Excellent Catalytic Performances of SBA-15-supported Vanadium Oxide for Partial Oxidation of Methane to Formaldehyde

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Vanadium oxide supported on SBA-15 exhibits superior catalytic performances for the partial oxidation of methane to formaldehyde. A space-time yield of formaldehyde as high as 93 mol $kg_{cat.}^{-1}h^{-1}$ has been obtained with a formaldehyde selectivity of 94% over 3 wt % VO_x/SBA-15 catalyst, significantly higher than those reported so far.

Partial oxidation of methane directly into useful oxygenates such as methanol and formaldehyde remains as one of the biggest challenges in chemistry. A large variety of solid catalysts have been reported for the partial oxidation of CH_4 to HCHO with O_2 under atmospheric pressure, but the reproducible HCHO yield is lower than 4%.[1–5] High HCHO space-time yield (STY) combined with high HCHO selectivity should be a key criterion for assessing a catalyst. So far, relatively high HCHO STY values have been reported over a few catalysts, e.g., ca. 40 and 27 mol $kg_{cat.}^{-1}h^{-1}$ over Fe–Nb–B oxides and silica-supported vanadium oxide, respectively.[6,7] Recently, it has been shown that HCHO STY up to 75 mol $kg_{cat.}^{-1}h^{-1}$ can be obtained over the vanadium oxide supported on MCM-41, a mesoporous silica with high surface area.[8] However, HCHO selectivity was lower than 30% over this catalyst under the conditions used for obtaining high STY values. As compared with MCM-41, SBA-15 possesses larger pores, thicker walls and higher thermal stability and may be a more appropriate support for the selective oxidation reactions occurring at high temperatures since the larger porous channels would be beneficial to the rapid desorption of a partial oxidation product. In this communication, for the first time, we report the excellent catalytic performances especially the high HCHO STY and selectivity of the SBA-15-suppoted vanadium oxide for the partial oxidation of CH_4 with O_2.

SBA-15 was synthesized in a similar manner as reported previously.[9] Typically, a homogeneous mixture containing Pluronic P123 triblock copolymers ($EO_{20}PO_{70}EO_{20}$) as a template and tetraethyl orthosilicate (TEOS) in hydrochloric acid was stirred at 35 °C for 24 h and further treated at 97 °C for 24 h to obtain as-synthesized SBA-15. The as-synthesized SBA-15 was collected by filtration followed by repeated washing with deionized water, drying in vacuum at 40 °C and calcination at 650 °C for 6 h. Vanadium oxide (VO_x) was introduced into SBA-15 by an impregnation method. SBA-15 was immersed into an aqueous solution of NH_4VO_3, followed by drying and calcination at 650 °C. Thus prepared VO_x/SBA-15 was characterized by X-ray diffraction and N_2-adsorption at 77 K to identify the mesoporous regularity. For comparison, VO_x/MCM-41 and VO_x/Cab-O-Sil were also prepared by the same impregnation method. The partial oxidation of CH_4 was performed on a fixed-bed flow reactor operated at atmospheric pressure. The products were analyzed by on-line gas chromatography.

Table 1 shows the BET surface area, pore volume and pore diameter obtained from N_2-adsorption measurements. BET surface area and pore volume both showed a decrease after introducing 1 wt % VO_x (calculated based on the amount of V_2O_5) into SBA-15, and then kept almost unchanged with increasing VO_x content up to 3 wt %. Further increase in vanadium content significantly decreased the surface area and pore volume. The pore diameter was kept at 5.4 nm for the samples with VO_x content lower than 3 wt % and decreased slightly to 5.3 nm for the samples with VO_x content of 5 and 10 wt %.

SBA-15 showed three X-ray diffraction peaks at 2θ of ca. 1.0, 1.6, and 1.9° assigned to its hexagonal mesoporous regularity. As shown in Figure 1, the three XRD peaks were also observed after the introduction of VO_x into SBA-15 and the intensities of the peaks were not significantly decreased, indicating

Table 1. Physical properties of the supported vanadium oxide catalysts

Catalyst	Surface area /m^2g^{-1}	Pore vol. /cm^3g^{-1}	Pore dia. /nm
SBA-15	645	0.80	5.4
1% VO_x/SBA-15	545	0.68	5.4
2% VO_x/SBA-15	549	0.69	5.4
3% VO_x/SBA-15	560	0.72	5.4
5% VO_x/SBA-15	418	0.63	5.3
10% VO_x/SBA-15	321	0.57	5.3
3% VO_x/MCM-41	871	0.89	2.3
3% VO_x/Cab-O-Sil	166	—	—

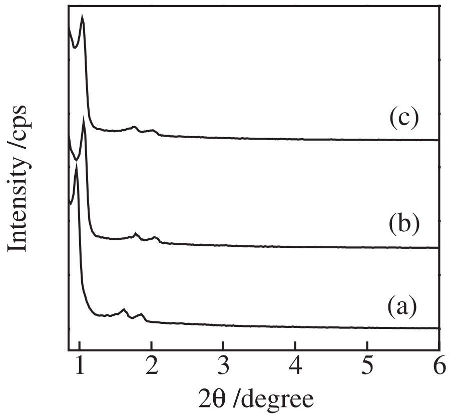

Figure 1. XRD patterns of (a) SBA-15, (b) 2 wt % VO_x/SBA-15, (c) 3 wt % VO_x/SBA-15.

the sustaining of the hexagonal regularity at long range. These XRD peaks were still observable even when VO$_x$ content increased to 10 wt % (not shown). It should be noted that no diffraction peaks of crystalline V_2O_5 were observed at high diffraction angles for the SBA-15-supported VO$_x$ samples with VO$_x$ content up to 10 wt %, suggesting that VO$_x$ species are highly dispersed on the wall surface of SBA-15 or form small vanadium oxide clusters in the mesoporous channels which are hard to be detected by XRD.

Table 2 shows the catalytic performances of the supported VO$_x$ samples for partial oxidation of CH_4 with O_2 at 625 °C. SBA-15 alone showed very low CH_4 conversion although HCHO selectivity was 100%. CH_4 conversion increased remarkably with introducing VO$_x$ into SBA-15 and reached a maximum at VO$_x$ content of 3 wt %. The introduction of VO$_x$ to SBA-15 formed CO in addition to HCHO. However, the selectivity to HCHO kept at >80% and only changed slightly with an increase in VO$_x$ content from 1 to 3 wt % while CH_4 conversion rose from 1.0 to 4.6% at the same time. Further increase in VO$_x$ content decreased both CH_4 conversion and HCHO selectivity significantly.

It is known that HCHO selectivity generally decreases with an increase in CH_4 conversion because of the consecutive oxidation of HCHO. HCHO selectivity versus CH_4 conversion obtained over the VO$_x$/SBA-15 with different VO$_x$ content was thus compared in Figure 2. This figure clearly shows that the 3 wt % VO$_x$/SBA-15 is the best one for the partial oxidation of CH_4 to HCHO. Probably, the concentration of the monomeric vanadyl species responsible for the selective oxidation of CH_4 is the highest over this catalyst. The highest HCHO STY value obtained at 625 °C over this catalyst was 93 mol $\mathrm{kg_{cat.}}^{-1}\mathrm{h}^{-1}$ with HCHO selectivity of 94% (Table 2). This STY value is significantly higher than those reported in literatures, and more importantly, much higher HCHO selectivity was obtained simultaneously.[1–8] HCHO selectivity of 94% could also be sustained at a single-pass HCHO yield of 3.4%. To our knowledge, this is the highest HCHO selectivity combined with a reasonably high single-pass HCHO yield.

Table 2. Catalytic performances of the supported vanadium oxide catalysts for partial oxidation of CH_4[a]

Catalyst	CH_4 conv. /%	HCHO select. /%	HCHO yield /%	HCHO STY /mol $\mathrm{kg^{-1}h^{-1}}$
SBA-15	0.08	100	0.08	0.4
1% VO$_x$/SBA-15	1.0	84	0.9	4.8
2% VO$_x$/SBA-15	3.0	86	2.6	14
3% VO$_x$/SBA-15	4.6	81	3.7	20
5% VO$_x$/SBA-15	2.9	76	2.2	12
10% VO$_x$/SBA-15	1.3	67	0.9	4.8
3% VO$_x$/SBA-15[b]	3.6	94	3.4	36
3% VO$_x$/SBA-15[c]	2.3	95	2.2	83
3% VO$_x$/SBA-15[d]	1.6	94	1.5	93
3% VO$_x$/Cab-O-Sil	2.7	78	2.1	11
3% VO$_x$/MCM-41	1.8	66	1.2	6.4

[a]Reaction conditions: $T = 625$ °C; catalyst, 0.1 g; total flow rate, 120 mL min^{-1}; $P(CH_4) = P(O_2) = 16.9$ kPa. [b]Total flow rate, 240 mL min^{-1}; $P(CH_4) = P(O_2) = 16.9$ kPa. [c]Total flow rate, 240 mL min^{-1}; $P(CH_4) = 59.1$ kPa; $P(O_2) = 4.2$ kPa. [d]Total flow rate, 240 mL min^{-1}; $P(CH_4) = 97.1$ kPa; $P(O_2) = 4.2$ kPa.

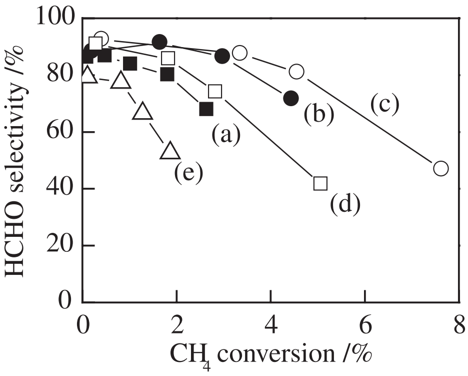

Figure 2. HCHO selectivity versus CH_4 conversion over the VO$_x$/SBA-15 with different VO$_x$ content. (a) 1 wt %, (b) 2 wt %, (c) 3 wt %, (d) 5 wt %, (e) 10 wt %.

It has recently been reported that the VO$_x$/SBA-15 catalyzes the oxidative dehydrogenation of C_3H_8 and photo-assisted oxidation of CH_4 at low temperatures more efficiently than VO$_x$/MCM-41 and VO$_x$/SiO$_2$, respectively.[10,11] Our results suggest that SBA-15 is also a better catalyst support for the partial oxidation of CH_4. CH_4 conversion and HCHO selectivity obtained over VO$_x$/SBA-15 were both higher than those over VO$_x$/Cab-O-Sil and VO$_x$/MCM-41. Further investigations on the advantages of SBA-15 as catalyst support for selective oxidations are underway.

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