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Effect of the metal oxide loading on the activity of silica supported MoO_3 and V_2O_5 catalysts in the selective partial oxidation of methane

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Precipitated silica catalysts loaded with either MoO_3 (0.2–4.0 wt%) or V_2O_5 (0.2–5.3 wt%) have been studied in the selective partial oxidation of methane to formaldehyde with molecular oxygen at 520°C. The functionality of the SiO_2 surface towards the formation of HCHO is significantly promoted by V_2O_5, while it is depressed by the MoO_3.

Keywords: Metal oxide loading; methane; selective oxidation; MoO_3/SiO_2 and V_2O_5/SiO_2 catalysts

Among the numerous catalysts proposed for the partial oxidation of methane to formaldehyde the silica based systems are the more promising ones [1,2]. MoO_3 [3–7] and V_2O_5 [8–10] have been generally recognised as promoters of the SiO_2 support in the title reaction. Though the influence of the metal oxide loading in oxidation catalysis has been largely investigated [11,12], several authors have particularly addressed the issue of the MoO_3 [5,7] and V_2O_5 [10] loading on both the overall activity and selectivity to HCHO in the partial oxidation of methane. The negative effect of high MoO_3 loading (>7.8 wt%) has been associated with the formation of multilayers of crystalline MoO_3 on the SiO_2 support which preferentially leads to CO_x [5,7]. A facile oxidation–reduction cycle from V^{5+} to V^{4+}/V^{3+} under reaction conditions has been invoked to explain that the optimum loading of V_2O_5 is in the range 1.8–7.1 wt% [10]. Catalysts featuring higher V_2O_5 loadings exhibit inferior performance. Similarly, the low-loaded V_2O_5 systems are also less

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active, this being attributed to limited amounts of extractable oxygen [10]. Pitchai and Klier (see ref. [14] of ref. [1]) found an optimum MoO_3 loading corresponding to 4.5 wt% in promoting HCHO formation on $MoO_3/SiO_2 \cdot Al_2O_3$ catalysts. Furthermore, a positive effect of the V_2O_5 loading on the catalytic activity of V_2O_5/SiO_2 catalysts has been envisaged for the partial oxidation of ethane [13,14] and ethanol [13]. In contrast, a negative effect of the V_2O_5 loading has been pointed out in the oxidation of toluene on V_2O_5/SiO_2 [15]. Bare SiO_2 itself exhibits a unique functionality in oxidising methane to HCHO [16,17]. In particular, in our previous work [17], dealing with the reactivity of various commercial SiO_2 samples, it has been ascertained that the efficacy of precipitated SiO_2 in the formation of HCHO is higher than those of MoO_3 and V_2O_5 promoted fumed silica catalysts. Such evidence led us to investigate the catalytic performance of differently loaded (0.2–4.0 wt%) MoO_3/SiO_2 and (0.2–5.3 wt%) V_2O_5/SiO_2 catalysts in the title reaction in order to assess the nature and the roles played by such oxides in the reactivity of the SiO_2 surface.

The supported MoO_3 and V_2O_5 catalysts have been prepared by incipient wetness impregnation of "precipitated" SiO_2 support (Si 4–5P grade, AKZO product; BET SA, 380 m^2 g^{-1}; pore volume, 1.14 cm^3 g^{-1}) with a basic solution (pH = 11) of ammonium heptamolybdate or ammonium metavanadate. The impregnated samples were dried at 90°C for 24 h and then calcined at 600°C for 16 h. MoO_3 and V_2O_5 loadings were determined by atomic absorption spectroscopy (AAS). BET surface areas were obtained by N_2 adsorption measurements at −196°C. XPS measurements were performed with an Escalab MK II SIMS/XPS instrument. Low temperature oxygen chemisorption (LTOC) uptakes were determined at −78°C in a pulse mode after reduction in a H_2 flow (50 Ncm^3 min^{-1} for 5 h at 500°C according to the procedure suggested by Nag et al. [18]. The list of the catalysts used along with their physico-chemical characteristics is given in table 1. Catalytic tests have

Table 1
Physico-chemical properties of the MoO_3/SiO_2 and V_2O_5/SiO_2 catalysts

Catalyst	Metal oxide loading (wt%)	BET SA (m^2 g^{-1})	Me/nm^2	Me/Si ratio ×10^4		LTOC uptake (μmol g_{cat}^{-1})
				theor.	XPS	
SiO_2	–	380	–	–	–	0.6
MoO_3/SiO_2	0.2	311	0.026	8	9	2.7
	1.1	314	0.146	46	13	28.6
	2.0	311	0.269	85	39	37.3
	4.0	187	0.895	174	48	106.7
V_2O_5/SiO_2	0.2	270	0.049	13	47	7.3
	1.0	272	0.240	67	48	21.7
	2.0	257	0.510	134	137	29.9
	5.3	231	1.510	370	139	92.7

been made by using a specifically designed batch reactor described elsewhere [15] operating at 1.7 bar and 520°C with a catalyst sample of 1.0 g and a recycle flow rate of 1000 $\mathrm{Ncm}^3\ \mathrm{min}^{-1}$. The reaction mixture consisted of 18 mmol of methane, 9 mmol of oxygen as oxidant ($CH_4/O_2 = 2$), 18 mmol of nitrogen as standard for gas chromatographic (GC) analysis and 53 mmol of helium as diluent.

Table 2 shows the activity data of MoO_3 and V_2O_5 catalysts expressed in terms of overall reaction rate ($10^{-7}\ \mathrm{mol_{CH_4}}\ \mathrm{g_{cat}^{-1}}\ \mathrm{s}^{-1}$) and specific reaction rate ($10^{-10}\ \mathrm{mol_{CH_4}}\ \mathrm{m}^{-2}\ \mathrm{s}^{-1}$) and product selectivity. A monotonically decrease in the activity with increasing metal oxide loading has been found for MoO_3 catalysts, while for V_2O_5 loading in the range 0.2–5.3 wt% a significant enhancing effect of the original activity of the SiO_2 has been noticed. The product selectivity indicates that: (i) both MoO_3 and V_2O_5 exert a higher oxidising action on the reaction mixture since the CO_2 selectivity found for the oxide catalysts is higher than that of unpromoted SiO_2 even at lower activity levels; (ii) a low extent of CO formation ranging between 1 and 7% has been found for all the catalysts; this indicates occurrence of a similar reaction pathway for both systems; and (iii) the HCHO selectivity increases with increasing MoO_3 loading and falls with increasing V_2O_5 loading; these trends reflect the inverse relationship between conversion and selectivity to HCHO generally observed for methane partial oxidation catalysts [6].

From table 1 it can be seen that in the case of both MoO_3 and V_2O_5 loaded catalysts there is a decrease in BET surface area with increasing the metal oxide loading. For both MoO_3 and V_2O_5 systems the XPS atomic ratios are lower than the theoretical ones. In MoO_3/SiO_2 catalysts the surface occupancy ($\mathrm{Mo/nm^2}$) is slightly lower than the occupancy ($\mathrm{V/nm^2}$) calculated for the V_2O_5/SiO_2 catalysts. These similarities in physico-chemical properties contrast with the differences in

Table 2
Activity and selectivity of the MoO_3/SiO_2 and V_2O_5/SiO_2 catalysts in the selective partial oxidation of methane at 520°C

Catalyst	Metal oxide loading (wt%)	Reaction rate		Selectivity (%)		
		($10^{-7}\ \mathrm{mol_{CH_4}}\ \mathrm{g_{cat}^{-1}}\ \mathrm{s}^{-1}$)	($10^{-10}\ \mathrm{mol_{CH_4}}\ \mathrm{m}^{-2}\ \mathrm{s}^{-1}$)	CO_2	CO	HCHO
SiO_2	–	2.38	6.3	38	5	57
MoO_3/SiO_2	0.2	1.82	5.8	56	3	41
	1.1	1.51	4.8	62	7	31
	2.0	1.34	4.3	65	2	33
	4.0	0.33	1.7	55	–	45
V_2O_5/SiO_2	0.2	1.12	4.1	48	1	51
	1.0	2.76	10.1	67	–	33
	2.0	4.44	17.3	69	4	27
	5.3	7.60	32.9	70	2	28

catalytic behaviour indicating that the catalytic action is determined by some other factor(s). It has been claimed by several workers [19,20] that LTOC measurements correlate with the activity of selective oxidation catalysts. In the present case such a correlation is not found for MoO_3 catalysts as shown in fig. 1 where activity is expressed in terms of space time yield to HCHO (STY_{HCHO}, g kg_{cat}^{-1} h^{-1}). It is proposed that a straight correlation exists between activity and the concentration of surface reduced sites of the working catalysts as reflected in HTOC (high temperature oxygen chemisorption) measurements [21]. Overall STYs for MoO_3/SiO_2 fall steadily with MoO_3 loading. For low-loaded V_2O_5/SiO_2 systems (up to 1 wt%) a decrease in specific activity and STY with respect to the SiO_2 support is seen. Such a behaviour is the consequence of a strong interaction between SiO_2 and V_2O_5 (much more stronger than that between SiO_2 and MoO_3) which results in a partial poisoning (blocking) of the active surface of the bare SiO_2. This hypothesis is further supported by the remarkable decrease in the specific surface area of the SiO_2 owing to small V_2O_5 addition [15]. In fact, the BET SA of the SiO_2 falls from 380 to 270 m^2 g^{-1} for 0.2% V_2O_5 addition. It is noteworthy that for tenfold higher loaded MoO_3/SiO_2 catalyst (2% MoO_3/SiO_2) a slighter decrease in BET surface area has been observed. This indicates the occurrence of a weaker interaction between MoO_3 and SiO_2 with respect to that occurring between V_2O_5 and SiO_2. The increase in activity found for higher loaded (> 1 wt%) V_2O_5 catalysts is likely due to the creation of new active sites on the supported V_2O_5 layer. These arguments allow us to propose for unpromoted SiO_2 and V_2O_5 or MoO_3 promoted silica catalysts the surface modelling depicted in fig. 2. According to this scheme we

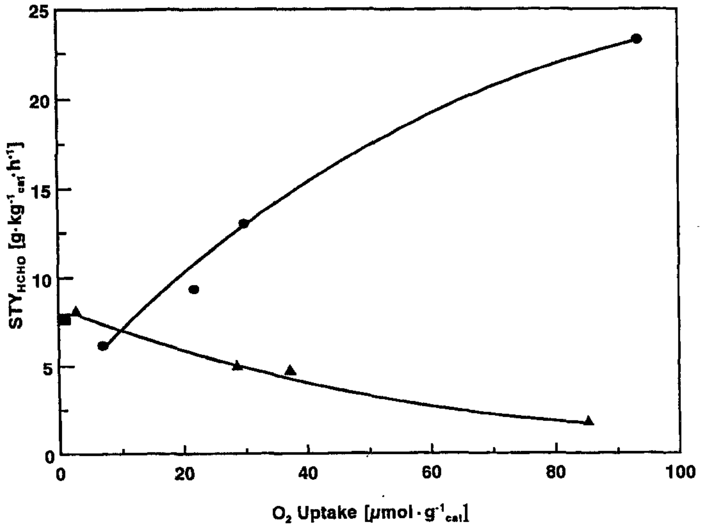

Fig. 1. Relationship between LTOC uptake and space time yield to HCHO on (■) bare SiO_2, (▲) MoO_3/SiO_2 and (●) V_2O_5/SiO_2 catalysts.

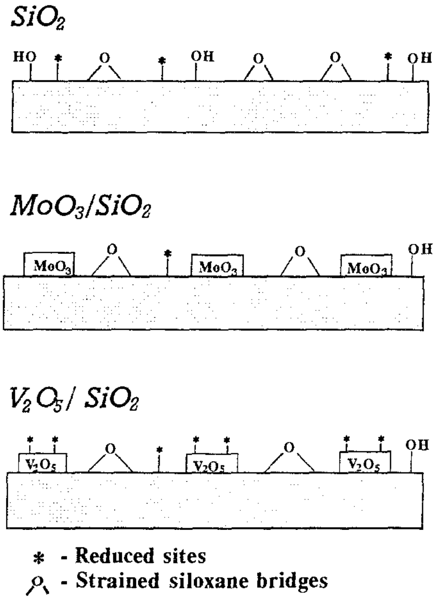

Fig. 2. Surface modelling for SiO_2, MoO_3/SiO_2 and V_2O_5/SiO_2 systems.

infer that the surface of the SiO_2 bears two kinds of active sites, i.e., * (reduced sites) and /O\ sites (strained siloxane bridges) which are effective in activating O_2 and CH_4 molecules respectively. Both MoO_3 and V_2O_5 can partially mask active sites of the precipitated SiO_2 surface with the difference that V_2O_5 generates own reduced active sites able to activate gas-phase oxygen. On the contrary, we observe that a peculiar interaction pathway between MoO_3 and SiO_2 has been already explained by inferring an encapsulation mechanism of MoO_3 within the SiO_2 which causes the hydrothermal structural changes of the SiO_2 (i.e., lowering in BET SA) and the formation of hardly reducible $SiMoO_x$ species [22]. This statement could account for the inability of the silica supported MoO_3 in assisting the formation and stabilisation of own reduced sites. The opposite effect exerted by MoO_3 (4 wt%) and V_2O_5 (5 wt%) dopants on the reactivity of the bare SiO_2 and particularly in the process of oxygen activation has been already correlated with the density of reduced sites determined by high temperature oxygen chemisorption measurements [21].

Finally, it is concluded that the activity observed with the bare SiO_2 is due to some specific surface sites possessing donor properties to activate molecular oxygen (i.e., Si^{3+} on structure defects of the precipitated silica [17]). These sites are influenced negatively by the presence of MoO_3 probably due to physically based masking of sites, but for V_2O_5 appreciable enhancement of activity is made possible by the introduction of additional specific reducible sites. The deeper understanding of the precise nature of the sites awaits the results of further surface characterization studies.

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