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On the Nature of the Catalytic Activity of Silica-Based Oxide Catalysts in the Partial Oxidation of Methane to Formaldehyde with O_2

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The partial oxidation of methane to formaldehyde with molecular O_2 has been investigated on various commercial bare SiO_2 samples and silica-supported MoO_3 and V_2O_5 catalysts at 550–650°C in batch, pulse, and continuous flow reactors at 1.7 bar. Amongst the different SiO_2 samples, the highest HCHO productivity expressed as space time yield (STY_{HCHO}, $g \cdot kg_{cat}^{-1} \cdot h^{-1}$) is found with "precipitated" silica, while "fumed" SiO_2 results in the least reactive silica. Incorporation of molybdena depresses the STY_{HCHO} value for the "precipitated" silica but enhances the STY_{HCHO} for bare "fumed" silica. In contrast, addition of vanadia to either "precipitated" or "fumed" silicas leads to higher STY_{HCHO} values. On the basis of a series of experiments performed by continuous scanning of the reaction mixture with a quadrupole M.S., the participation of lattice oxygen in the main reaction pathway has been ruled out. The acidic properties of the catalysts have been compared by ZPC and NH_3-TPD measurements. A straight correlation between the density of reduced sites (ρ, 10^{16} $s_r \cdot g_{cat}^{-1}$), evaluated in steady-state conditions by O_2 chemisorption, and the reaction rate has been disclosed. MoO_3 and V_2O_5 dopants modify the catalytic properties of SiO_2 by affecting the process of oxygen activation on the catalyst surface. © 1994 Academic Press, Inc.

INTRODUCTION

The great amount of research interest focused during the past decade on the catalytic partial oxidation of methane to formaldehyde has led us to ascertain that the more effective catalysts are the SiO_2-based ones (1, 2). Despite the fact that several kinetic studies on SiO_2 (3, 4) and silica-supported MoO_3 (5, 6), V_2O_5 (7–9), or heteropolyacids (10) involving the use of either oxygen or nitrous oxide as oxidant have been performed, very few studies have attempted to correlate catalytic activity with the physicochemical properties of the solids. Barbaux *et al.* (11), studying the title reaction on a series of differently loaded MoO_3/SiO_2 catalysts, observed that the yield and selectivity to HCHO increase with the amount of silicomolybdic acid in the catalyst. The promoting effect of MoO_3, up to a surface coverage of 0.1 monolayers, on the reactivity of bare silica catalysts has been claimed by Spencer (6). Recently, Hodnett and co-workers (12) have reported the inability of Fe, Ag, Cr, Na, and Co ions to improve the activity of silica-supported MoO_3 and V_2O_5 catalysts. For unpromoted V_2O_5/SiO_2 catalysts, they found that V_2O_5 loading in the range 1.8–7.2 wt% gave the best performance. Such a higher activity of the medium loaded V_2O_5 catalysts has been attributed to their capability to readily undergo a reduction–reoxidation process in the reaction conditions. However, the results achieved by the different research groups, either in terms of selectivity or yield to formaldehyde, appear to be controversial and not very encouraging (2). Several authors have seriously questioned the catalytic nature of the title reaction (3, 13, 14). Indeed, Burch and co-workers (13) have raised serious doubts regarding the convenience of using solid catalysts, stating that the yields of HCHO obtained from the catalytic reaction are lower than that obtained from the purely homogeneous gas-phase reaction. Nevertheless, Garibyan and Margolis (14), in reviewing the mechanism of methane oxidation over SiO_2 catalysts, proposed a heterogeneous–homogeneous reaction scheme which predicts the generation of HCHO on the catalyst surface only. On this account, we have previously pointed out (15, 16) the unique suitability of the SiO_2 surface in catalysing the title reaction, assessing also the influence of the preparation methods, Na loading, and thermal and mechanical pretreatments on its reactivity (15). In addition, we have also disclosed that the functionality of the very active "precipitated" SiO_2 towards the formation of HCHO is significantly promoted by V_2O_5, while it is depressed by the MoO_3 (17, 18). Namely, a monotonic 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

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effect of the original activity of the SiO_2 has been noted (17). Such peculiar results have been correlated with the density of reduced sites evaluated under reaction conditions on the surface of the different oxide catalysts (19).

The surface and the structure features of MoO_3 (20) and V_2O_5 (21) supported on silica have been extensively studied. The influence of the MoO_3 loading on its dispersion and reactivity has been assessed (20). In particular, on medium loaded MoO_3 catalysts (4.2–11.2 wt% MoO_3) the formation of polymeric molybdate species with octahedral coordination of the Mo ions has been detected (20). On the contrary, it has been claimed that V ions form surface compounds with a lower coordination number in medium loaded V_2O_5/SiO_2 catalysts (21). In fact, the presence of both oligomers with tetrahedral coordination around a V ion and ribbons with V ions in the centre of a square pyramid has been identified (21). Similarly, Centi *et al.* (22) have elucidated the coordination and nature of V sites in V-silicalite catalysts, providing further evidence of the presence of V^{4+} ions in a tetrahedral environment which give rise to the formation of very reactive O_2^- species. Oyama *et al.* (23) have recently developed an oxygen chemisorption method to characterise unsupported and silica-supported MoO_3 (24) and V_2O_5 (23), observing an interesting effect of structure on the reaction pathway of ethane partial oxidation on V_2O_5/SiO_2 catalysts (25). However, a valid attempt aimed at evaluating the amount of active sites present on the catalyst surface in steady-state conditions during the partial oxidation of methane or higher hydrocarbons is still lacking (25, 26).

In this paper we present a comparative study of the catalytic properties of various bare SiO_2 samples and differently loaded MoO_3/SiO_2 and V_2O_5/SiO_2 catalysts in the partial oxidation of methane to formaldehyde. The role of the acidic properties and reduced sites, evaluated in steady-state conditions, is addressed. A cooperative reaction pathway, involving the presence of two kinds of active sites capable of methane activation and oxygen binding, is proposed.

EXPERIMENTAL

Catalyst

Four different SiO_2 samples (Si 4-5P, Akzo product, $S.A._{BET}$ = 381 $m^2 \cdot g^{-1}$; Cab-O-Sil M5, Cabot product, $S.A._{BET}$ = 200 $m^2 \cdot g^{-1}$; 250 MP, Grace product, $S.A._{BET}$ = 180 $m^2 \cdot g^{-1}$; and D11-11, BASF product, $S.A._{BET}$ = 137 $m^2 \cdot g^{-1}$) have been used. Silica Si 4-5P and D11-11 were obtained by precipitation method (therefore these samples will be termed "precipitated" SiO_2), while Cab-O-Sil M5 and 250 MP were prepared by pyrolytic ("fumed or pyrolytic") and sol-gel ("silica gel") processes, respectively. The concentrations of alkali and alkaline-earth oxide impurities of the silica samples, determined by X-ray fluorescence (XRF) analysis using an ARL 8410 spectrometer, are listed in Table 1.

Differently loaded MoO_3 and V_2O_5 catalysts have been prepared by incipient wetness impregnation of precipitated Si 4-5P and fumed M5 SiO_2 samples with a basic solution (pH = 11) of ammonium heptamolybdate or ammonium metavanadate, respectively. The impregnated samples were dried at 90°C for 24 h and then calcined at 600°C for 16 h. All the catalysts were compressed at 100 bar and subsequently crushed to obtain the used particle size fraction 16–25 mesh.

BET surface areas were obtained by N_2 adsorption measurements at −196°C. MoO_3 and V_2O_5 loadings were determined by atomic absorption spectroscopy (AAS).

Catalyst Testing

Batch reactor. Methane partial oxidation experiments were performed using a specifically designed batch reactor, provided with an external recycle pump and a liquid product condenser placed downstream of the reactor and maintained at −15°C, which traps the oxygenated products and prevents their further oxidation (18). The quartz tube reactor measured 4 mm in diameter (i.d.) and 90 mm in length. The reaction mixture consisted of 18.2 mmol of methane, 9.1 mmol of oxygen ($CH_4/O_2 = 2$), 9.1 mmol of nitrogen as standard for GC analysis, and 54.6 mmol of helium as diluent. All the runs were carried out with 0.05 g of catalyst (particle size, 16–25 mesh), at 1.7 bar, and in the T range 550–650°C with a flow rate of 1.0×10^3 N $cm^3 \cdot min^{-1}$. This reactor device allows us to obtain experimental data unaffected by mass and heat-transfer limitations by operating in isothermal mode and at quasi-zero conversion per pass (18). The catalyst samples were pretreated *in situ* in an air flow at the reaction temperature for 2 h. Care was taken to avoid oxygen-limiting conditions and hence methane conversion data obtained only for O_2 conversions below 20% have been used for the calculation of reaction rates. In all our catalytic experiments the hourly CH_4 conversion ranged between 1 and 8%. In the adopted experimental conditions, on the basis

TABLE 1

Alkali and Alkaline-Earth Oxide Impurity Content of Various Commercial SiO_2 Samples

Sample	Na_2O (ppm)	MgO (ppm)	CaO (ppm)	BaO (ppm)	Total content
Si 4-5P	630	190	380	6	1206
D11-11	920	350	100	94	1464
250 MP	1700	320	38	180	2238
M 5	630	270	12	—	912

of preliminary blank tests, the contribution of the homogeneous gas-phase reaction or blank effect on the "wall" of the reactor can be completely neglected (18).

All the gaseous products were analysed on-line by automatic sampling with a Hewlett–Packard 5890A gas-chromatograph equipped with 2 columns in series: (i) a 2.5-m Porapak QS 80/100 and (ii) a 2.5-m Molecular Sieve 5A kept at 70°C and connected to a thermal conductivity detector (TCD). HCHO was cumulatively determined by GC at the end of the run on the condensed mixture by using a 1.8-m Haysep R 100/120 column kept at 130°C and connected to a TCD. Carbon and oxygen mass balances were generally better than 98–99% in all the runs.

Pulse-flow reactor. A conventional flow apparatus operating in both continuous and pulse mode has been used. Catalyst samples (0.05 g) were heated *in situ* up to reaction temperature (550–650°C) in a He carrier flow (50 N $cm^3 \cdot min^{-1}$), and then 5.5 N cm^3 $CH_4/O_2/He$ ($P_{CH_4} : P_{O_2} : P_{He} = 2:1:7$) or CH_4/He ($P_{CH_4} : P_{He} = 2:8$) pulses were injected onto the sample until a constant level of reaction products was reached. The pulse time was 6.6 sec. The reactor stream was analysed by an on-line connected "Thermolab" (Fisons Instruments) quadrupole mass spectrometer (QMS).

Catalyst Characterisation

Oxygen chemisorption measurements. Measurements were performed in the above flow apparatus using He as carrier gas (30 N $cm^3 \cdot min^{-1}$). Prior to chemisorption measurements, catalyst samples (0.25–1.00 g) were treated *in situ* for 15 min in a flow of $CH_4/O_2/He$ ($P_{CH_4} : P_{O_2} : P_{He} = 2:1:7$) reaction mixture at 550–650°C. The residence time of this treatment was selected properly for each sample to provide a CH_4 conversion extent lower than 10 mol% in order to prevent in the end zone of the catalytic bed overreduction of the catalyst due to the high level of O_2 conversion. O_2 uptakes were determined in a pulse mode ($V_{O_2 pulse} = 1.7$ μmol) at the same temperature of the pretreatment by using a TCD connected to a DP 700 data processor (Carlo Erba Instruments). The number of reduced sites was calculated by assuming the chemisorption stoichiometry O_2/"reduced site" of 1/2.

NH_3–TPD measurements. Measurements were performed in the same apparatus. Prior to NH_3 saturation, the samples (0.05 g) were treated at 600°C in O_2/He or $CH_4/O_2/He$ flowing mixtures for half an hour. After NH_3 saturation at 150°C, the samples were purged at the same temperature in the He carrier flow (30 N $cm^3 \cdot min^{-1}$) for 1 h.

The TPD process was run in the range 150–510°C with a heating rate of 12°C · min^{-1}, the NH_3 desorption being monitored and quantified by the QMS.

Zero point charge (ZPC) measurements. Potentiometric titration of samples (3.0 g) was carried out in an aqueous suspension (500 ml electrolytic KNO_3 solution) according to the procedure reported by Parks (27).

RESULTS AND DISCUSSION

A. Bare Silica Catalysts

In our previous paper (15) we reported that the reactivity of the SiO_2 surface in the title reaction is mainly controlled by the preparation method. Although there is a general consensus on such argument (3, 4, 10), no attempts have been made to rationalise the catalytic behaviour of the different SiO_2 samples in terms of physico-chemical properties. Therefore, in order to shed some light on this issue, the activity of four kinds of commercial SiO_2 samples, namely Si 4-5P, 250 MP, M5, and D11-11, was evaluated at the same reaction conditions in batch, flow, and pulse reactors. All three techniques lead to similar results. The catalytic behaviour of these four SiO_2 samples at 600 and 650°C is presented in Table 2 in terms of reaction rate, product selectivity, and HCHO productivity (STY_{HCHO}, $g \cdot kg_{cat}^{-1} \cdot h^{-1}$). These data indicate that "precipitated" SiO_2 Si 4-5P possesses the highest activity, while "fumed" M5 SiO_2 sample is the least active SiO_2. The great difference in reactivity between the various SiO_2 samples cannot be rationalised in terms of alkali and alkaline earth oxide impurities (see Table 1). In fact, it is evident that Si 4-5P and M5 SiO_2 samples contain the same amount of Na_2O (630 ppm), while their reactivities differ for more than one order of magnitude (see Table 2). The total content of alkali and alkaline-earth oxides does not allow us to draw any relationship between reactivity and concentration of impurities since M5 and 250 MP samples, containing the least (912 ppm) and the highest (2238 ppm) amount of impurities, respectively, result in the less active SiO_2 catalysts. We have recently proposed that one of the most important properties of oxide catalysts in the title reaction is the capability to create special active species of oxygen leading to the HCHO formation (17, 19). This process likely involves the gas-phase O_2 activation on the reduced sites of the catalyst surface (19). Therefore, in order to check the validity of such a hypothesis, the density of reduced sites (ρ, 10^{16} $s_r \cdot g_{cat}^{-1}$) of the different SiO_2 catalysts was measured. This measurement was performed after treatment of the catalyst with the reaction mixture under the same conditions adopted for the evaluation of the catalytic activity. Thus, the density of reduced sites determined by such procedure corresponds to that of the working catalysts. In Fig. 1 the density of reduced sites at 600°C (Fig. 1a) and 650°C (Fig. 1b) for the different bare SiO_2 samples is plotted versus the STY_{HCHO}. Such data indicate the existence of a strong

TABLE 2

Activity and Formaldehyde Productivity of Various Commercial SiO_2 Samples in the Partial Oxidation of Methane[a]

Sample	Preparation method	S.A.$_{BET}$ ($m^2 \cdot g^{-1}$)	T_R (°C)	Reaction rate (10^{-7} $mol_{CH_4} \cdot g_{cat}^{-1} \cdot s^{-1}$)	Selectivity (%) HCHO	CO	CO_2	STY_{HCHO} ($g \cdot kg_{cat}^{-1} \cdot h^{-1}$)
Si 4-5P	Precipitation	381	600	14.36	75	18	7	115.85
			650	44.29	63	23	14	303.84
D11-11	Precipitation	137	600	8.93	56	31	13	54.43
			650	31.35	47	30	23	159.17
250 MP	Sol–gel	180	600	2.33	73	20	7	18.58
			650	7.99	70	19	11	60.11
M5	Pyrolysis	200	600	0.40	79	11	10	3.28
			650	2.53	75	13	12	20.76

[a] The catalytic activity data were obtained by batch reactor tests.

correlation between activity and density of reduced sites of the silica surface. All these findings prove definitively that the preparation method is fundamental in determining the reactivity of the SiO_2 surface in the partial oxidation of methane (15). In fact, for the various SiO_2 samples the following reactivity scale referring to the preparation method can be drawn: pyrolysis < sol-gel < precipitation.

B. Silica-Supported MoO_3 and V_2O_5 Catalysts

The catalytic behaviour of silica-supported MoO_3 and V_2O_5 catalysts in the partial oxidation of methane has been widely addressed by many research groups (1, 2, 5–12). It is generally recognised that both MoO_3 (1, 2, 5, 6, 11, 12) and V_2O_5 (1, 2, 7–9, 12) enhance the catalytic activity of the bare SiO_2 support. In the present work, the catalytic performance of differently loaded MoO_3 and V_2O_5 catalysts supported on "fumed" M5 (the least reactive SiO_2) and "precipitated" Si 4-5P (the highest reactive SiO_2) silicas in the range 550–650°C was studied.

The activity data of the oxide catalysts supported on "fumed" M5 silica are summarised in Table 3 in terms of reaction rate, product selectivity, and STY_{HCHO}. These results indicate that MoO_3 and V_2O_5 really improve the catalytic properties of "fumed" SiO_2. The promoting effect of V_2O_5 is more pronounced than that of MoO_3 even if the loading of V_2O_5 is lower than that of MoO_3. On the whole, this promoting effect of MoO_3 and V_2O_5 is in agreement with that already reported in the literature (8, 12). The density of reduced sites of these oxide catalysts, measured according the procedure above reported for bare SiO_2 samples, is plotted in Fig. 2 against the STY_{HCHO} at 600°C (Fig. 2a) and 650°C (Fig. 2b). For sake of comparison therein is also included the data of bare "fumed"

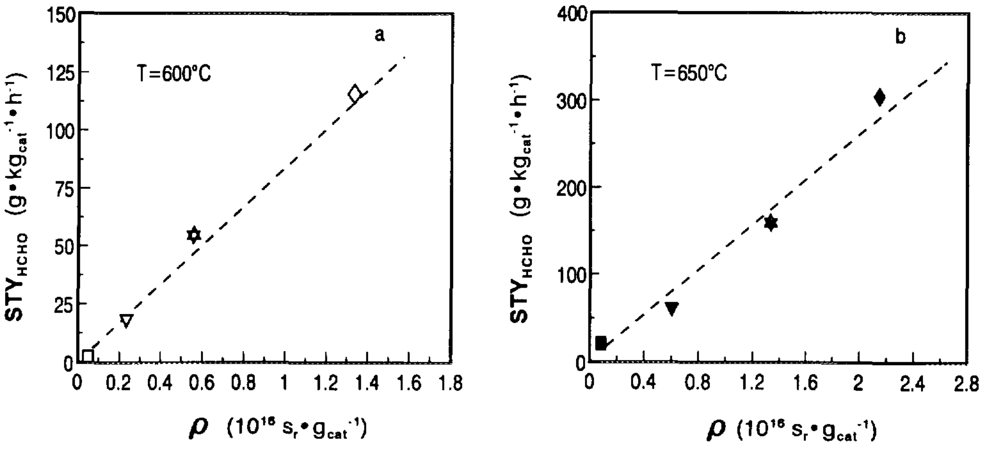

FIG. 1. Relationship between density of reduced sites (ρ) and STY_{HCHO} in the partial oxidation of methane on "precipitated" Si 4-5P (◇, ◆), "precipitated" D11-11 (✡, ✱), "silica gel" 250MP (▽, ▼), and "fumed" M5 (□, ■) SiO_2 catalysts at 600°C (◇, ✡, ▽, □) and 650°C (◆, ✱, ▼, ■).

TABLE 3

Activity and Formaldehyde Productivity of "Fumed" M5 SiO_2-Supported MoO_3 and V_2O_5 Catalysts in the Partial Oxidation of Methane[a]

Sample	S.A.$_{BET}$ ($m^2 \cdot g^{-1}$)	T_R (°C)	Reaction rate (10^{-7} $mol_{CH_4} \cdot g_{cat}^{-1} \cdot s^{-1}$)	Selectivity (%)			STY_{HCHO} ($g \cdot kg_{cat}^{-1} \cdot h^{-1}$)
				HCHO	CO	CO_2	
4.5% MoO_3/SiO_2 M5	165	550	0.57	95	—	5	6.16
		600	2.93	91	5	4	29.51
		650	13.65	86	9	5	126.78
2.2% V_2O_5/SiO_2 M5	191	550	9.98	82	15	3	88.31
		600	58.34	50	23	27	318.05
		650	216.98	30	35	35	687.46

[a] The catalytic activity data were obtained by batch reactor tests.

SiO_2. These results confirm the validity of the straight correlation between activity and density of reduced sites of silica based oxide catalysts (19).

The activity data of the oxide catalysts supported on "precipitated" Si 4-5 P SiO_2 are presented in Table 4. These data are qualitatively different from those observed for "fumed" silica-based systems (see Table 3). In fact, V_2O_5 exerts a promoting effect on the activity of "precipitated" SiO_2 similar to that observed for the addition of V_2O_5 to the "fumed" SiO_2. This being still in agreement with the literature data (1, 7, 8, 12), while MoO_3 decreases the original activity of the bare "precipitated" SiO_2 sample. These batch reactor data have been checked by flow and pulse reactor experiments. The comparison of the different experimental techniques is reported in Table 5. The good agreement between the data obtained by such different reactors strengthens the reliability of the negative effect of MoO_3 on the catalytic activity of the bare "precipitated" SiO_2. Figure 3 shows the relationship between density of reduced sites and STY_{HCHO} for the "precipitated" SiO_2-based catalysts at 600°C (Fig. 3a) and 650°C (Fig. 3b). These data confirm further the straight correlation between density of reduced sites and catalytic activity of silica-based oxide systems. It is worth noting that MoO_3 addition causes a decrease in both the catalytic activity and the density of reduced sites of the unpromoted "precipitated" SiO_2 surface. Such a different effect of MoO_3 and V_2O_5 addition on the reactivity of the "precipitated" SiO_2 surface can be explained by inferring that 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 its own reduced active sites which are able to activate gas-phase oxygen (17, 19). On the contrary, a strong interaction pathway between MoO_3 and SiO_2, which causes the hydrothermal structural changes of the SiO_2 (i.e., lowering in BET S.A. from 381 $m^2 \cdot g^{-1}$ of the bare "precipitated" SiO_2 to 187 $m^2 \cdot g^{-1}$ of the 4.0% MoO_3/SiO_2 Si 4-5P sample) and the formation of hardly reducible $SiMoO_x$ species (28), could account for the inability of the silica-supported MoO_3 to assist in the formation and

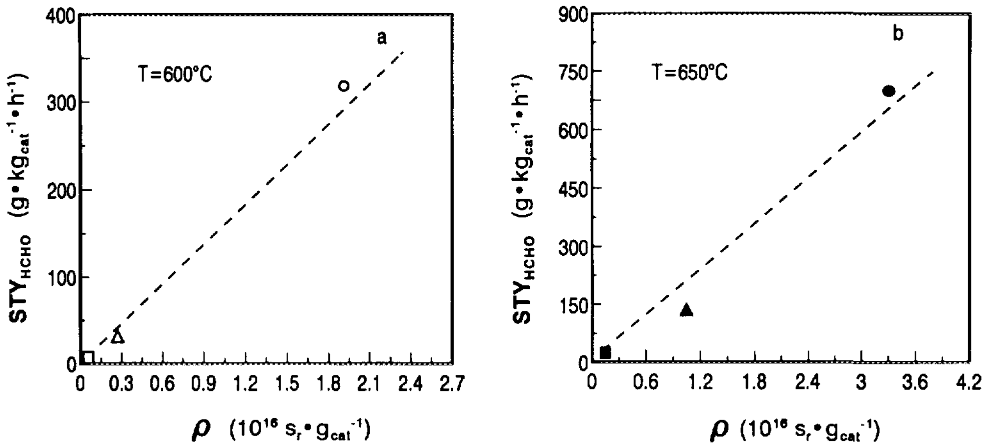

FIG. 2. Relationship between density of reduced sites (ρ) and STY_{HCHO} in the partial oxidation of methane on "fumed" M5 SiO_2 (□, ■), 4.5% MoO_3/SiO_2 M5 (△, ▲), and 2.2% V_2O_5/SiO_2 M5 (○, ●) catalysts at 600°C (□, △, ○) and 650°C (■, ▲, ●).

TABLE 4

Activity and Formaldehyde Productivity of "Precipitated" Si 4-5P SiO_2-Supported MoO_3 and V_2O_5 Catalysts in the Partial Oxidation of Methane[a]

Sample	S.A.$_{BET}$ ($m^2 \cdot g^{-1}$)	T_R (°C)	Reaction rate (10^{-7} $mol_{CH_4} \cdot g_{cat}^{-1} \cdot s^{-1}$)	Selectivity (%) HCHO	CO	CO_2	STY$_{HCHO}$ ($g \cdot kg_{cat}^{-1} \cdot h^{-1}$)
4.0% MoO_3/SiO_2 Si 4-5P	187	550	1.00	70	—	30	7.60
		600	3.13	70	—	30	22.70
		650	10.50	70	2	28	76.10
5.3% V_2O_5/SiO_2 Si 4-5P	231	550	15.27	61	2	37	100.55
		600	60.87	48	14	38	318.05
		650	210.61	35	51	14	793.48

[a] The catalytic activity data were obtained by batch reactor tests.

stabilisation of its own reduced sites. In addition, it can be also argued that such strong interaction involves an electron transfer process between Mo ions and silica support which negatively affects the concentration of reduced sites of the SiO_2 surface. On other hand, for "fumed" oxide catalyst, the weaker interaction between MoO_3 and inert SiO_2 surface, documented by the slight decrease in BET S.A. (from 200 $m^2 \cdot g^{-1}$ of the bare "fumed" SiO_2 to 165 $m^2 \cdot g^{-1}$ of the 4.5% MoO_3/SiO_2 M5 sample), could allow the stabilisation of reduced sites on supported MoO_3 patches or crystallites which well accounts for the promoting effect of MoO_3 on the "fumed" silica. Besides, we observe that 2.2% V_2O_5/SiO_2 M5 catalyst displays a catalytic behaviour analogous to that of 5.3% V_2O_5/SiO_2 Si 4-5P. This analogous promoting effect of V_2O_5, even if at different oxide loading, can be the consequence of a weaker interaction occurring between V_2O_5 and "fumed" SiO_2 with respect to that between V_2O_5 and "precipitated" SiO_2. This hypothesis is again supported by the different decrease in BET S.A. observed for the two silica-supported V_2O_5 catalysts. In fact, this decrease is very slight for the 2.2% V_2O_5/SiO_2 M5, while it is well pronounced for the 5.3% V_2O_5/SiO_2 Si 4-5P.

However, the different promoting effect of MoO_3 and V_2O_5 on the reactivity of the silica surface can be explained by invoking a different capability of such supported oxides in stabilising reduced states of metal ions (1, 20–23, 29). According to the literature data, on the SiO_2 surface Mo ions exist in octahedral coordination (20) which assist the stabilisation of the highest oxidation state (Mo^{VI}). On the contrary, for V_2O_5/SiO_2 catalysts it has been claimed that V ions form surface compounds with lower coordination number which assist the stabilisation of lower oxidation states (21).

C. Pulse Reaction Tests in Presence and Absence of Molecular Oxygen

The rate of the partial oxidation of methane both on bare "precipitated" Si 4-5P SiO_2 and MoO_3- and V_2O_5-doped "precipitated Si 4-5P SiO_2 catalysts in the presence and in the absence of molecular oxygen was measured in

TABLE 5

Activity and Formaldehyde Productivity of SiO_2 Si 4-5P and 4% MoO_3/SiO_2 Si 4-5P in the Partial Oxidation of Methane Measured by Different Reactors at 650°C

Reactor	Reaction rate (10^{-7} $mol_{CH_4} \cdot g_{cat}^{-1} \cdot s^{-1}$)	Selectivity (%) HCHO	CO	CO_2	STY$_{HCHO}$ ($g \cdot kg_{cat}^{-1} \cdot h^{-1}$)
SiO_2 Si 4-5P					
Batch	44.29	63	23	14	303.84
Continuous flow	41.64	37	52	11	167.18
Pulse	44.60	13	63	24	62.67
4.0% MoO_3/SiO_2 Si 4-5P					
Batch	10.50	70	2	28	76.10
Continuous flow	7.73	48	20	32	40.12
Pulse	13.90	30	43	27	45.08

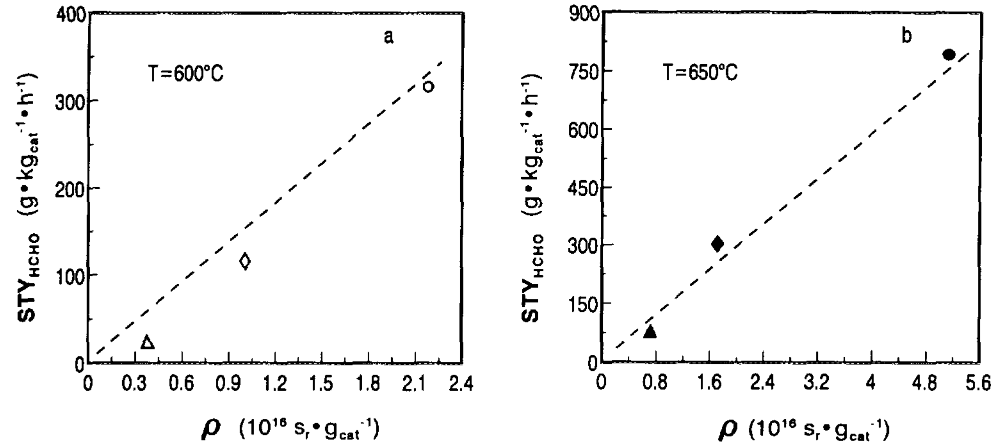

FIG. 3. Relationship between density of reduced sites (ρ) and STY_{HCHO} in the partial oxidation of methane on "precipitated" Si 4-5P SiO_2 (◇, ◆), 4.0% MoO_3/SiO_2 Si 4-5P (△, ▲), and 5.3% V_2O_5/SiO_2 Si 4-5P (○, ●) catalysts at 600°C (◇, △, ○) and 650°C (◆, ▲, ●).

the T_R range 550–650°C by a pulse reactor connected to a QMS. In the procedure of such tests, special attention was paid to avoid a decline of the state of the catalytic surface from the steady-state conditions. This was checked by pulsing reaction mixture (CH_4 + O_2) before and after reducing pulse (CH_4). The results presented in Table 6 definitively confirm that (i) V_2O_5 promoted catalyst is more active than bare "precipitated" SiO_2 and (ii) the addition of MoO_3 produces a considerable decrease in the activity of the bare "precipitated" SiO_2 surface. From the comparison of the rate of formation of fully and partially oxidised products with and without O_2 in the reaction mixture it emerges that the oxidation reaction proceeds in the presence of gas-phase oxygen. Only a small amount of products has been detected in the absence of gas-phase O_2 at the highest T_R (650°C) on V_2O_5/SiO_2 catalysts. Then, as the reaction rates in the mixture of reactant and in separate steps differ (26), these data exclude the participation of lattice oxygen in the partial oxidation of methane via a two-step redox mechanism

TABLE 6

Methane Partial Oxidation on Silica and Silica-supported MoO_3 and V_2O_5 Catalysts in the Presence and in the Absence of Gas-Phase Oxygen

Catalyst		T_R (°C)	Reagents	Rate of product formation (10^{17} molec · g_{cat}^{-1} · s^{-1})		
				HCHO	CO	CO_2
SiO_2	Si 4-5P	550	CH_4 + O_2	0.63	2.61	12.30
			CH_4	—	—	—
		600	CH_4 + O_2	1.68	6.90	2.61
			CH_4	—	—	—
		650	CH_4 + O_2	3.54	16.80	6.33
			CH_4	—	0.75	—
4.0% MoO_3/SiO_2	Si 4-5P	550	CH_4 + O_2	0.30	0.48	1.08
			CH_4	—	—	—
		600	CH_4 + O_2	0.90	1.05	1.95
			CH_4	—	—	—
		650	CH_4 + O_2	2.55	3.60	2.25
			CH_4	—	—	—
5.3% V_2O_5/SiO_2	Si 4-5P	550	CH_4 + O_2	1.68	2.46	1.38
			CH_4	—	—	—
		600	CH_4 + O_2	3.60	20.04	8.28
			CH_4	—	1.35	—
		650	CH_4 + O_2	5.76	76.50	16.80
			CH_4	0.30	7.20	3.30

as main reaction pathway proving the occurrence of a "concerted mechanism" (26).

D. *Acidity Characterisation of Silica-Based Oxide Catalysts*

The acidic properties of bare "fumed" and "precipitated" SiO_2 samples and MoO_3- and V_2O_5-silica-based oxide catalysts were comparatively evaluated by NH_3-TPD tests and ZPC measurements. The results of these tests, listed in Table 7, allow us to draw the following order of acidity both for "precipitated" and "fumed" silica-based oxide catalysts: $MoO_3/SiO_2 > V_2O_5/SiO_2 > SiO_2$. This order is essentially different from the reactivity scale in the partial oxidation of methane.

E. *O_2 Activation and Reaction Mechanism*

Apart from the generally accepted theory of the pure homogeneous gas-phase oxidation of methane, based on a chain reaction of free radicals (1) three distinct theoretical approaches have been adopted in formulating the mechanism of the partial oxidation of methane to formaldehyde on oxide catalysts. One consists of a classical Langmuir–Hinshelwood model, where all the reactions take place on the surface (30). It is assumed that the reacting molecules interact simultaneously with the catalyst surface and the reaction between such activated species gives rise to the formation of the reaction products without the participation of oxygen from the oxide lattice (31). Different schools of thought state that the formation of HCHO occurs through the involvement of lattice oxygen (32–34). A third approach deals with the proposition of a heterogeneous–homogeneous mechanism (14). Even if the HCHO is assumed to be formed on the surface, it essentially entails the generation of radicals on the surface and formation of products in gas phase. This last theory still presents some undefined points providing on the whole semiquantitative analyses of such processes (14). On the other hand, it is generally accepted that the redox properties of the selective oxidation catalysts control the oxygen activation as well as the surface stabilisation of the oxygen activated species and their reactivity (26). In particular, the stabilisation of the active oxygen forms requires the presence of reduced sites on the surface. In fact, the peculiar behaviour of Mo, V, and Fe oxides in selective oxidation reactions is strictly linked with the stabilisation of reduced sites (26). This point has stimulated a growing interest in providing correlation between the degree of reduction (29) or the extent of reduced sites (25) and the reactivity in selective oxidation of light alkanes.

Therefore, two fundamental issues still remain under debate: (i) the direct participation of lattice oxygen in the formation of selective oxidation products and (ii) the role of the acidic properties of the catalysts on their reactivities (29).

The reactions of partial oxidation of organic compounds usually proceed via a stepwise mechanism (26), while the data presented in Table 6 allow to conclude that the partial oxidation of methane to HCHO on silica-based oxide catalysts in the T_R range 550–650°C occurs mainly through a concerted mechanism without participation of lattice O_2. It can be then proposed that O_2 species more active than lattice O_2 ions ($O^{2-}_{(l)}$) are involved in the title reaction. These active species can be created in the process of interaction of gas-phase O_2 ($O_{2(g)}$) with the reduced sites (*RS*) of the catalyst surface. If such interaction proceeds with rather low rate some intermediate species $(O)^*_S$ (between initial state ($O_{2(g)}$) and final state ($O^{2-}_{(l)}$)) can have a long lifetime. This condition likely occurs on the catalyst

TABLE 7

Acidity Characterisation of Silica-Supported MoO_3 and V_2O_5 Catalysts

			NH_3-TPD		
Catalyst		ZPC	Treatment at 600°C	$\mu mol_{NH_3} \cdot g_{cat}^{-1}$	T_M (°C)
SiO_2	Si 4-5P	4.7	O_2	—	—
			$CH_4 + O_2$	—	—
4.0% MoO_3/SiO_2	Si 4-5P	3.0	O_2	141.8	217
			$CH_4 + O_2$	140.4	213
5.3% V_2O_5/SiO_2	Si 4-5P	3.1	O_2	43.0	184
			$CH_4 + O_2$	22.0	185
SiO_2	M5	4.0	O_2	—	—
			$CH_4 + O_2$	—	—
4.5% MoO_3/SiO_2	M5	3.3	O_2	61.6	188
			$CH_4 + O_2$	60.5	184
2.2% V_2O_5/SiO_2	M5	3.5	O_2	5.0	179
			$CH_4 + O_2$	2.8	173

surface having rather low density of electrons which avoid a quickly deep reduction of molecular oxygen up to lattice ions ($O^{2-}_{(l)}$):

$$O_{2(g)} \xrightarrow{RS} (O)^*_S \longrightarrow O^{2-}_{(l)}.$$

Taking into account that our catalysts possess a very low concentration of reduced sites (≅0.01% of O_2 monolayer) for O_2 activation, the above condition related to the long lifetime of active intermediate O_2 species $(O)^*_S$ should be realised on our catalysts. Then, it can be proposed that the amount of specific reduced sites having the capability to activate gas-phase O_2 and stabilise surface active O_2 species $(O)^*_S$ governs the catalytic behaviour of silica-supported oxide catalysts in the partial oxidation of methane. This statement is strictly supported by the straight correlation between density of reduced sites and STY_{HCHO} presented above (see Figs. 1–3) for different silica-supported oxide catalysts.

The next important point of the partial oxidation lies in the activation of the hydrocarbon molecule. This activation can occur on acidic site of the oxide surface (1, 35). Our data clearly show that the CH_4 activation process is not the rate-determining step of the partial oxidation of methane. Indeed, a different order in acidity and activity properties for the unpromoted and MoO_3- and V_2O_5-doped SiO_2 catalysts has been found. Therefore, it can be argued that all catalysts provide a suitable extent of CH_4 activation and change in the acidity, for this set of catalysts does not have any effects on the catalytic activity. As shown above the reason for the different catalytic activities observed in such oxide catalysts lies in their different abilities to activate gas-phase oxygen. This means that redox properties play a prominent role in controlling the activity of the oxide catalysts in the partial oxidation of CH_4 to HCHO. Then, taking into account the above experimental findings as well as the literature data (36) dealing with the suitability of the SiO_2 surface in activating CH_4 molecules, the following reaction pathway seems adequate to describe the partial oxidation of methane with O_2 on silica-based oxide catalysts,

$$CH_4 + L \rightleftarrows (CH_4)^*_S + \underset{\substack{\uparrow \\ RS \\ + \\ O_{2(g)} \quad \text{or} \quad O_{2(S)}}}{(O)^*_S} \rightarrow P$$

where $(CH_4)^*_S$ and $(O)^*_S$ indicate CH_4 and O_2 surface activated species respectively, P refers to HCHO and CO_2, and L and RS represent specific surface centres for CH_4 activation and reduced surface site providing molecular oxygen activation from gas-phase ($O_{2(g)}$) or adsorbed form ($O_{2(S)}$), respectively.

CONCLUSIONS

- The partial oxidation of methane to formaldehyde with molecular O_2 over bare SiO_2 and silica-supported MoO_3 and V_2O_5 catalysts proceeds mainly via a concerted mechanism without participation of lattice oxygen.
- The acidic properties of silica-based oxide catalysts seems to exert no direct influence on the reaction pathway of the methane partial oxidation.
- A direct relationship exists between the density of reduced sites and the reactivities of oxide catalysts in the partial oxidation of methane to formaldehyde. Then, the catalytic activity of these catalysts is controlled by the capability to provide activation of gas-phase oxygen into active species by reduced sites of catalyst surface.

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