conversion of methane to methanol or formaldehyde, with the majority of the studies involving supported metal oxide catalysts [18–27] primarily molybdenum [12,17,19,25,26] and vanadium oxides [7,12,20,26,27]. Surface vanadium oxide species have been reported to be more reactive and lead to

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higher methane conversion at lower temperature than the molybdenum oxide species, whereas, the latter exhibit higher selectivity to formaldehyde at similar methane conversion [26]. As a support for the transition metal oxide catalysts, silica was reported to be the most effective for the selective partial oxidation [28,29]. Moreover, the silica support itself can also act as a catalyst for the formation of formaldehyde [30]; however, the activity is much lower than the metal oxide catalysts studied.

The active site was proposed to be the isolated tetrahedral vanadium oxide species with terminal oxygen sites ($V=O$) [31–33], whereas, the surface species without terminal $V=O$ sites leads to the over oxidized products. Thus, the dispersion and nature of the metal oxide species have great influence on the reactivity and selectivity of the catalysts for the selective oxidation of methane. The relationship between methane conversion and formaldehyde selectivity and the dispersion of the surface species have been reported by Banares and Fierro [25], Faraldos et al. [26] and Kartheuser and Hodnett [34]. A decrease of formaldehyde selectivity could be seen when the vanadium loading was higher than 2 wt.% in V_2O_5/SiO_2 catalysts, due to the formation of polyvanadates or aggregated vanadium species [34]. Monolayer coverage has been shown to produce the optimized formaldehyde selectivity and productivity for silica stabilized isolated vanadium catalysts [25,35,36] and mesoporous silica supported catalyst, i.e. $VO_x/SBA-15$ catalyst [37].

High active site dispersion is considered to be the key to optimize the productivity of formaldehyde and avoid the consecutive oxidation of formaldehyde to undesired carbon oxides. The dispersion of metal oxide species at moderate loading on the support with high surface area is crucial to improve the catalyst system and thus, enhance the formaldehyde yield. Recently, the mesoporous siliceous material MCM-41 has been used as the support for highly dispersed vanadium oxide species by Berndt et al. [38]. By impregnation, a high concentration of isolated vanadium active species was obtained compared to amorphous silica, resulting in significantly higher formaldehyde space time yield (STY_{HCHO}) of $2255 \text{ g kg}^{-1} \text{ h}^{-1}$ at 895 K and GHSV of $280,000 \text{ l kg}^{-1} \text{ h}^{-1}$ over $VO_x/MCM-41$ with 2.5 wt.% V, albeit, with a low HCHO selectivity of only 26.3%. More recently, Fornes et al. [37] reported the catalytic performance of mesoporous $VO_x/SBA-15$ catalysts by impregnation of vanadium species on the ordered mesoporous material SBA-15. A space time yield of formaldehyde reached about $2383 \text{ g kg}^{-1} \text{ h}^{-1}$ at 891 K and GHSV of $417,000 \text{ l kg}^{-1} \text{ h}^{-1}$ over $VO_x/SBA-15$ with vanadium loading of 3.85 wt.%, again, with a relatively low HCHO selectivity of 39.9%.

Almost all of the heterogeneous catalysts investigated for the partial oxidation of methane are impregnated catalysts, and no studies of this reaction have been published to date using incorporated catalysts (catalyst with V atomically dispersed in a silica matrix) with high dispersion. One study has compared partial oxidation reactions of a range of small alkanes over an MCM-41 catalyst with vanadium dispersed on the wall surface and one in which vanadium was incorporated into the

framework [39], which showed that the two types of catalysts behaved profoundly different. For example, the MCM-41 supported vanadium catalyst showed moderate selectivity for ethane to ethylene and propane to propylene whereas the V-MCM-41 catalyst showed high selectivity for propane to propylene and isobutane to isobutene [39]. In addition, a highly ordered vanadium incorporated MCM-41 catalyst has been successfully synthesized and developed in our previous work [40] such that the physical and chemical properties can be controlled precisely. Our previous work has already shown that V-MCM-41 is a good catalyst for the gas phase conversion of methanol to formaldehyde showing up to 98% selectivity [41]. The aim of this work is to develop V-MCM-41 catalysts with a high density of isolated active sites and to optimize the catalytic reaction conditions for the partial oxidation of methane directly to formaldehyde in order to enhance both the formaldehyde selectivity and the yield. In this work, a series of catalysts with highly ordered structure and highly dispersed vanadium active species are synthesized by direct incorporation of vanadium into the silica framework, characterized by N_2 physisorption and evaluated for the partial oxidation of methane to formaldehyde using molecular oxygen.

2. Experimental

2.1. Catalyst preparation

The sources of silica were Cab-O-Sil (Cabot) and tetramethylammonium silicate (Aldrich). The vanadium source was $VOSO_4 \cdot 3H_2O$ (Sigma–Aldrich). Hexadecyl trimethylammonium bromide ($C_{16}H_{33}(CH_3)_3NBr$, Sigma–Aldrich) surfactant was used as a template material. The surfactant solutions were prepared by ion-exchanging the 20 wt.% $C_{16}H_{33}(CH_3)_3NBr$ aqueous solution with equal molar exchange capacity of Amberjet-4400(OH) ion-exchange resin (Sigma) by overnight batch mixing. The resulting solution was filtered and ready for use. The anti-foaming agent was Antifoam A (Sigma), which is a silane polymer alkyl terminated by methoxy groups. Acetic acid (Fisher Scientific) was used for pH adjustment of the synthesis solution.

All of the samples studied in this work are based on C16 V-MCM-41 (16 carbon chain length surfactant). The fumed silica Cab-O-Sil (2.5 g) was added into tetramethylammonium silicate aqueous solution (10.4 g of 16.9 wt.% sol. containing 1 g of SiO_2) and stirred vigorously for 30 min. Deionized water (50.7 ml) was added to improve mixing. The vanadium aqueous solution ($VOSO_4 \cdot 3H_2O$, 2.0 wt.%) was added with continued stirring for another 30 min. Two drops of antifoam agent (0.2 wt.% of surfactant) were added, followed by adding the surfactant ($C_{16}H_{33}(CH_3)_3N \cdot OH$ 20 wt.%) solution (28.7 g) slowly and continuously. The pH was adjusted to 11.5 by adding acetic acid. After additional mixing for about 120 min, this synthesis solution was poured into a polypropylene bottle and placed in the autoclave at 373.2 K for 6 days. After cooling to room temperature, the resulting solid was recovered by filtration, washed with deionized water and dried under ambient conditions. The pre-dried solid was heated at a constant rate

from room temperature to 813.2 K over 20 h under He and held for 1 h under the same condition, followed by calcination at 813.2 K for 6 h with air to remove the residual surfactant. Because the preparation process may cause some loss of V and silica in the byproducts, the final vanadium content was determined by ICP analysis at Galbraith Laboratories, Inc. (Knoxville, TN).

2.2. Catalyst characterization

2.2.1. Nitrogen physisorption

Nitrogen adsorption–desorption isotherms at 77 K were measured with a Quantachrome Autosorb-3b static volumetric instrument. Prior to measurement, the samples were outgassed at 473 K to a residual pressure below 10^{-4} Torr. A Baratron pressure transducer (0.001–10 Torr) was used for low-pressure measurements. The specific surface area was calculated following the method of Brunauer, Emmet and Teller (BET) [42]. The pore size and pore size distribution were calculated by the Barrett, Joyner and Halenda (BJH) method [43] using the desorption isotherm branch.

2.3. Catalytic activity testing

The catalytic properties of V-MCM-41 catalysts for the partial oxidation of methane to formaldehyde were investigated in an isothermal fixed-bed down-flow quartz reactor. In order to obtain reliable data, the reactor is specifically designed to reduce the dead volume, which can be critical in minimizing the combustion and the gas-phase reaction [44]. The inside diameter of the first half of the quartz reactor is approximately 10 mm and narrowed down to 2 mm after the catalyst bed in order to increase the local flow rate of the reactant stream, thereby effectively decreasing the possibility of consecutive reaction of formaldehyde to carbon oxides in the gas phase. Typically, 50 mg of catalyst was loaded in the reactor with the thermocouple inserted into the catalyst bed for better control of the actual pretreatment and reaction temperature. The reactor was installed vertically inside a 127 mm i.d. tubular furnace controlled by a programmable PID temperature controller (CN2011J, Omega). All the gases were controlled by calibrated mass flow controllers (Brooks). The pressure was adjusted with a needle valve and measured on a pressure gauge (Matheson, 0–100 psi).

Before reaction, the catalysts were pretreated in situ in a stream of 10 ml/min ultrazero grade air at 773 K for 40 min to get a clean surface of the catalysts. After pretreatment, the catalysts were then flushed with ultrahigh purity He for 20 min. Methane combined with the balance gas, helium, was introduced into the reactor at the same temperature first, followed by the introduction of oxygen in order to keep the gas mixture above the upper explosion limit. Then the temperature was increased to the reaction temperature at a rate of as low as 5 K/min in order to avoid catalytic combustion in the bed.

The catalytic activity tests were conducted at various pressures ranged from 6 to 21.5 psi in the temperature range

from 753 to 953 K. The reactants of CH₄ and O₂ were mixed at different ratios ranging from 1 to 13 (molar ratio) by means of mass flow controllers, and the gas mixture was balanced by ultrahigh purity He. The effect of gas hourly space velocity was studied in a wide range from 1.0×10^5 to 1.7×10^6 l kg⁻¹ h⁻¹.

The feed and products were analyzed by an on-line programmable gas chromatograph (HP 6890) equipped with TCD, Hayesep D column (100/120 mesh 20 ft) and Hayesep T column (100/120 mesh 5 ft). Separation of the products and reactants was achieved by twice injection of the GC with temperature programming, giving a complete separation of O₂, CO, CH₄, CO₂, C₂H₆, C₂H₄, HCHO and H₂O. The outlet of the reactor to the GC was heated to 423 K to avoid the condensation of the products. For each steady state study, the results typically corresponded to the catalytic activity after stabilization for 100 min.

Methane conversion was calculated from the products, i.e. the sum of the major products converted from methane divided by the amount of input methane, which is different from the method used by some other authors, who calculate the quotient of the consumed methane and the input methane. For the method used in this work, one can possibly obtain underestimated conversion because some of the minor products are uncounted in the numerator. However, the latter method will result in larger error because of the low possible conversion to products. The selectivity to products is defined as the amount of each product produced from methane divided by the sum of all the products.

3. Results and discussion

3.1. Catalyst characterization

As the primary measurement to compare the structure of V-MCM-41, nitrogen physisorption was conducted for a series of V-MCM-41 samples with different vanadium loading (0.56–1.86 wt.%). For samples with a uniform pore diameter, a step increase of infinite slope in the adsorption isotherm due to the capillary condensation at a characteristic relative pressure should be ideally shown. The incorporation of vanadium ions in the silica framework increases pore diameter because of a larger transition metal ion size resulting in greater metal oxygen bond length than the Si–O bond while the unimodal pore size distribution is maintained. The isotherms and the pore size distributions for V-MCM-41 samples with different vanadium loading are shown in Fig. 1. It can be observed that all the samples exhibit a sharp capillary condensation, high adsorption volume and unimodal pore size distribution, suggesting that highly ordered V-MCM-41 catalysts were successfully synthesized regardless of the increase of vanadium content. On the other hand, all of the samples exhibit a step increase around a relative pressure = 0.9–1 due to the filling of interparticle spaces (macropores). Very narrow pore size distributions can be observed for all of the samples with different vanadium loading. The physical properties of the V-MCM-41 samples with varying vanadium contents are shown in Table 1. The samples with different vanadium content

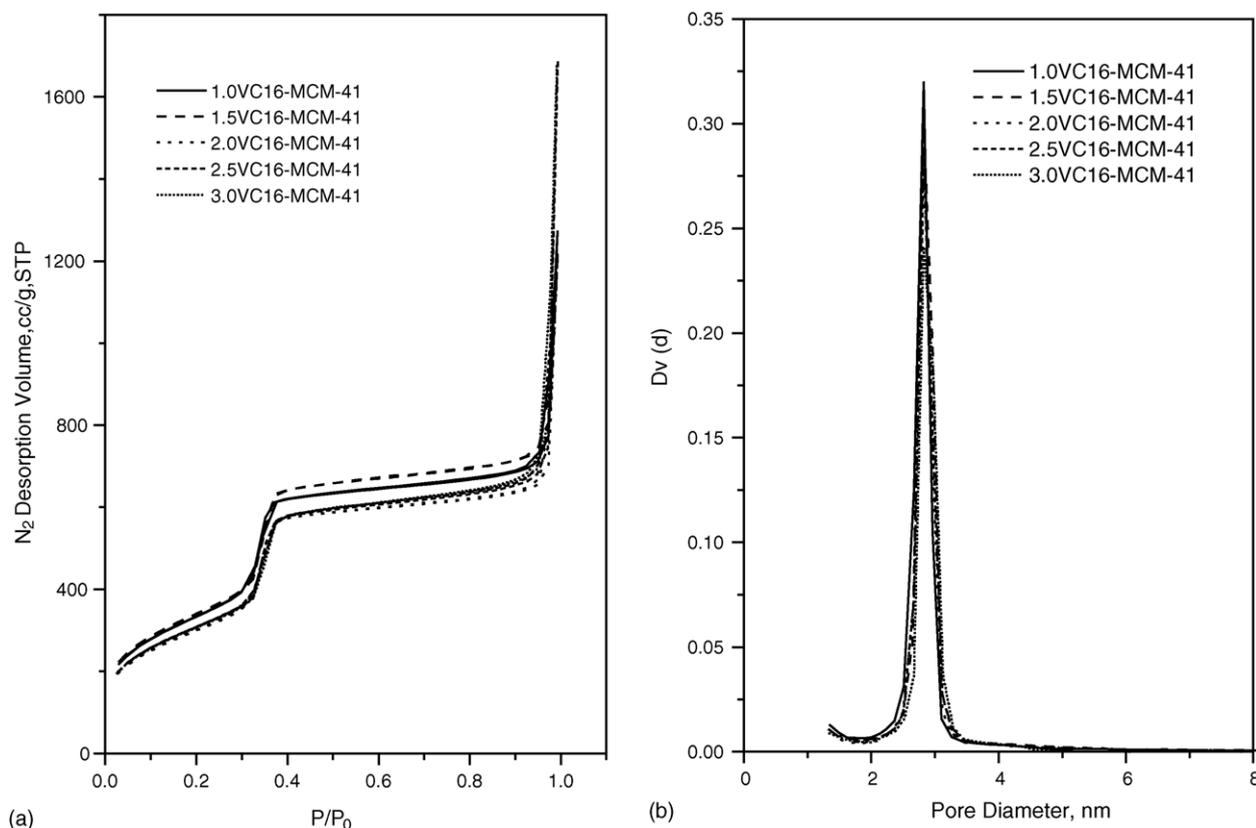


Fig. 1. Nitrogen physisorption for C16 V-MCM-41 samples with different vanadium loading.

exhibit typical MCM-41 BET surface area ($>1000 \text{ m}^2/\text{g}$) and almost the same average pore size. The slope of the capillary condensation slightly decreases with the vanadium loading.

Note that there is a discontinuity in total pore volume between vanadium loadings of 0.56–1.15 and 1.45–1.86 wt.%, which may indicate a change in particle morphology reflected in the macropores formed by particle packing. On the basis of XANES [45,51] and V-NMR [40] results, it is deduced that the vanadium (+5) is substituted into the silica framework of MCM-41 by replacing V for Si, mostly occupying isolated distorted tetrahedral coordination sites possessing one double V=O bond and three single V–O bonds. Thus, the vanadium is stabilized most favorably on the surface of pore walls tetrahedrally with a V=O bond exposed on the surface of pore walls. Because the vanadium ion is substituted for the silica ion in the framework, not deposited on the surface of the pore walls

as for impregnated catalysts, formation of aggregated vanadium species on the surface of the pore channels is minimized. Increasing the vanadium content results in an increase of nominal surface density, however, still equal to or less than $0.2 \text{ V atoms nm}^{-2}$, suggesting highly dispersed vanadium species on the pore wall. The measurements of the physical properties of the V-MCM-41 catalysts as a function of vanadium content indicates that the pore diameter and pore volume can be precisely controlled using the preparation method described in our previous work [40].

3.2. Catalytic tests

In order to evaluate the significance of the bulk (non-catalytic) reaction of CH_4 and O_2 , a series of preliminary experiments were carried out with an empty reactor at the same conditions as used for the catalytic reactions. The results

Table 1
Physical properties of C16 V-MCM-41 with different vanadium loading

Sample ID	V-loading (wt.%)	BET (m^2/g)	Pore diameter (nm)	Mesopore volume (cm^3/g)	Total pore volume (cm^3/g)	Slope of capillary condensation (cm^3/g)	Nominal surface density V (atoms/nm^2)	FWHM (nm)
1.0VC16-MCM-41	0.56	1220	2.83	1.08	2.06	5210	0.054	0.23
1.5VC16-MCM-41	0.93	1240	2.82	1.12	1.98	4990	0.089	0.28
2.0VC16-MCM-41	1.15	1100	2.82	1.01	1.93	4780	0.12	0.25
2.5VC16-MCM-41	1.45	1130	2.83	1.00	2.70	4670	0.15	0.26
3.0VC16-MCM-41	1.86	1120	2.82	0.99	2.67	4030	0.20	0.30

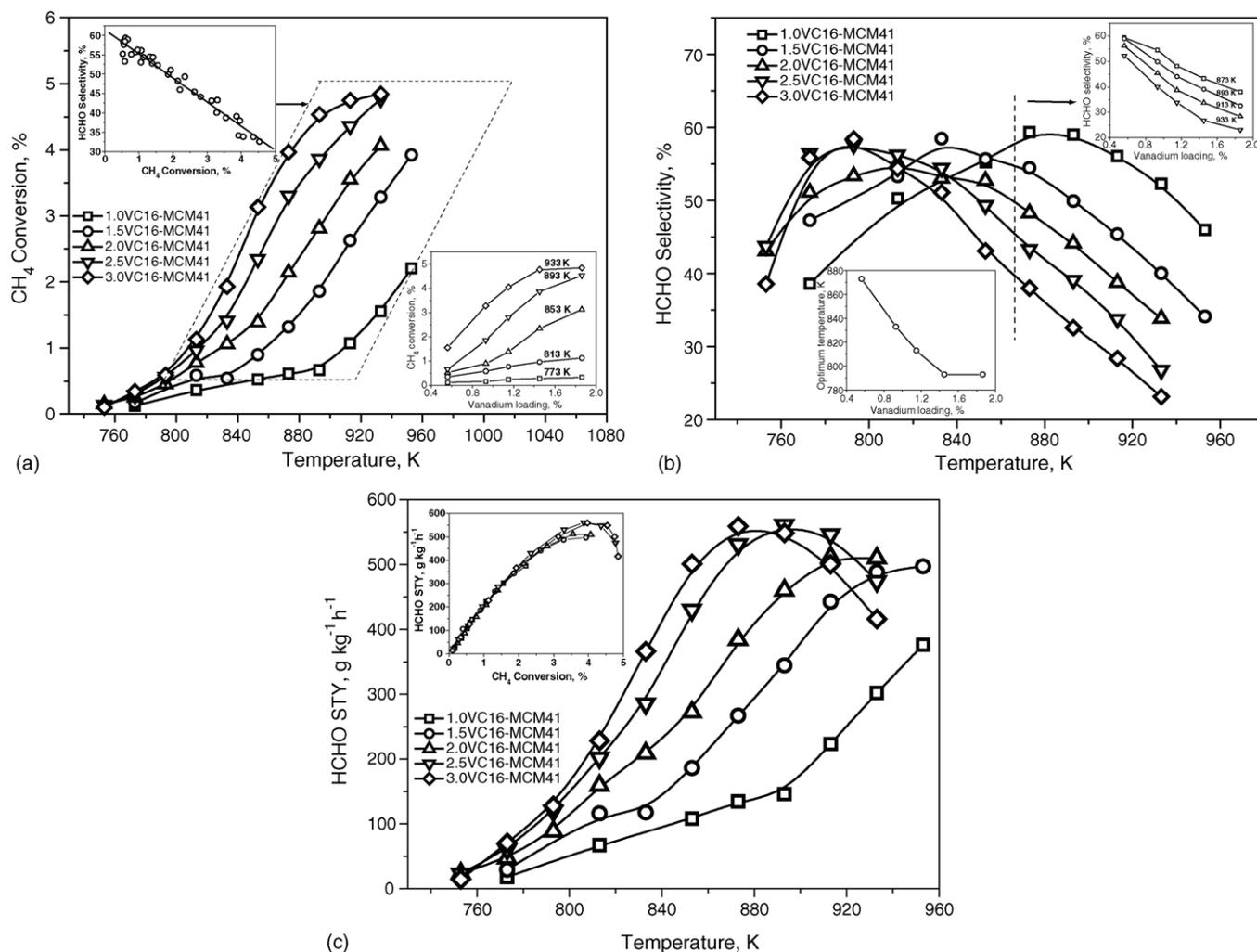


Fig. 2. (a) The influence of temperature on methane conversion, (b) HCHO selectivity and (c) HCHO space time yield over V-MCM-41 catalyst with different vanadium loading from 0.56 to 1.86 wt.% V at reaction pressure of 12 psi, $\text{CH}_4:\text{O}_2$ ratio of 13:1 and GHSV of $200,040 \text{ l kg}^{-1} \text{ h}^{-1}$.

showed that the contribution of the non-catalytic gas phase oxidation of methane at the conditions studied is negligible. Blank experiments using pure Cab-O-Sil MCM-41 were also performed, showing no significant activity at high temperatures ranging from 893 to 933 K. These experiments do not, of course, rule out desorption of species from the active catalyst that then react in the gas phase.

The partial oxidation of methane on V-MCM-41 catalysts yielded essentially formaldehyde, carbon monoxide, carbon dioxide and water. Trace amounts of dimerization products, such as ethane and ethylene, as well as methanol were also observed.

3.2.1. Effect of temperature and vanadium loading

The influence of temperature on the catalytic performance of V-MCM-41 samples with increasing vanadium loading was studied at a reaction temperature ranged from 753 to 953 K, pressure of 12 psi, gas hourly space velocity of $200,040 \text{ l kg}^{-1} \text{ h}^{-1}$ and a feed composition of 24.1 vol.% methane, 1.8 vol.% oxygen and 74.1 vol.% helium. The reaction temperature had a significant influence on the catalytic performance of V-MCM-41 catalysts. The conversion of

methane, selectivity of formaldehyde as well as the space time yield (STY_{HCHO}) obtained as a function of vanadium loading are shown in Fig. 2. It can be seen that, in the range of reaction temperatures studied, for each V-MCM-41 sample with different vanadium loading, methane conversion increases gradually with the temperature, as shown in Fig. 2a. Methane conversion increased almost linearly with the vanadium loading at all temperatures below 933 K. The catalyst 3.0VC16-MCM-41 with the highest vanadium loading (1.86 wt.% V) exhibited the highest activity with which the highest conversion (up to 5%) can be obtained at around 933 K at the expense of almost complete consumption of molecular oxygen with oxygen conversion of about 91%. With a further increase in reaction temperature, the increase of methane conversion slowed. For stoichiometric conversion to formaldehyde, the methane to oxygen ratio is 1:1. At the methane to oxygen ratio of 13:1 used here, the maximum conversion of methane is only 7.7% assuming 100% of the methane consumed is converted to formaldehyde. Thus, higher conversion is restricted by the oxygen concentration in the feed.

Even with sufficient oxygen, however, STY_{HCHO} is expected to decrease with increasing temperature. For the impregnated

catalysts, as temperature increases, the concentration of the most active isolated vanadium species on the surface decreases due to agglomeration. When the vanadium content exceeds the dispersion-limit loading, e.g. the monolayer capacity [26,36,37], aggregated species predominate even at lower temperatures. For the conventional VO_x/SiO_2 catalysts, the highest activity can be achieved at low vanadium loading (1–2 wt.% V) with nominal surface density below ca. 1 V atoms nm^{-2} , where isolated surface active species are dominant [26]. While at higher vanadium loading than the dispersion limit, aggregated V species or even crystalline V_2O_5 particles are present, causing a decrease in the accessible vanadium active sites thus lowering the catalytic activity to formaldehyde [26]. Similar behavior has been observed for catalysts with higher vanadium loadings on supports with higher surface area, e.g. $\text{VO}_x/\text{MCM-41}$ [38], $\text{VO}_x/\text{SBA-15}$ [37]. However, the much higher BET surface area of the V-MCM-41 catalysts synthesized and studied in this work allows the nominal surface density of the catalysts to be below 0.2 V atoms nm^{-2} , which is substantially lower at given vanadium content in comparison to VO_x/SiO_2 , $\text{VO}_x/\text{MCM-41}$ or $\text{VO}_x/\text{SBA-15}$ catalysts. Thus, the consecutive oxidation of formaldehyde on the surface is highly restrained over a much broader reaction temperature range allowing higher selectivity, and thus STY_{HCHO} , to be achieved.

The selectivity to formaldehyde shows a similar “parabola” pattern as for V-MCM-41 samples with different vanadium loading as shown in Fig. 2b. Selectivity to formaldehyde increased with temperature, passing through a broad maximum and then constantly dropping with the further increase of the temperature. The wide temperature range of the maximum HCHO selectivity represents a significant advantage for the industrial application of the V incorporated MCM-41 catalysts synthesized in this work. For V-MCM-41 samples with different vanadium contents, the maximum HCHO selectivity was within the range of 55.1–59.4%, however, the temperature for the maximum selectivity was observed to shift to lower temperatures for the catalysts with higher vanadium loadings, i.e. the increase of vanadium loading lowers the optimum temperature for highest HCHO selectivity at a given space velocity. This suggests that the number of active site determines the optimum temperature, i.e. for the samples with more active sites accompanying higher vanadium loading, the optimum temperature of the highest HCHO selectivity is much lower than the low vanadium loading samples. It can be clearly seen from Fig. 2b that, for temperatures above 853 K, the selectivity to formaldehyde sequentially decreased with increasing vanadium loading, which was also reported by Fornes et al. [37] on $\text{VO}_x/\text{SBA-15}$ at 873 K. Since the polymeric vanadium species are unlikely to exist in the catalysts synthesized in this work, as supported by the Raman spectrum of V-MCM-41 used for methanol oxidation reported by Yang et al. [41], the decline of the formaldehyde selectivity likely has to do with its high reactivity on the catalyst surface at high temperature in favor of consecutive products. The direct conversion of methane to formaldehyde involves activation of the C–H bond through

rupture of the relatively inert CH_4 by adsorbed oxygen to generate reaction intermediates, and then the formation of formaldehyde by the as-generated $\text{CH}_3\cdot$ radical reacting with lattice oxygen of the catalyst surface [46]. The partial oxidation of methane to formaldehyde is thermodynamically favorable ($\Delta G_{700\text{K}}^0 = -293 \text{ kJ mol}^{-1}$) [6]. However, at high temperature (above 800 K), which is necessary to activate the relatively inert methane (C–H bond strength 438 kJ mol^{-1}) in the first place, the activation of the C–H bond in formaldehyde (C–H bond strength 364 kJ mol^{-1}) is much easier than that in CH_4 [46,47], resulting in the total oxidation products ($\Delta G_{700\text{K}} = -569, -791 \text{ kJ mol}^{-1}$ for CO and CO_2 , respectively) [6] by consecutive oxidation. Spencer and Pereira reported that the kinetic constant for the consecutive undesirable HCHO oxidation to CO_x is typically ~ 70 times larger than that of partial oxidation of CH_4 to HCHO at 873 K [20]. As shown in the inset of Fig. 2a, for a certain conversion range and for all the samples with various vanadium loading, the formaldehyde selectivity decreases strictly with the increase of methane conversion, giving an inverse selectivity-conversion relationship. This result also suggests that in this temperature range, changing vanadium loading does not result in varying active site configuration and/or a change in mechanism.

For the combination of methane conversion and formaldehyde selectivity, the patterns of the space time yields showed a similar shift as that of formaldehyde selectivity as shown in Fig. 2c. Initially, the STY_{HCHO} increases with the temperature followed by a rapid drop due to the undesirable consecutive oxidation of HCHO to carbon oxides. For the samples with higher vanadium loading, the decline of HCHO production took place at lower temperature than the samples with lower vanadium loading. When methane conversion is below 3.5%, V-MCM-41 samples with different vanadium loading showed similar STY_{HCHO} at the same CH_4 conversion. With the further increase of CH_4 conversion, the STY_{HCHO} of the samples with higher vanadium loading were observed to decrease, which reflects the consecutive oxidation of formaldehyde to carbon oxides at high reaction temperature. A maximum STY_{HCHO} of

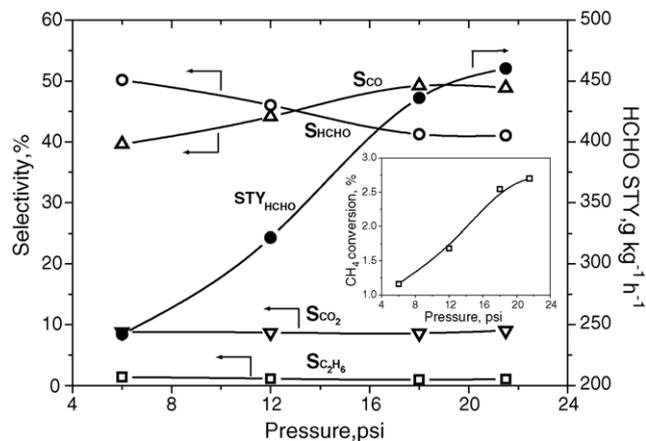


Fig. 3. The influence of the reaction pressure on product selectivities and STY_{HCHO} over V-MCM-41 catalyst with 0.56 wt.% V at a temperature of 933 K, $\text{CH}_4:\text{O}_2$ ratio of 6:1 and GHSV of $232,920 \text{ l kg}^{-1} \text{ h}^{-1}$.

560 g kg⁻¹ h⁻¹, at the expense of a decreased HCHO selectivity to 38%, can be achieved at around 873 K for 3.0VC16-MCM-41 catalyst at the conditions used here.

As an exothermic reaction, a majority of the enthalpy of the reaction, combined with the temperature gradients in the furnace, makes the reaction temperature very difficult to control at a temperature higher than 993 K. Slow catalytic combustion was observed above 993 K, which was also reported elsewhere [18]. The self-propagating characterization [18] of this high temperature oxidation reaction restricted the reaction temperature to be below 993 K. The combustion leads to high methane conversion producing large amount of carbon oxides. The considerations discussed above in this section suggest that significant improvement may be possible in a short contact time reactor.

3.2.2. Pressure effect

The effect of pressure on the partial oxidation of methane to formaldehyde is shown in Fig. 3. As the pressure was increased, methane conversion increased rapidly at the expense of a drop in the formaldehyde selectivity resulting from the consecutive oxidation of HCHO at high pressure. With the increase of pressure, there was little change on the selectivities of CO₂ and C₂ compounds. This suggests that at higher pressure, the rate of decomposition of HCHO increases in favor of the increase in CO selectivity, thus showing a complementary selectivity trends between HCHO and CO. However, the space time yield increased from 242 to 460 g kg⁻¹ h⁻¹ due to the increase of methane conversion, when the pressure was increased from 6 to 21.5 psi. With a further increase in the reaction pressure, catalytic

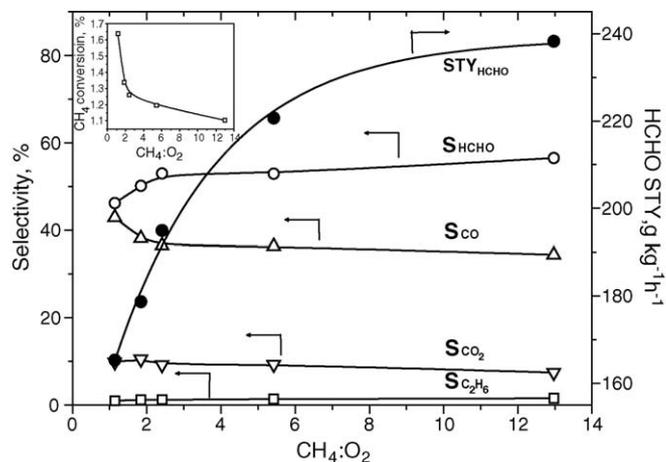


Fig. 4. The influence of the reactant ratio on product selectivities and STY_{HCHO} over V-MCM-41 catalyst with 0.56 wt.% V at a temperature of 933 K, pressure of 7.5 psi and GHSV of 206,400 l kg⁻¹ h⁻¹.

combustion occurred in the catalyst bed, producing a large amount of CO and CO₂, as well as H₂O. Since the influence of the pressure on the catalytic data achieved is considerable, it is important to keep constant the pressure in the reactor when comparing a certain reaction parameter with different samples.

3.2.3. Reactant ratio effect upon the catalytic activity

The stoichiometric ratio of methane to oxygen in the partial oxidation reaction to form formaldehyde is 1:1. However, a larger reactant ratio of CH₄:O₂ was usually used in most of

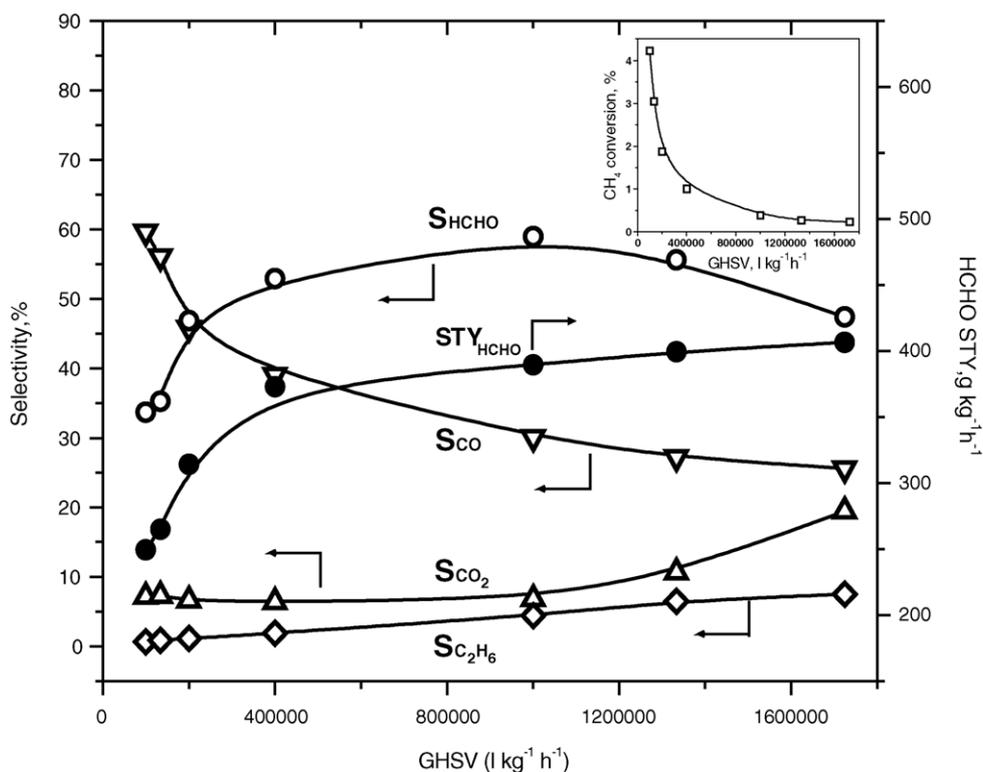


Fig. 5. The influence of space velocity on product selectivities and STY_{HCHO} over V-MCM-41 catalyst with 0.56 wt.% V at a temperature of 933 K, pressure of 18 psi and CH₄:O₂ ratio of 13:1.

published work [20,37,38,48]. As one of the main reaction parameters, the influence of $\text{CH}_4:\text{O}_2$ molar ratio was studied at reaction temperature of 933 K, reaction pressure of 7.5 psi and gas hourly space velocity (GHSV) of $206,400 \text{ l kg}^{-1} \text{ h}^{-1}$, with the increase of $\text{CH}_4:\text{O}_2$ molar ratio from 1:1 to 13:1 as shown in Fig. 4. The conversion of methane was observed to decrease dramatically when the $\text{CH}_4:\text{O}_2$ molar ratio was increased from 1:1 to 2.4:1, simultaneously, the HCHO selectivity increased substantially. With a further increase of the $\text{CH}_4:\text{O}_2$ molar ratio, the rate of decrease of methane conversion slowed down, as shown in the inset of Fig. 4. Above $\text{CH}_4:\text{O}_2=2.4:1$, any further increase of reactant ratio did not dramatically affect the HCHO selectivity. A decrease of CO selectivity can be observed corresponding to increase of HCHO selectivity, however, no significant impact of the reactant ratio on the selectivities of CO_2 and C_2 compounds was observed. A reactant molar ratio of 13:1 produced the highest HCHO selectivity and STY_{HCHO} at the present reaction conditions. So, subsequent studies used this high $\text{CH}_4:\text{O}_2$ molar ratio in the feed. For a commercial process, a lower reactant molar ratio (approximately 2.4:1 to 5.4:1) is

likely optimal. However, this ratio is difficult to use in a packed bed reactor because catalytic combustion occurs at temperatures lower than 973 K, making the temperature control very difficult. A fast flow reactor probably will allow the use of the higher oxygen concentrations because hot spots are minimized and temperature control is more precise. In our packed bed experiment, both the selectivity and the space time yield of HCHO increased strongly with a corresponding decrease of the carbon oxides until about 5.4:1 and then increased slowly as the $\text{CH}_4:\text{O}_2$ molar ratio increased to 13:1.

3.2.4. Space velocity effect

The influence of the gas hourly space velocity (GHSV) on the methane conversion, product selectivity, and STY_{HCHO} was studied at 933 K, pressure of 18 psi, $\text{CH}_4:\text{O}_2$ molar ratio of 13:1, with a wide range of GHSV from 1.0×10^5 to $1.7 \times 10^6 \text{ l kg}^{-1} \text{ h}^{-1}$ using the catalyst 1.0V-MCM-41. As shown in Fig. 5, the gas hourly space velocity distinctly affected the catalytic performance of V-MCM-41 catalyst. With the increase of space velocity, the methane conversion gradually

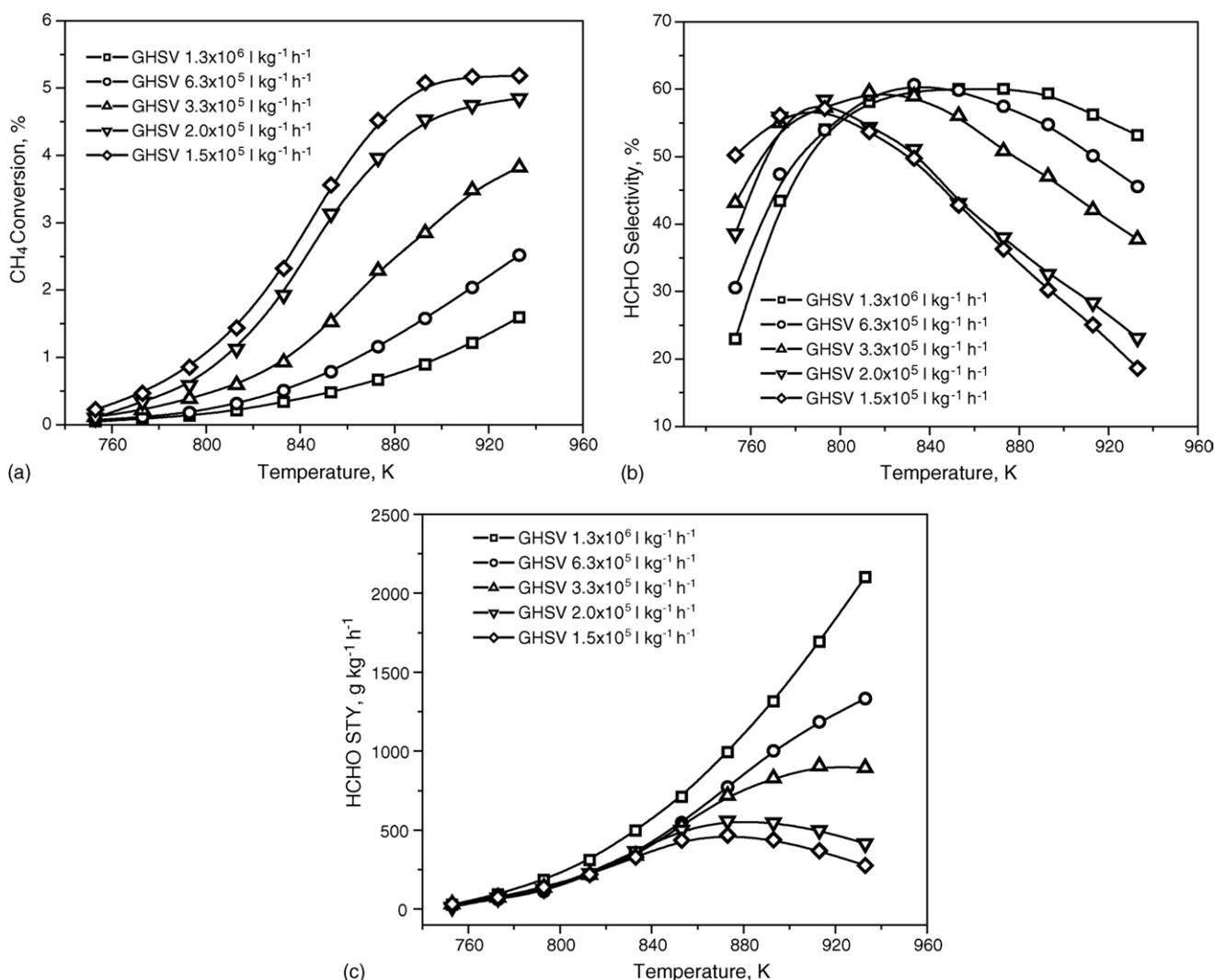


Fig. 6. (a) The influence of temperature on methane conversion, (b) HCHO selectivity and (c) HCHO space time yield over 3.0V-MCM-41 catalyst with 1.86 wt.% V at different space velocities, reaction pressure of 12 psi and $\text{CH}_4:\text{O}_2$ ratio of 13:1.

decreased because of the decrease of the contact time. Decreased contact time also minimizes undesired consecutive oxidation to carbon oxides. Formaldehyde selectivity increased significantly from 34 to 53% when the space velocity was increased from around 1.0×10^5 to 4.0×10^5 $\text{l kg}^{-1} \text{h}^{-1}$. The curve of HCHO selectivity versus space velocity exhibits a wide range of near maximum values, with the highest selectivity of 59% at 1.0×10^6 $\text{l kg}^{-1} \text{h}^{-1}$, followed by a decrease with the further increase of space velocity. At the same time, CO selectivity constantly decreased with an increase of the CO_2 and C_2H_6 selectivity. On the other hand, the STY_{HCHO} increased significantly below GHSV of 4.0×10^5 $\text{l kg}^{-1} \text{h}^{-1}$ due to the rapid increase of HCHO selectivity, compensating for the decreasing methane conversion. The increase in HCHO yield continued but only slightly with the further increase of space velocity. At elevated temperature, the oxidation of methane to carbon oxides is more favorable because of the instability of HCHO produced at this temperature. Some as-produced formaldehyde is oxidized on the catalyst, producing undesired carbon oxides, thus the enhancement of the space velocity is favorable for the formaldehyde synthesis with

respect to the selectivity and the space time yield. Shimamura et al. suggested that shorter residence time moving the produced formaldehyde from the catalyst zone of the reactor more quickly, may provide a key for minimizing the decomposition of formaldehyde to carbon oxides and improving the overall yield [49]. Thus, short contact time reactors will allow high selectivity by reducing the consecutive oxidation.

In order to maximize the yield of formaldehyde in the partial oxidation of methane using vanadium incorporated MCM-41 catalysts, the catalyst with the highest vanadium loading (1.86 wt.%) was studied by means of varying the reaction temperature and space velocity. The influence of reaction temperature and space velocity on the conversion of methane, formaldehyde selectivity and space time yield at a reaction pressure of 12 psi, the $\text{CH}_4:\text{O}_2$ molar ratio of 13:1 was demonstrated in Fig. 6. As shown in Fig. 6a, with the decrease of the GHSV, the increase of the methane conversion was more pronounced at higher temperature. The maximum selectivity to formaldehyde increased slowly with higher space velocity, with the optimum temperature shifting to higher value, as shown in Fig. 6b. The highest formaldehyde selectivity of 60% was

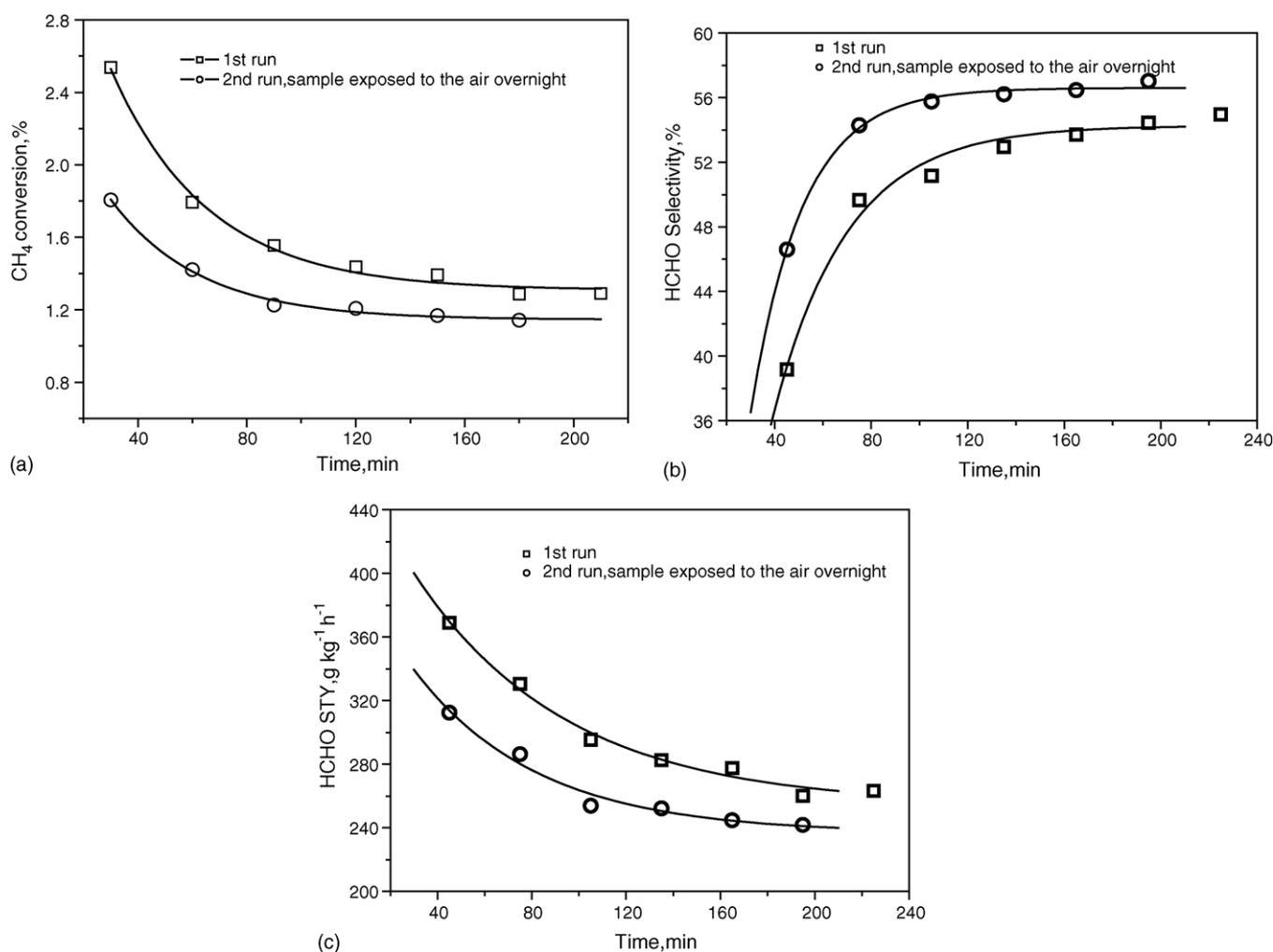


Fig. 7. Comparison of the (a) CH_4 conversion, (b) HCHO selectivity and (c) STY_{HCHO} of the V-MCM-41 with 0.56 wt.% V at first run of reaction and the second run of reaction using the same sample after exposure to air overnight, at a temperature of 933 K, pressure of 12 psi, $\text{CH}_4:\text{O}_2$ ratio of 13:1 and GHSV of 207,600 $\text{l kg}^{-1} \text{h}^{-1}$.

Table 2
Physical properties of C16 0.56 wt.% V-MCM-41 under different conditions

Sample ID	BET (m ² /g)	Pore diameter (nm)	Mesopore volume (cm ³ /g)	Total pore volume (cm ³ /g)	Slope of capillary condensation (cm ³ /g)	FWHM (nm)
1.0VC16-MCM-41 before reaction	1220	2.83	0.95	2.06	5210	0.23
1.0VC16-MCM-41 after reaction	1060	1.97	0.81	2.79	4560	0.21

achieved with a high gas hourly space velocity of $1.3 \times 10^6 \text{ l kg}^{-1} \text{ h}^{-1}$. From Fig. 6c, it can be seen that a maximum STY_{HCHO} of $2103 \text{ g kg}^{-1} \text{ h}^{-1}$ with a relatively high HCHO selectivity of 53.2% was obtained at the highest gas hourly space velocity ($1.3 \times 10^6 \text{ l kg}^{-1} \text{ h}^{-1}$) used, at the reaction temperature of 933 K. At 893 K, the STY_{HCHO} is $1315 \text{ g kg}^{-1} \text{ h}^{-1}$ at GHSV of $1.3 \times 10^6 \text{ l kg}^{-1} \text{ h}^{-1}$ for V-MCM-41 (1.86 wt.%), which is lower than the maximum STY_{HCHO} of $2255 \text{ g kg}^{-1} \text{ h}^{-1}$ on vanadium impregnated MCM-41 catalyst ($\text{VO}_x/\text{MCM-41}$, 2.5 wt.% V) at 895 K reported by Berndt et al. [38] and the maximum STY_{HCHO} of $2383 \text{ g kg}^{-1} \text{ h}^{-1}$ on vanadium impregnated SBA-15 catalyst ($\text{VO}_x/\text{SBA-15}$, 3.85 wt.%) at 891 K reported by Fornes et al. [37] and is higher than the maximum STY_{HCHO} of $1282 \text{ g kg}^{-1} \text{ h}^{-1}$ reported for vanadium impregnated SiO_2 catalyst (VO_x/SiO_2 , 2 wt.% V) at a temperature of 898 K [7]. Importantly, however, the selectivity to formaldehyde ($\sim 59.4\%$) at the above

conditions achieved with the V incorporated MCM-41 catalyst is significantly higher than any other reported catalyst, i.e. 26.3% for $\text{VO}_x/\text{MCM-41}$, 39.9% for $\text{VO}_x/\text{SBA-15}$ and 30.3% for VO_x/SiO_2 . Between selectivity and space time yield of formaldehyde as concerned for the catalytic performance, the former is significantly more important because the separation of formaldehyde from methane and the products is not difficult. Therefore, it is proposed that, by using a short contact time reactor with continuous separation and removal of the desired products, a high yield of formaldehyde is expected to be achieved with high efficiency. Moreover, the vanadium loading in the vanadium substituted MCM-41 samples studied in this work is much lower than that of the impregnated samples discussed above. Thus, the high formaldehyde selectivity with a high space time yield achieved with the V incorporated MCM-41 catalysts in our work makes it an outstanding system for the partial oxidation of methane.

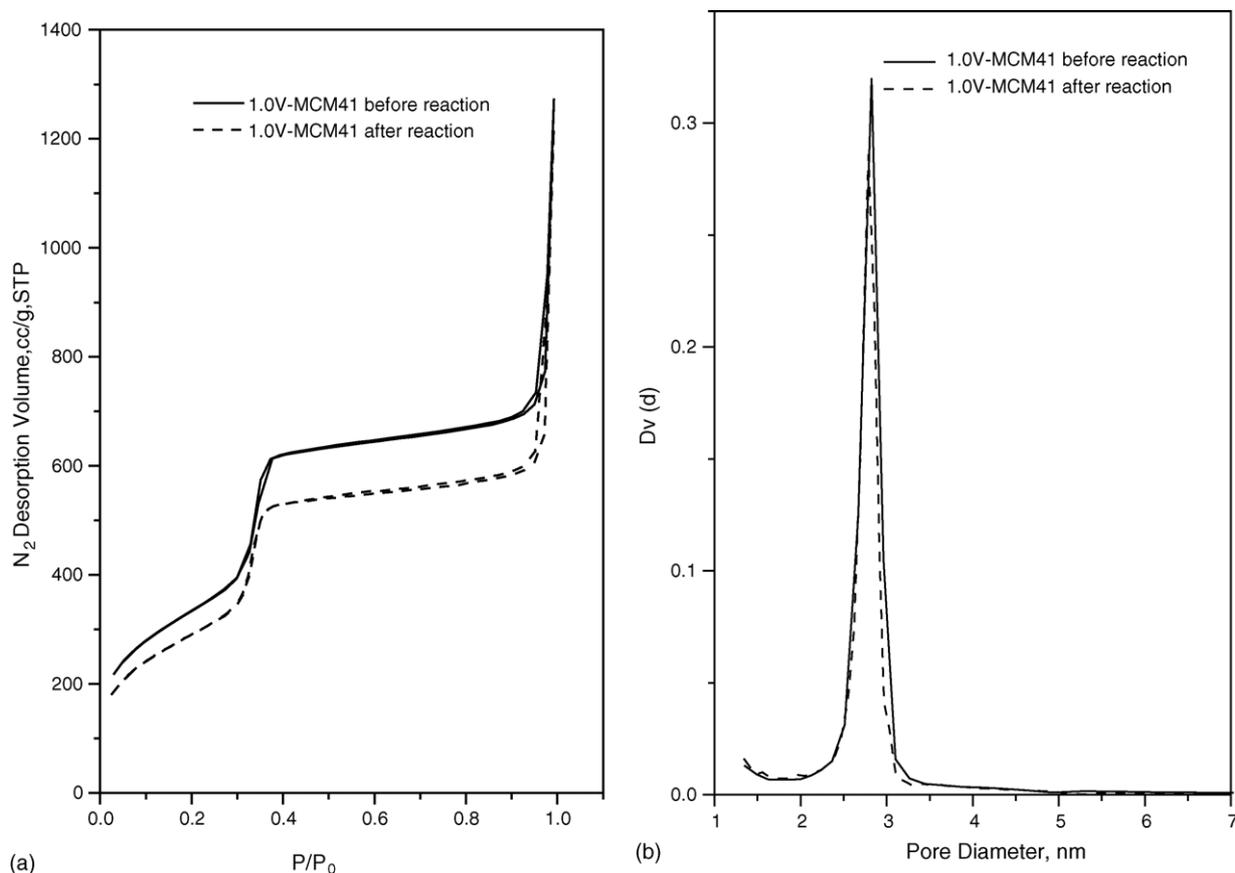


Fig. 8. Nitrogen physisorption for C16 V-MCM-41 with 0.56 wt.% V before and after methane partial oxidation.

3.3. Catalyst stability

In order to test the stability of the catalytic properties of the V-MCM-41 catalysts, a second experiment was carried out using the catalyst from a previous experiment after exposure to air overnight. The same air pretreatment was performed before each experiment. The data of the second experiment showed a pattern similar to the first experiment as shown in Fig. 7. The reaction reached its steady state after a similar amount of time. The methane conversion of the second run was slightly lower than that of the first experiment, however, the HCHO selectivity was a little higher after exposure to air between experiments. The STY_{HCHO} was lower for the second run than the first run due to the decrease of methane conversion. Nevertheless, the difference was not significant at steady state. This result indicates that the catalyst synthesized and studied in this work maintained its catalytic activity even after reaction and hydration in air overnight.

The physical stability of V-MCM-41 before and after partial oxidation of methane was measured by N_2 physisorption as shown in Table 2 and Fig. 8. Fig. 8 shows the nitrogen physisorption isotherm of the fresh V-MCM-41 (typically 1.0V-MCM-41) catalyst and the catalyst after methane partial oxidation at normal reaction conditions for about 10 h. The isotherm for the used catalyst still retains a steep capillary condensation step of $4560 \text{ cm}^3/\text{g}$ compared to that of the fresh sample of $5210 \text{ cm}^3/\text{g}$, although the mesoporous adsorption

volume decreased after reaction because of dehydroxylation. The pore size distribution of both catalysts calculated by the BJH method showed identical narrow sharp peaks. Apparently, the V-MCM-41 catalyst still maintained a highly ordered structure. As shown in Table 2, the BET surface area, the pore diameters, mesopore volume and the slope of the capillary condensation of V-MCM-41 catalyst decreased after reaction because of the dehydroxylation. However, the total pore volume is observed to increase, which is because the result of enlargement of the interparticle volume after reaction. The full width at half maximum (FWHM) remains almost the same for both the used and fresh catalysts. In conclusion, the nitrogen physisorption experiments prove that the V-MCM-41 does not show any significant structural change after methane partial oxidation producing substantial amounts of H_2O at high temperature. This is consistent with the XRD patterns (not shown) that are substantially the same before and after reaction. This suggests that V-MCM-41 synthesized in this study is very stable against hydrothermal degradation.

The V-MCM-41 catalysts have been extensively characterized in our previous work. As reported by Lim and Haller [50], the vanadium in the V-MCM-41 catalyst remains in a distorted tetrahedral coordination after the methanol oxidation reaction, which was confirmed by the comparison of the UV–vis spectroscopies of the fresh and used V-MCM-41 catalysts on the same reaction studied by Yang et al. [41]. As supplemental support for this finding, our previous study of the XANES of

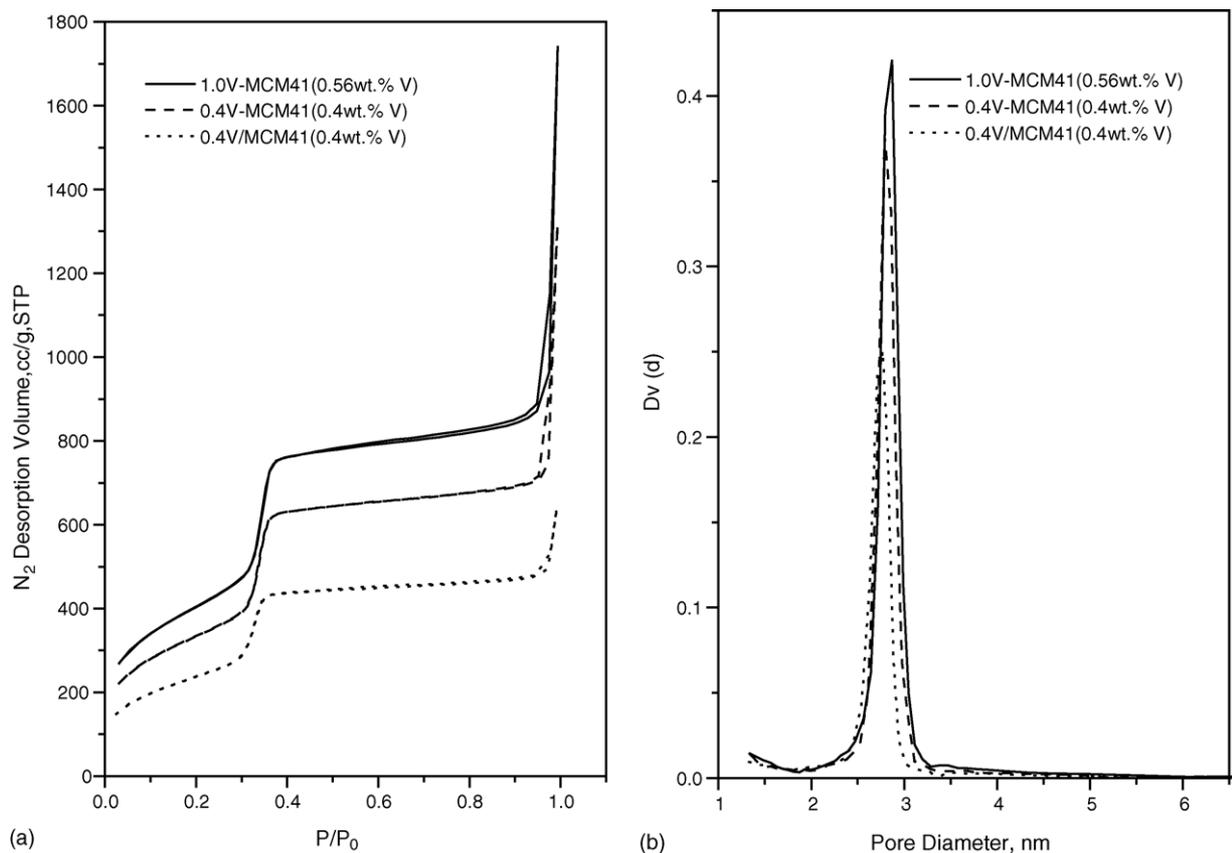


Fig. 9. Nitrogen physisorption for incorporated V-MCM-41 and impregnated V/MCM-41 catalysts.

Table 3
Physical properties of incorporated V-MCM-41 and impregnated V/MCM-41 catalysts

Sample ID	V-loading (%)	BET (m ² /g)	Pore diameter (nm)	Total pore volume (cm ³ /g)	Slope of capillary condensation (cm ³ /g)	Nominal surface density V (atoms/nm ²)	FWHM (nm)
1.0VC16-MCM-41	0.56	1220	2.83	2.06	5210	0.054	0.23
0.4VC16-MCM-41 ^a	0.40	1210	2.79	2.13	6020	0.039	0.20
0.4VC16/MCM-41 ^a	0.40	860	2.77	1.07	3920	0.055	0.22

^a 0.4VC16-MCM-41 is the label for incorporation, while 0.4VC16/MCM-41 indicates impregnation.

V-MCM-41 showed that, even at high temperature reduction with hydrogen (823 K, 1 h), the vanadium ions cannot be completely reduced to V⁴⁺ [51]. Thus, it is a reasonable assumption that the vanadium ions remain in the framework after methane partial oxidation.

3.4. Comparison of vanadium impregnated and incorporated MCM-41

The N₂ physisorption results and physical properties of the incorporated V-MCM-41 and impregnated V/MCM-41 are

compared as shown in Fig. 9 and Table 3. Fig. 9a shows the nitrogen physisorption isotherms of the incorporated (0.56 wt.% V and 0.40 wt.% V) and impregnated (0.40 wt.% V) samples. The isotherm capillary condensation step is much steeper for the incorporated V-MCM-41 catalyst (5210 and 6020 cm³/g) than the impregnated V/MCM-41 (3920 cm³/g) with similar vanadium loading. The pore size distribution as shown in Fig. 9b exhibits a narrow sharp distribution, with the pore size of the incorporated catalyst slightly greater than that of the impregnated catalyst because of the framework substitution of V for Si. From Table 3, the BET surface area

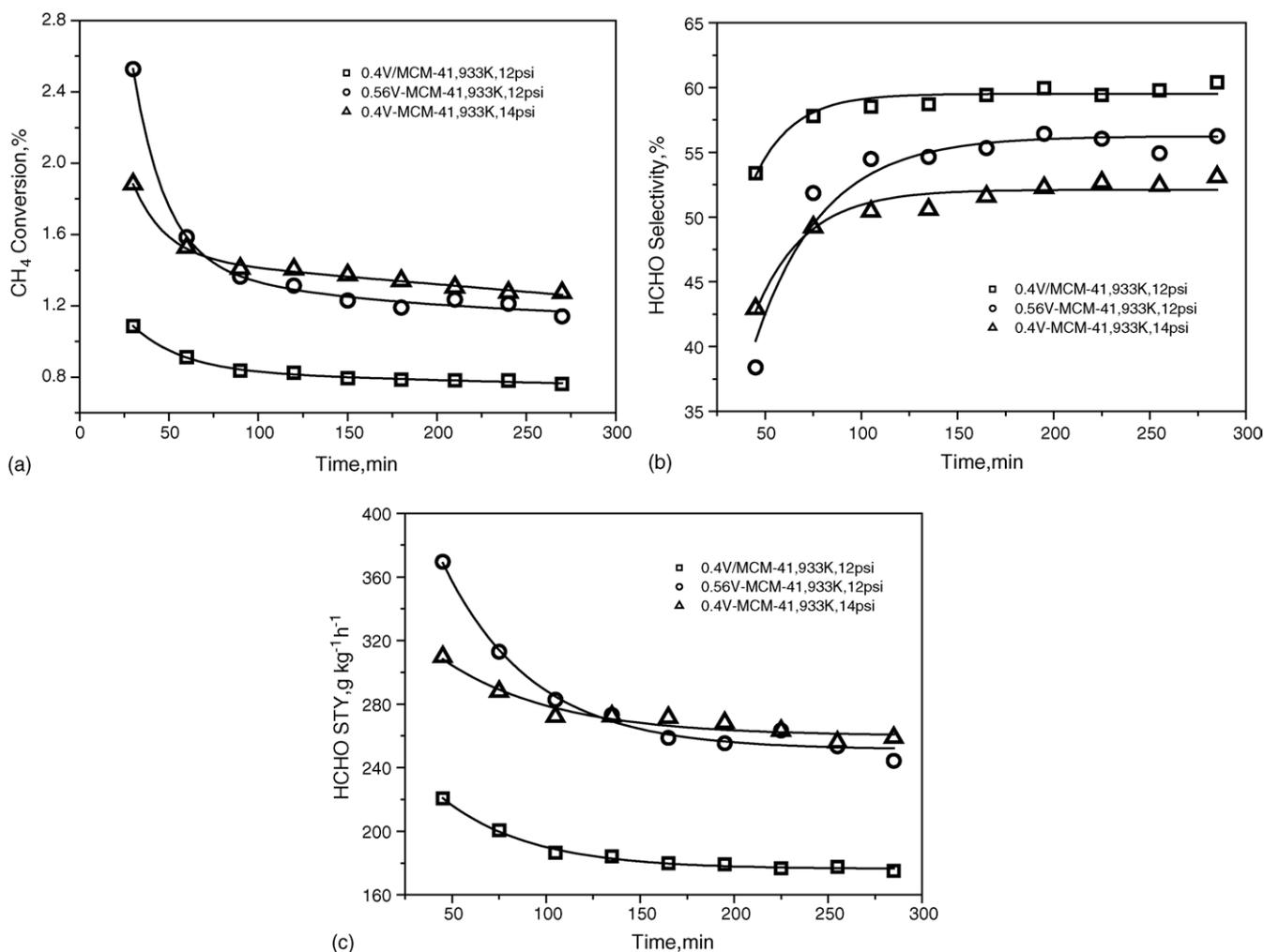


Fig. 10. Comparison of the (a) CH₄ conversion, (b) HCHO selectivity and (c) STY_{HCHO} of the incorporated V-MCM-41 and impregnated V/MCM-41 catalysts with CH₄:O₂ ratio of 13:1 and GHSV of 200,040 l kg⁻¹ h⁻¹.

and the total pore volume is much higher for the incorporated catalyst (0.4V-MCM-41) than the impregnated catalyst (0.4V/MCM-41) with the same vanadium loading (0.40 wt.%), giving a lower nominal surface density for the incorporated catalyst than its counterpart. The full width at half maximum are almost the same for both kinds of catalysts.

The methane conversion, the HCHO selectivity, and the STY_{HCHO} are illustrated in Fig. 10. As shown in Fig. 10a, the incorporated V-MCM-41 samples displayed much higher catalytic activity than the impregnated V/MCM-41 sample, showing a CH_4 conversion value of almost 1.5 times that of its impregnated counterpart. The reactivity for methane conversion is essentially related to the dispersed isolated surface metal oxide species, resulting in the higher methane conversion of incorporated V-MCM-41 catalysts. However, it should also be noted that, although both catalysts have the same vanadium loading of 0.40 wt.%, because some vanadium is buried in the wall, the incorporated catalyst has a somewhat lower site density.

The impregnated V/MCM-41 catalyst showed apparently higher HCHO selectivity than the incorporated catalyst as shown in Fig. 10b. However, in order to properly compare the incorporated and impregnated catalyst, they must be compared at the same conversion. While we do not have the experimental data to do this, we can estimate what the selectivity would be if we extrapolate (at 275 min) the incorporated catalyst selectivity to about the same conversion, using the correlation given in Fig. 2a. Doing this comparison demonstrates that the selectivity for impregnated and incorporated catalyst are identical, within experiment error, for these low loading catalysts.

The fraction of vanadium on the surface is greater for the impregnated V/MCM-41 catalyst than the incorporated V-MCM-41 catalyst at the same vanadium loading, because the synthetic method of incorporation causes a fraction of the vanadium species to be buried into the pore wall of the V-MCM-41. For the incorporated catalyst, the surface active sites are anchored by partially reduced vanadium ions in the matrix preventing aggregation under reaction conditions. There is a high possibility of aggregation of the vanadium species of the impregnated V/MCM-41 on the surface of the MCM-41 pore wall resulting in faster deactivation. As for the STY_{HCHO} shown in Fig. 10c, the incorporated V-MCM-41 catalysts led to much higher yield than the impregnated V/MCM-41 catalyst at 933 K as a result of the much higher catalytic activity of the incorporated V-MCM-41 catalyst. Furthermore, considering the high catalytic stability, V-MCM-41 will be the superior catalyst compared to the impregnated catalyst. Moreover, the advantage of the incorporated vanadium catalyst over impregnated catalyst will likely increase with vanadium loading (here compared at a low value of 0.40 wt.%) because aggregation becomes an increasing problem especially for impregnated catalysts at higher loadings.

4. Conclusions

The mesoporous catalyst, V-MCM-41, with vanadium contents ranging from 0.56 to 1.86 wt.% have been successfully

synthesized by incorporation of vanadium into the silica framework, characterized by N_2 physisorption and tested in the partial oxidation of methane to formaldehyde by molecular oxygen over a wide range of temperatures and space velocities. Owing to the large BET surface area of the V-MCM-41, the nominal surface density of the samples is essentially below ca. $0.2 \text{ V atoms nm}^{-2}$ with all the catalysts prepared in this work, providing the V-MCM-41 catalysts highly dispersed isolated vanadium active species stabilized against aggregation. For the wide range of reaction temperatures studied, the incorporated V-MCM-41 sample with the highest vanadium loading was shown to have the highest catalytic activity and formaldehyde yield. Although, at temperatures higher than 853 K, the selectivity of formaldehyde decreases with the increase of vanadium loading, however, it should be noticed that the same HCHO selectivity could be achieved at much lower reaction temperature, which provides a path to optimize the selectivity and space time yield of partial oxidation of methane through reactor engineering. Elevated pressure has a negative effect on the HCHO selectivity, yet increases the methane conversion. The effect of reactant ratio ($CH_4:O_2$) was also investigated in this work, and $CH_4:O_2 = 2.4:1$ is considered to be the optimum ratio taking both methane conversion and formaldehyde selectivity into account. Increasing the $CH_4:O_2$ ratio to 13:1 gives higher space time yield of formaldehyde. At the optimum conditions, a very high formaldehyde space time yield of about $2103 \text{ g kg}^{-1} \text{ h}^{-1}$ with a high HCHO selectivity of 53.2% was achieved with the sample of the highest vanadium loading prepared in this work at a reaction temperature of 933 K, $CH_4:O_2$ ratio of 13:1, GHSV of $1.3 \times 10^6 \text{ l kg}^{-1} \text{ h}^{-1}$. At 893 K, a high formaldehyde selectivity level of $\sim 60\%$ with a fairly high STY_{HCHO} of $1315 \text{ g kg}^{-1} \text{ h}^{-1}$ was obtained with the V incorporated MCM-41 catalyst (1.86 wt.%), which is significantly higher than the best results reported for other catalysts. The mesoporous catalyst is confirmed to be a very promising catalyst for the partial oxidation of methane, in addition to high selectivity and yield, the highly ordered structure was maintained confirming the high stability of the V-MCM-41 catalyst. Moreover, because of the extremely high BET surface area of the V-MCM-41 synthesized by the method developed in this lab, samples with low nominal surface density at even higher vanadium loading could be achieved, making possible the high efficiency production of formaldehyde by partial oxidation of methane at much lower temperature. The high selectivities to formaldehyde offered also provide the opportunity of further yield improvements through engineering of the reactor and reaction process.

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