Superior catalytic performance of phosphorus-modified molybdenum oxide clusters encapsulated inside SBA-15 in the partial oxidation of methane

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Small phosphorus-modified molybdenum oxide clusters encapsulated inside the mesoporous channels of SBA-15 exhibit excellent catalytic performance for the partial oxidation of methane to formaldehyde with oxygen. A formaldehyde selectivity of 90% has been obtained at a single-pass methane conversion of 5.8%.

Partial oxidation of methane directly into useful oxygenates such as methanol and formaldehyde remains as one of the greatest challenges in chemistry in the new century. A large number of catalysts have been reported for the partial oxidation of CH_4 to HCHO with O_2, but the reproducible HCHO yield is lower than 4%.[1–6] HCHO selectivity combined with an acceptable CH_4 conversion should be the first criterion in evaluating a catalyst at the current stage. Silica-supported MoO_3 and V_2O_5 are two widely studied catalysts showing good selectivities for the partial oxidation of CH_4 to HCHO. HCHO selectivities of *ca.* 80% and 70% were observed by Spencer and Pereira[7] only at very low CH_4 conversions (< 0.5%) over silica-supported MoO_3 and V_2O_5, respectively. Parmaliana and Arena[8] reported that a HCHO selectivity of 91% could be obtained at a CH_4 conversion of 0.58% over MoO_3 supported on a "precipitated" silica, but an increase in CH_4 conversion decreased HCHO selectivity sharply. Since mesoporous molecular sieves possess well-ordered mesoporous channels and large surface areas, the high dispersion of active components may be achieved in their nano-ordered space. Recently, a few studies have shown that the use of mesoporous silica such as MCM-41 or SBA-1 as supports of V_2O_5 and MoO_3 could increase the rate of HCHO formation.[9,10] The selectivity, as well as the single-pass yield to HCHO, however, was not significantly enhanced and the yield was limited to *ca.* 1–2% due to the rapid decrease in HCHO selectivity with increase in CH_4 conversion.

SBA-15, which possesses larger pores, thicker walls and higher thermal stability as compared with other mesoporous silicas[11] may be used as a promising catalyst support, particularly for reactions occurring at high temperatures. Furthermore, due to the larger pores (5–30 nm) of SBA-15 the partial oxidation product would facilely leave the catalyst, decreasing the probability of its consecutive oxidation. Recently, we have focussed on the tailoring of the catalytic components inside SBA-15 for the selective oxidation of hydrocarbons. In this communication, we report for the first time the high catalytic performance and in particular the excellent selectivity of SBA-15-encapsulated molybdenum oxide clusters modified with a small amount of phosphorus for the partial oxidation of CH_4 to HCHO with O_2.

SBA-15 prepared in this work showed three X-ray diffraction peaks at 2θ values of *ca.* 0.8°, 1.7° and 2.0° assigned to its hexagonal regularity. These XRD peaks were also observed after the introduction of molybdenum oxide (denoted as MoO_x hereafter) into SBA-15 with an impregnation method as the MoO_x content (calculated on the basis of the amount of MoO_3) did not exceed 10 wt % irrespective of the presence of the phophorus modification, indicating that the mesoporous regularity was sustained after the impregnation. This regularity was further confirmed by HRTEM observations. As a typical example, HRTEM images of the 10 wt % MoO_x/SBA-15 are shown in Fig. 1. The pore diameter evaluated from the TEM images is *ca.* 5 nm, consistent with that obtained from N_2
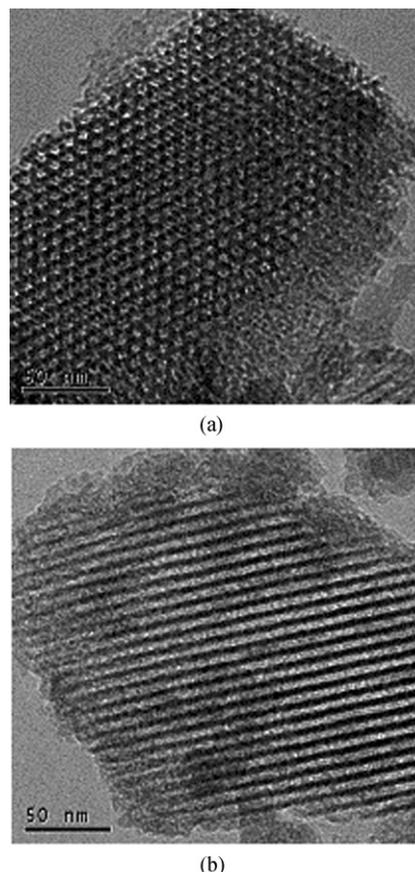

(a)

(b)

Fig. 1 HRTEM images of the 10 wt % MoO_x/SBA-15 taken with the beam parallel (a) and perpendicular (b) to the pore direction.

adsorption measurments as shown in Table 1. Table 1 also shows that both the BET surface area and the pore volume decrease with an increase in the MoO_x content. The pore diameter was also slightly reduced with increasing MoO_x content up to 10 wt %. These changes suggest that the MoO_x exist inside the porous channels of SBA-15 and may be located on the internal walls. The BET surface area and the pore volume became notably small as the MoO_x content reached 15 wt %, possibly indicating that most of the pores are blocked by the MoO_x clusters at such a high content. The pore diameter of MCM-41 synthesized in this work was 2.6 nm, smaller than that of SBA-15. Decreases in the surface area, pore volume and pore diameter were likewise observed after the introduction of MoO_x into MCM-41.
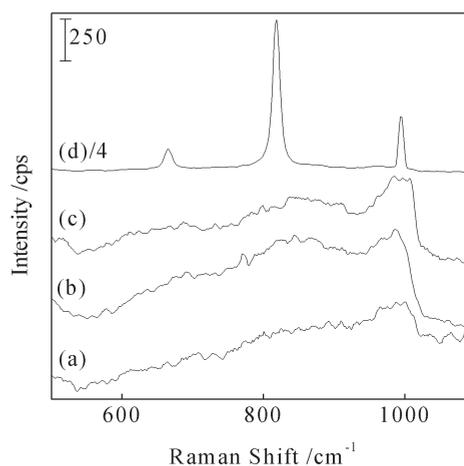
No diffraction peaks of crystalline MoO_3 were observed for the SBA-15- and MCM-41-supported samples with a MoO_x content lower than 10 wt %. Strong and sharp XRD peaks assigned to MoO_3 suddenly appeared as the MoO_x content reached 15 wt %. However, crystalline MoO_3 was clearly observed for the 10 wt % MoO_x/Cab–O–Sil sample. Fig. 2 shows the Raman spectra of the SBA-15-supported MoO_x samples. Sharp and intense bands at 993, 818 and 665 cm^{-1} appeared as the MoO_x content reached 15 wt %. The band at 993 cm^{-1} is assigned to the stretching mode of terminal Mo=O while that at 818 cm^{-1} could be assigned to the Mo–O–Mo stretching of crystalline MoO_3.[12] On the other hand, for samples with MoO_x contents of 5 and 10 wt %, only weak and broad bands at 985 and ca. 850 cm^{-1} appeared. The weak and broad features of the Raman bands are probably related to the encapsulation of molybdenum oxide clusters inside the mesoporous channels of SBA-15. Furthermore, the positions of these bands are similar to those observed for polymolybdates.[12] Therefore, the Raman results suggest that the molybdenum species located inside the mesoporous channels are probably nano-sized molybdenum oxide clusters, which cannot be observed by XRD. Fig. 3 shows the Raman spectra of MoO_x (10 wt %) introduced into SBA-15 and MCM-41, as well as deposited on Cab–O–Sil. On Cab–O–Sil, sharp bands at 995 and 820 cm^{-1} ascribed to crystalline MoO_3 were observed, while one distinct band at 990 cm^{-1} appeared in the case of MCM-41. The absence of the Mo–O–Mo stretching band at ca. 850 cm^{-1} in this case may indicate that molybdenum oxide is highly dispersed on the wall surface of MCM-41.

For the phosphorus-modified samples, the current characterization results are still insufficient to gain much insight into the state of phosphorus. No crystalline phase was observed from XRD as the MoO_x content was lower than 10 wt % in the P–MoO_x/SBA-15 samples, while only MoO_3 appeared when the MoO_x content exceeded 10 wt %. No crystalline phase containing phosphorus was observed for all of the samples investigated in this work. The Raman spectrum of the 10 wt % P–MoO_x/SBA-15 (curve c of Fig. 2) did not show any distinct differences with that of the 10 wt % MoO_x/SBA-15.
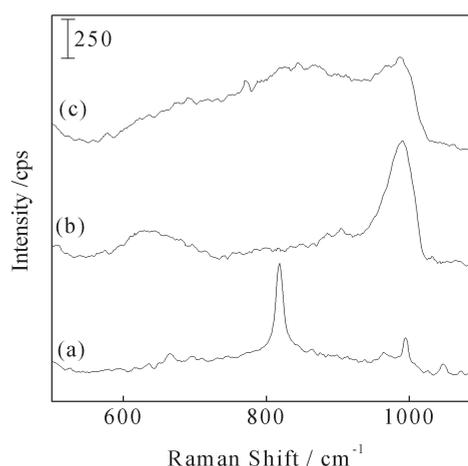

Fig. 2 Raman spectra of MoO_x introduced into SBA-15 with different MoO_x content. (a) 5 wt % MoO_x/SBA-15; (b) 10 wt % MoO_x/SBA-15; (c) 10 wt % P–MoO_x/SBA-15; (d) 15 wt % MoO_x/SBA-15.

Further studies are needed to elucidate the location and nature of phosphorus.

Table 2 shows the catalytic performances of these molybdenum oxide based samples for the partial oxidation of CH_4 with O_2. SBA-15 alone showed high HCHO selectivity but low CH_4 conversion. CH_4 conversion was raised from 0.63% to 3.8% and 5.0% with MoO_x encapsulated in SBA-15 at 5 and 10 wt %, respectively. HCHO selectivity decreased slightly from 90% to 83% and 73% at the same time. As the MoO_x content was further increased to 15 wt %, CH_4 conversion decreased to 1.1%, only slightly higher than that for SBA-15 alone. MoO_x/Cab–O–Sil (10 wt %) exhibited a similarly low catalytic activity. This, combined with the characterization results, suggests that crystalline MoO_3 particles outside the mesopores are almost inactive in the reaction under our conditions. Although CH_4 conversion over the 10 wt % MoO_x/MCM-41 was slightly higher than that over the 10 wt % MoO_x/SBA-15, HCHO selectivity was remarkably lower and thus HCHO yield was lower over this catalyst. Further comparisons under different conditions revealed that HCHO selectivity over MoO_x/SBA-15 was always higher than that over MoO_x/MCM-41 at similar CH_4 conversions. This probably arises from the different states of the MoO_x species inside these two mesoporous materials, as suggested by Raman spectroscopy. The larger pore diameter of SBA-15 (Table 1), which allows rapid

Table 1 Porous properties of the samples

Sample	Surface area/m^2 g^{-1}	Pore volume/ cm^3 g^{-1}	Pore diameter/nm
SBA-15	645	0.80	5.4
5 wt % MoO_x/SBA-15	382	0.57	5.3
10 wt % MoO_x/SBA-15	318	0.46	5.1
15 wt % MoO_x/SBA-15	66	0.06	n.d.
10 wt % P–MoO_x/SBA-15	350	0.48	5.1
MCM-41	983	1.59	2.6
10 wt % MoO_x/MCM-41	610	0.21	2.0
10 wt % MoO_x/Cab–O–Sil	41	n.d.^{a}	n.d.^{a}

^{a} n.d. = not detectable

Fig. 3 Raman spectra of MoO_x introduced into (a) Cab–O–Sil, (b) MCM-41 and (c) SBA-15. The MoO_x content is 10 wt % in all the cases.

Table 2 Catalytic performance in the partial oxidation of CH_4 to $HCHO^a$

Catalyst	$T/^\circ C$	% CH_4 conversion	% HCHO selectivity	% HCHO yield
SBA-15	650	0.63	90	0.6
5 wt % MoO_x/SBA-15	650	3.8	83	3.1
	686	11	42	4.6
	700^b	7.9	62	4.9
10 wt % MoO_x/SBA-15	650	5.0	73	3.7
15 wt % MoO_x/SBA-15	650	1.1	89	1.0
5 wt % P–MoO_x/SBA-15	650	5.1	87	4.4
	675	9.8	61	6.0
	675^b	5.8	90	5.2
	700^b	9.5	64	6.1
10 wt % P–MoO_x/SBA-15	650	5.1	82	4.1
	675	9.4	49	4.6
10 wt % MoO_x/MCM-41	650	6.6	48	3.2
10 wt % MoO_x/Cab–O–Sil	650	1.1	90	1.0

^{a} Reaction conditions: catalyst, 0.2 g; $P(CH_4) = P(O_2) = 16.9$ kPa; total flow rate, 0.16 mol (STP) h^{-1}. ^{b} Total flow rate, 0.32 mol (STP) h^{-1}.

desorption of HCHO, may also contribute to the high selectivity of MoO_x/SBA-15.

As shown in Table 2, the modification of MoO_x/SBA-15 with phosphorus enhanced HCHO yield by increasing CH_4 conversion or HCHO selectivity. P–MoO_x/SBA-15 with a 5 wt % MoO_x content showed better catalytic performance for HCHO formation. HCHO selectivity of 90% was achieved at a CH_4 conversion of 5.8% at 675 °C. To the best of our knowledge, this is the highest HCHO selectivity combined with a reasonably high single-pass CH_4 conversion. A single-pass HCHO yield of 6.1% could be obtained with HCHO selectivity of 64%. Such a HCHO yield is higher than those reported so far over a large variety of catalysts in the literatures. The HCHO space-time yield was calculated to be 16 mol kg_{cat}^{-1} h^{-1} at the same time. This value is significantly higher than those obtained over other supported molybdenum oxide catalysts under similar reaction conditions.[7,8] Therefore, SBA-15-encapsulated nano-sized molybdenum oxide clusters modified with phosphorus are unique in the partial oxidation of CH_4 to HCHO with O_2. The investigation of the role of phosphorus in the catalyst is now underway.

In summary, we have found that phosphorus-modified nano-sized molybdenum oxide clusters encapsulated inside the mesoporous channels of SBA-15 exhibit excellent HCHO selectivity at a reasonably high single-pass CH_4 conversion in the partial oxidation of CH_4 with O_2. At this time, a single-pass HCHO yield of *ca.* 6% has been achieved.

Experimental

SBA-15 was synthesized in a similar manner as reported elsewhere.[11,13] Typically, a homogeneous mixture comprised of Pluronic P123 triblock copolymers ($EO_{20}PO_{70}EO_{20}$) 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 separated by filtration, followed by repeated washing with deionized water, drying in vacuum at 40 °C and calcination at 650 °C for 6 h. Molybdenum oxide was introduced into SBA-15 by an impregnation method. SBA-15 was immersed into an aqueous solution of $(NH_4)_6Mo_7O_{24}$, followed by stirring for 8 h and allowing to rest for 10 h. The resultant powder was dried and finally calcined at 650 °C for 6 h. The catalyst thus prepared is denoted as MoO_x/SBA-15. For comparison, *via* the same method, molybdenum oxide was also introduced into MCM-41, which was prepared with the procedure described elsewhere,[14] and also deposited on Cab–O–Sil, a nonporous silica purchased from Acros Organics. The catalysts modified with phosphorus were prepared by co-impregnating SBA-15 with $(NH_4)_6Mo_7O_{24}$ and $NH_4H_2PO_4$ (denoted as P–MoO_x/SBA-15, the molar ratio of P to Mo was kept at 1:12).

The prepared materials were characterized by X-ray diffraction (XRD), N_2 adsorption at 77 K, high resolution transmission electron microscopy (HRTEM) and Raman spectroscopy to identify the mesoporous regularity and the possible nature and location of the molybdenum and phosphorus species.

The partial oxidation of CH_4 was performed on a fixed-bed flow reactor operated at atmospheric pressure. The inner diameter of the U-typed quartz reactor was 5 mm at the catalyst bed, decreasing to 2 mm downstream to remove the products rapidly from the hot zone of the reactor. The product was analyzed by on-line gas chromatography.

Acknowledgements

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