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On the nature of active sites of silica based oxide catalysts in the partial oxidation of methane to formaldehyde

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Abstract

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. Amongst the different SiO_2 samples, the highest HCHO productivity (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. 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.

1. Introduction

In spite of the great research effort dedicated during the last years to the partial oxidation of methane to formaldehyde (MPO) over silica based oxide catalysts, the understanding of the reaction mechanism and the nature of the active sites still remain two challenging issues. Three distinct theoretical models have been proposed to describe the working mechanism of MPO catalysts: i) Langmuir–Hinshelwood model or concerted mechanism; ii) Mars–van Krevelen model or redox mechanism and iii) heterogeneous–homogeneous model or surface assisted gas-phase reaction mechanism [1]. In order to probe the origin of the oxygen species incorporated into reaction products isotopic labelling techniques have been used [2,3]. However, such techniques did not allow to obtain a definitive proof of the participation of lattice or gas-phase oxygen in the product formation since also the reaction products undergo isotopic exchange with labelled oxygen [3]. On the basis of a comparison of the reaction rates of MPO in the presence and in the absence of O_2 in the reaction mixture, we have previously argued that the MPO on SiO_2 based oxide catalysts, in the range 550–650°C, proceeds via a concerted mechanism involving the activation of gas-phase O_2 on surface reduced sites [4]. In particular, a straight relationship between 'density of reduced sites' under steady-state conditions and the reactivity of SiO_2 based oxide catalysts in MPO has been disclosed [4,5]. A number of studies have been recently addressed to disclose a

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basic relationship between surface properties and reactivity of MoO_3/SiO_2 catalysts in the MPO [6,7]. Smith et al. [6] reported that on low loaded (≤ 1.8 wt%) MoO_3/SiO_2 catalysts highly dispersed silicomolybdic species allow the selective formation of HCHO, while on medium loaded (5.8–9.8 wt%) catalysts the formation of Mo–O–Mo bridging sites in polymolybdate moieties leads to complete oxidation. By contrast, Bañares et al. [7], on the basis of XRD and XPS evidences, pointed out that the best HCHO selectivity for MoO_3/SiO_2 catalysts is obtained in the composition range where polymolybdates are developed. Kennedy et al. [8] claimed a facile oxidation–reduction cycle from V^{5+} to V^{4+}/V^{3+} to explain the highest performance of medium loaded (1.8–7.1 wt%) V_2O_5/SiO_2 catalysts.

The present paper is aimed to shed light on the role of the redox properties of silica based oxide catalysts in the reactivity and working mechanism in the MPO.

2. Experimental

2.1. Catalyst

Four different SiO_2 samples (Si 4-5P Grade, 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.

Differently loaded MoO_3 (2.0% $MoO_3/SiO_{2\,Si\,4\text{-}5P}$, $S.A._{BET} = 290\ m^2 \cdot g^{-1}$, 4.0% $MoO_3/SiO_{2\,Si\,4\text{-}5P}$, $S.A._{BET} = 187\ m^2 \cdot g^{-1}$, 6.8% $MoO_3/SiO_{2\,Si\,4\text{-}5P}$, $S.A._{BET} = 74\ m^2 \cdot g^{-1}$ and 4.5% $MoO_3/SiO_{2\,M5}$, $S.A._{BET} = 165\ m^2 \cdot g^{-1}$) and V_2O_5 (5.3% $V_2O_5/SiO_{2\,Si\,4\text{-}5P}$, $S.A._{BET} = 231\ m^2 \cdot g^{-1}$, 10.1% $V_2O_5/SiO_{2\,Si\,4\text{-}5P}$, $S.A._{BET} = 198\ m^2 \cdot g^{-1}$, 20.8% $V_2O_5/SiO_{2\,Si\,4\text{-}5P}$, $S.A._{BET} = 193\ m^2 \cdot g^{-1}$, 52.0% $V_2O_5/SiO_{2\,Si\,4\text{-}5P}$, $S.A._{BET} = 168\ m^2 \cdot g^{-1}$ and 2.2% $V_2O_5/SiO_{2\,M5}$, $S.A._{BET} = 191\ m^2 \cdot g^{-1}$) catalysts were prepared by incipient wetness impregnation of 'precipitated' Si 4-5P and 'fumed' M5 samples with a basic solution (pH = 11) of ammonium heptamolydbate or ammonium metavanadate respectively according to the procedure elsewhere described [9].

2.2. Catalyst testing

Methane partial oxidation experiments in the T range 550–650°C were performed using a specifically designed batch reactor elsewhere described [9]. Pulse reaction tests in the presence and in the absence of O_2 have been performed in a conventional flow apparatus by using a 'Thermolab' (Fisons Instruments) QMS for analysis of the reaction stream [9].

2.3. Catalyst characterization

Oxygen chemisorption measurements were performed in the above flow apparatus according to the procedure elsewhere described [9]. O_2 uptakes were determined in a pulse mode ($V_{O2\ pulse} = 4.8 \cdot 10^{-2}\ \mu mol$) 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.

3. Results and discussion

3.1. Bare silica catalysts

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 the T range 550–650°C. These data have indicated 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

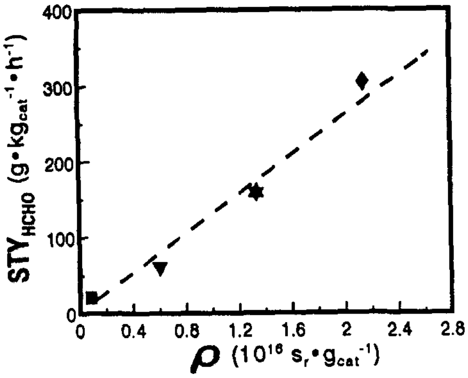


Fig. 1. Relationship between density of reduced sites (ρ) and STY_{HCHO} in the partial oxidation of methane on 'precipitated' Si 4-5P (♦), 'precipitated' D11-11 (★), 'silica-gel' 250 MP (▼) and 'fumed' M5 (■) SiO_2 catalysts at 650°C.

cannot be rationalised in terms of alkali and alkaline-earth oxide impurities [9]. 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 [4]. Therefore, in order to check the validity of such hypothesis, the density of reduced sites (ρ, $10^{16} s_r \cdot g_{cat}^{-1}$) of the different SiO_2 catalysts was measured. In Fig. 1 the density of reduced sites at 650°C for the different bare SiO_2 samples is plotted vs. the STY_{HCHO} ($g \cdot kg_{cat}^{-1} \cdot h^{-1}$). Such data indicate the existence of a strong 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 [9,10]. In fact, for the various SiO_2 samples the following reactivity scale referred to the preparation method can be drawn: pyrolysis < sol–gel < precipitation.

3.2. Silica supported MoO_3 and V_2O_5 catalysts

In our previous paper we have shown that the addition of V_2O_5 enhances the activity of both precipitated Si 4-5P and fumed M5 silicas in the MPO by factors of 2 and 70 respectively, while MoO_3 incorporation improves the activity of the fumed silica by a factor of 6 and depresses that of the precipitated one [9]. The density of reduced sites of 4.5% $MoO_3/SiO_{2\,M5}$ and 2.2% $V_2O_5/SiO_{2\,M5}$ (a) and of 4.0% $MoO_3/SiO_{2\,Si\,4\text{-}5P}$ and 5.3% $V_2O_5/SiO_{2\,Si\,4\text{-}5P}$ (b) catalysts is plotted in Fig. 2 against the STY_{HCHO} at 650°C. For sake of comparison also the data of bare 'fumed' M5 (a) and 'precipitated' Si 4-5P (b) silicas are therein included. These results confirm the validity of the straight correlation between activity and density of reduced sites of bare silica and low and medium (MoO_3 or $V_2O_5 \leq 5$ wt%) loaded silica supported oxide catalysts [4,9]. However, in order to better assess the role of MoO_3 and V_2O_5 on the reactivity of the SiO_2 surface the effect of oxide loading on the reaction rate at 650°C and density of reduced sites has been also evaluated. The data presented in Fig. 3 point out that (i) the addition of MoO_3

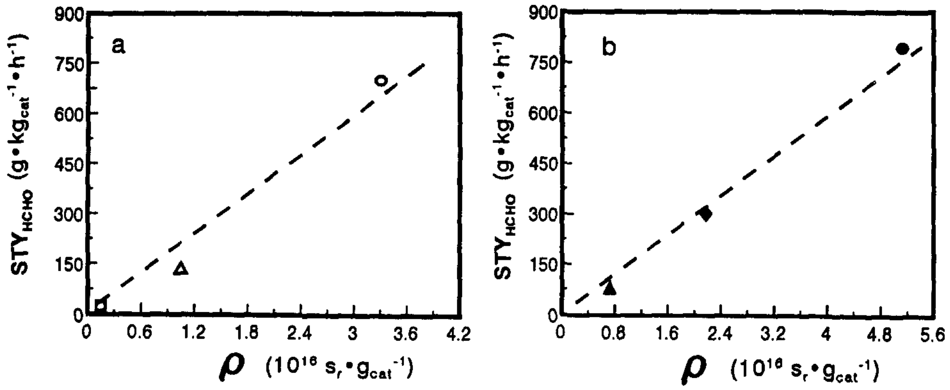


Fig. 2. Relationship between density of reduced sites (ρ) and STY_{HCHO} in the partial oxidation of methane on: (a) 'fumed' M5 SiO_2 (□), 4.5% $MoO_3/SiO_{2\,M5}$ (△) and 2.2 $V_2O_5/SiO_{2\,M5}$ (○); and (b) 'precipitated' Si 4-5P SiO_2 (♦), 4.0% $MoO_3/SiO_{2\,Si\,4\text{-}5P}$ (▲) and 5.3% V_2O_5/SiO_2 $_{Si\,4\text{-}5P}$ (●) catalysts at 650°C.

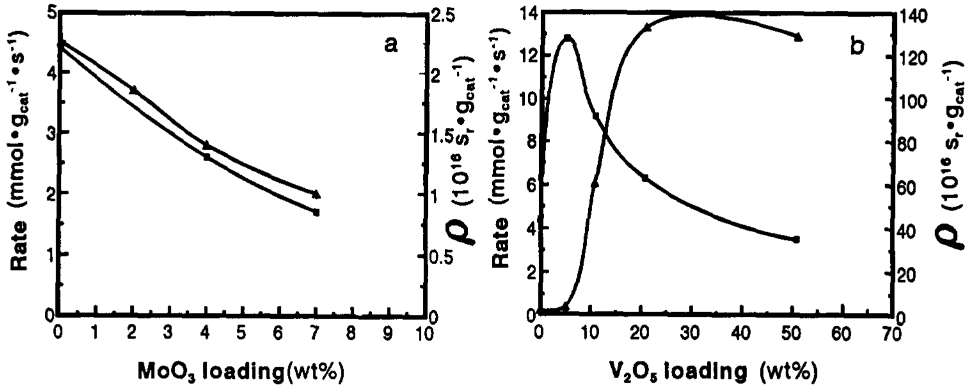


Fig. 3. Effect of oxide loading on the (■) reaction rate in the partial oxidation of methane and (▲) density of reduced sites (ρ) on (a) $MoO_3/SiO_{2\ Si\ 4\text{-}5P}$ and (b) $V_2O_5/SiO_{2\ Si\ 4\text{-}5P}$ catalysts at 650°C.

(a) induces a negative effect, proportional to the MoO_3 loading, on both the reactivity of the SiO_2 surface and the value of ρ and (ii) the addition of V_2O_5 (b) up to 5 wt% enhances both the reaction rate and ρ, whereas higher V_2O_5 loadings (> 5 wt%) determine a gradual drop in the reaction rate and a steep increase in ρ. The behaviour of higher loaded V_2O_5/SiO_2 catalysts likely signals the occurrence of a working mechanism which cannot be explained in terms of density of reduced sites and surface reaction pathway [4,9]. It is worth noting that MoO_3 addition causes a decrease in both catalytic activity and density of reduced sites of the unpromoted 'precipitated'. 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 own reduced active sites able to activate gas-phase oxygen [4,11]. On the other hand, for 'fumed' oxide catalysts, the weaker interaction between MoO_3 and such rather inert SiO_2 surface 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. 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 [1,12,13]. According to the literature data, on the SiO_2 surface Mo ions exist in octahedral coordination [12] which assists 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 [13]. On the basis of the above findings, in Fig. 4 is presented the surface model accounting for the different redox properties of precipitated (a) and fumed (b) silica based oxide catalysts.

3.3. Pulse reaction tests in presence and absence of O_2 and reaction mechanism

The values of reaction rate both on bare 'precipitated' $SiO_{2\ Si\ 4\text{-}5P}$ 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 in the T_R range 550–650°C are presented in Table 1. Such results 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

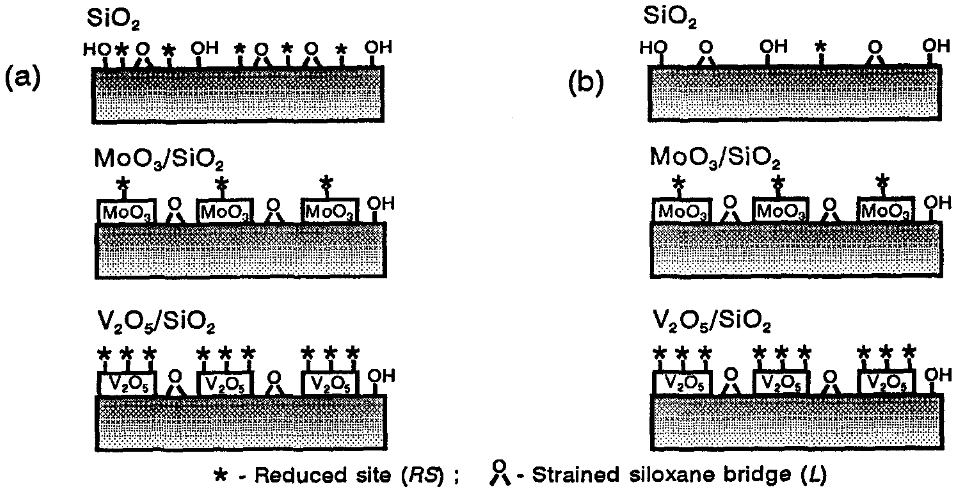
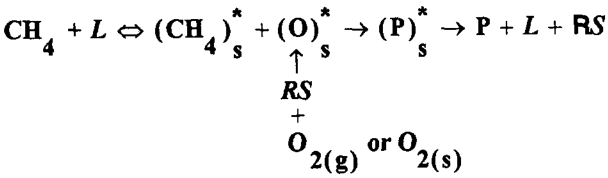


Fig. 4. Surface model of precipitated (a) and fumed (b) SiO_2 based MoO_3 and V_2O_5 catalysts.

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 catalyst. Then, as the reaction rates in the mixture of reactant and in separate steps differ, these data exclude the participation of lattice oxygen in the partial oxidation of methane via a two step redox mechanism as main reaction pathway proving the occurrence of a 'concerted mechanism' [5]. On this account, it can be 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

Table 1. 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	1.30
		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+O2	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



$$CH_4 + L \Leftrightarrow (CH_4)^*_s + \underset{\substack{\uparrow \\ RS \\ + \\ O_{2(g)}\ \text{or}\ O_{2(s)}}}{(O)^*_s} \rightarrow (P)^*_s \rightarrow P + L + RS$$

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

$$O_{2(g)} \xrightarrow{RS} (O)^*_s \rightarrow O^{2-}_{(l)}$$

Taking into account that our catalysts possess a very low concentration of reduced sites ($\cong$ 0.01% of O_2 monolayer) for O_2 activation, it means that 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 MPO. This statement is strictly supported by the straight correlation between density of reduced sites and STY_{HCHO} presented above (Figs. 1–2) for different silica supported oxide catalysts. The next important point of the partial oxidation lies in the activation of hydrocarbon molecule. This activation can occur on acidic site of the oxide surface [1]. However, 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 [4,5]. 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 ability to activate gas-phase oxygen [5]. This means that redox properties play a prominent role in controlling the activity of the oxide catalysts in the MPO. Then, taking into account the above experimental findings as well as the literature data [14] 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, 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 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.

4. Acknowledgements

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5. References

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