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A comparative study of the partial oxidation of methane to formaldehdye on bulk and silica supported MoO_3 and V_2O_5 catalysts

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Abstract

The mechanism of the partial oxidation of methane to formaldehdye with O_2 has been investigated on bulk and differently loaded silica supported (4–7 wt%) MoO_3 and (5–50 wt%) V_2O_5 catalysts at 600–650°C in a pulse reactor connected to a quadrupole mass spectrometer. The reaction rate and product distribution in the presence and in the absence of gas-phase O_2 have been evaluated. On bare SiO_2, low and medium loaded silica supported MoO_3 and V_2O_5 catalysts the reaction proceeds via a concerted mechanism involving the activation of gas-phase oxygen on the reduced sites of the catalyst surface as proved by the direct correlation between catalytic activity and density of reduced sites evaluated in steady-state conditions, while on highly loaded catalysts as well as on bulk MoO_3 and V_2O_5 the reaction rate drops dramatically and the reaction pathway via redox mechanism becomes predominant. The results indicate that the surface mechanism is essentially more effective than the redox mechanism enabling also a higher selectivity to HCHO.

Keywords: Comparative study; Partial oxidation of methane to formaldehdye; Bulk and silica supported MoO_3 and V_2O_5 catalysts; MoO_3; V_2O_5

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1. Introduction

Notwithstanding the great research effort, the working mechanism of bulk and supported oxide catalysts in the partial oxidation of methane to formaldehyde with molecular oxygen (MPO) still remains undecided. A number of studies based on the use of transient kinetic [1,2] and isotopic labelling techniques [3–6] have been addressed to ascertain the oxygen insertion pathway in the MPO on bulk and silica supported V_2O_5 and MoO_3 catalysts. However, isotopic techniques do not provide definitive proof about the participation of lattice or surface activated gas-phase oxygen in the product formation since the reaction products (HCHO and CO_2) undergo fast isotopic exchange with labelled oxygen [2,6] and therefore no definitive conclusions have been drawn about the occurrence of a redox (Mars–van Krevelen model) or surface (Langmuir–Hinshelwood model) mechanism [1,3,6]. Various physico-chemical characterization methods such as TPR, XRD, XPS and

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'in situ' LRS have been used in order to correlate the redox properties of such transition metal oxide catalysts with their reactivity and to highlight the nature of the active sites [5,7,8]. Smith and Ozkan [9] concluded that the MPO on bulk MoO_3 is a structure sensitive reaction claiming that Mo = O sites are responsible for production of HCHO, while Mo–O–Mo bridging oxygen sites promote total oxidation. Bañares et al. [8] reported that the active sites of MoO_3/SiO_2 catalysts leading to HCHO lie in polymolybdate moieties, while Smith and Ozkan [5] stated that such selective sites are associated with highly dispersed silicomolybdic species. Similarly, no direct and definitive evidences have been achieved about the active sites of V_2O_5/SiO_2 catalysts since it is speculated that highly dispersed tetrahedral surface vanadia species catalyze the primary oxidation reaction, whereas O associated with the bulk-like vanadia and with the SiO_2 lattice is involved in the secondary oxidation reactions of HCHO or CO [6]. However, ruling out the occurrence of purely homogeneous and/or surface assisted gas-phase reaction pathways, it is evident that the step-wise redox mechanism can rationalize the catalytic action of transition metal oxides which are able to provide lattice oxygen through a cyclic reduction/oxidation scheme, while it is absolutely inadequate to explain the action of the SiO_2 surface in catalyzing the MPO reaction [10,11]. On this account, we have proposed that silica based oxide catalysts have the capability to provide activation of gas-phase oxygen into active species by reduced sites of the catalyst surface [12]. In particular, since the direct relationship between the density of reduced sites and the reactivity of such oxide catalysts, we have argued that the MPO on bare SiO_2 and medium-loaded silica supported MoO_3 and V_2O_5 catalysts proceeds via a concerted mechanism without participation of lattice oxygen [12]. As it has been ascertained that the catalytic behaviour of silica supported MoO_3 and V_2O_5 catalysts is controlled by the extent of oxide loading [8,13], this paper deals with a comparative study of the reaction mechanism of the MPO on bulk and differently loaded silica supported MoO_3 and V_2O_5 catalysts in order to highlight the reasons for their different catalytic action.

2. Experimental

2.1. Catalyst

Supported MoO_3 (MPS) and V_2O_5 (VPS) catalysts were prepared by the incipient wetness method adding step-by-step a basic solution (pH = 11) of ammonium heptamolybdate or metavanadate to a 'precipitated' SiO_2 support (Si 4-5P, Akzo product, BET surface area = 400 m^2 g^{-1}). After impregnation all the catalysts were dried overnight at 110°C and then calcined at 600°C for 16 h. Bulk MoO_3 and V_2O_5 samples were commercial products and were used 'as received'. The list of the studied samples is presented in Table 1.

2.2. Pulse reaction tests

Pulse reaction tests were performed at 600–650°C in a conventional flow apparatus operating in both continuous and pulse modes using a linear quartz microreactor and He as carrier gas flowing at 50 STP cm^3 min^{-1}. 5.5 cm^3 of $CH_4/O_2/He$ ($P_{CH_4}:P_{O_2}:P_{He}$ = 2:1:7) or CH_4/He ($P_{CH_4}:P_{He}$ = 2:8) pulses were injected

Table 1
List of samples

Code	Chemical composition (wt%)	BET surface area (m^2 g^{-1})
PS	SiO_2	400
VPS 5	5.3% V_2O_5/SiO_2	230
VPS 10	10.1% V_2O_5/SiO_2	200
VPS 20	20.8% V_2O_5/SiO_2	190
VPS 50	50.8% V_2O_5/SiO_2	160
V	V_2O_5	5
MPS 4	4% MoO_3/SiO_2	190
MPS 7	7% MoO_3/SiO_2	75
M	MoO_3	2

onto the sample until a constant level of reaction products was reached. The reactor stream was analyzed by a quadrupole mass spectrometer (QMS) connected on line to the reactor by a heated ($\approx 180°C$) inlet capillary. The mass sample was 0.05 g unless otherwise specified.

2.3. Continuous flow measurements

Continuous flow tests in the MPO were carried out using 0.05 g of sample and the $CH_4/O_2/He$ reaction mixture flowing at 50 STP $cm^3\ min^{-1}$. The reaction products were analyzed by the analytical setup described elsewhere [12].

2.4. Reaction temperature oxygen chemisorption (RTOC)

RTOC measurements in the range 500–750°C were performed in a pulse mode using He as carrier gas. After treatment in the $CH_4/O_2/He$ reaction mixture flow, the sample was purged in the carrier flow and then O_2 pulses (4×10^{-8} mol O_2) were injected into the carrier gas until saturation of the sample was attained. The density of reduced sites (ρ) was calculated from the O_2 uptakes by assuming a chemisorption stoichiometry O_2/'reduced site' of 1/2. Catalyst samples releasing oxygen during pulses injection did not reach the saturation (full oxidation state) as after the first pulse the area of the pulses attained a constant value (A_f) considerably lower than that of the standard value (A_0). Then, for such samples the value of ρ was calculated on the basis of O_2 uptake corresponding to the difference between A_f and the area (A_1) of the first pulse, while the difference between A_0 and A_1 was taken for calculating the total density of reduced sites (ρ_{tot}).

3. Results and discussion

3.1. General

The key point of the mechanistic studies of MPO on oxide catalysts is to ascertain the origin of the oxygen incorporated in the reaction products. Indeed, the direct participation of the lattice oxygen proves the occurrence of a stepwise redox mechanism while the involvement of the surface activated gas-phase O_2 probes a concerted or a two-site surface reaction path [14]. As the attempts made to elucidate the oxygen insertion pathway under steady-state conditions resulted not completely convincing [3,6], a valid and alternative approach which could contribute to shed light into this issue is that based on the evaluation of the reaction rate in the mixture of reactants ($CH_4 + O_2$) and in the absence of gas-phase O_2 [15]. On this account, it has been documented that the presence of O_2 in the reaction mixture does not enhance

Table 2
Activity data of bulk and silica-supported oxide catalysts in the MPO at 650°C. Comparison between pulse reaction (PR) and continuous flow (CF) measurements

Catalyst	Reaction rate ($\mu mol\ g_{cat}^{-1}\ s^{-1}$)		Product distribution (%)					
	PR	CF	HCHO		CO		CO_2	
			PR	CF	PR	CF	PR	CF
PS	4.3	3.2	28	40	62	51	10	9
VPS 5	12.7	13.9	10	11	79	81	11	8
VPS 20	3.0	3.7	10	11	67	43	23	12
VPS 50	1.1	1.6	10	8	62	80	28	12
V	0.3	0.2	17	3	74	85	9	12
MPS 4	1.6	0.7	30	48	43	20	27	32

the rate of product formation when the reaction proceeds via a step-wise redox mechanism [15].

Then, a series of pulse reaction tests in the MPO on bulk and differently loaded silica supported MoO_3 and V_2O_5 catalysts in the presence and in the absence of gas-phase O_2 has been carried out. Care was taken to avoid during the pulsing 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).

In order to probe the reliability of the kinetic data obtained by Pulse reaction tests, a significant comparison of reaction rate and product selectivity values attained at 650°C on various catalytic systems by pulse (PR) and continuous flow (CF) reactors is outlined in Table 2. It is evident that in spite of the transient regime of the pulse reaction technique the activity data obtained by the two methods are analogous or at least similar in terms of both reaction rate and product distribution.

3.2. VPS catalysts

The activity data of PS, V and differently loaded VPS catalysts in the presence and in the absence of gas-phase oxygen, expressed in terms of reaction rate on unit oxide or catalyst weight basis and product distribution, are comparatively shown in Table 3.

These data indicate that (i) the bare PS catalyst in absence of gas-phase O_2 is not effective in the MPO at 600°C while at 650°C it enables a reaction rate value which is two orders of magnitude lower than that measured in the full

Table 3
Activity data of bulk and supported V_2O_5 catalysts at 600 and 650°C in the presence and in the absence of gas-phase O_2

Catalyst	T_R	Reaction mixture	Reaction rate		Product distribution		
	(°C)		(μmol g_{ox}^{-1} s^{-1})	(μmol g_{cat}^{-1} s^{-1})	HCHO (%)	CO (%)	CO_2 (%)
PS	600	CH_4+O_2	1.9	1.9	35	58	7
		CH_4	0.0	0.0			
	650	CH_4+O_2	4.3	4.3	28	62	10
		CH_4	0.1	0.1	38	60	2
VPS 5	600	CH_4+O_2	106.0	5.3	11	63	26
		CH_4	4.0	0.2		100	
	650	CH_4+O_2	240.0	12.7	10	79	11
		CH_4	37.7	2.0	10	76	14
VPS 10	600	CH_4+O_2	47.2	5.1	11	81	8
		CH_4	20.4	2.2	6	83	11
	650	CH_4+O_2	77.8	8.4	12	80	8
		CH_4	25.0	2.7	13	83	4
VPS 20	600	CH_4+O_2	8.2	1.7	20	66	14
		CH_4	3.8	0.8	8	87	5
	650	CH_4+O_2	14.6	3.0	10	67	23
		CH_4	8.5	1.7	5	73	22
VPS 50 [a]	600	CH_4+O_2	1.4	0.7	25	53	22
		CH_4	0.7	0.4	18	80	2
	650	CH_4+O_2	2.2	1.1	10	62	28
		CH_4	1.4	0.8	16	75	9
V [b]	600	CH_4+O_2	0.14	0.14	26	62	12
		CH_4	0.10	0.10	29	65	6
	650	CH_4+O_2	0.28	0.28	17	74	9
		CH_4	0.17	0.17	17	81	2

[a] $W_{cat} = 0.15$ g.
[b] $W_{cat} = 0.30$ g.

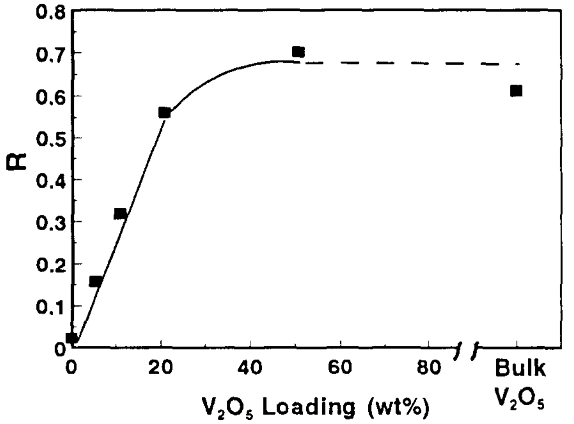

Fig. 1. Influence of the V_2O_5 loading on the ratio (R, r_1/r_0) between the value of reaction rate in the absence (r_1) and presence (r_0) of gas-phase oxygen on the VPS catalysts at 650°C.

reaction mixture; (ii) V_2O_5 addition up to a loading of 20 wt% implies a promoting effect on the activity of the PS carrier even if the optimum loading, ensuring the best HCHO yield, corresponds to the 5 wt%; (iii) on highly loaded (> 5 wt%) V_2O_5/SiO_2 samples, the drop in activity is not counterbalanced by a corresponding increase in the HCHO selectivity; (iv) bulk V_2O_5 possesses a similar activity in the presence and in the absence of gas-phase O_2. Besides, it can be noted that the extent of the reaction rate in full reaction mixture and in CH_4 depends upon the V_2O_5 loading. A clear picture of such an effect is presented in Fig. 1 by plotting the ratio (R, r_1/r_0) between the value of the reaction rate in the absence (r_1) and in the presence (r_0) of gas-phase O_2 at 650°C against the V_2O_5 loading. It results that the value of R increases steadily up to a V_2O_5 loading of 20%, thereafter it levels off to a value of ca. 0.6 for VPS 50 and bulk V samples. The above findings clearly suggest that PS ($R = 0.023$) and VPS 5 ($R = 0.15$) catalysts act in the MPO via a surface mechanism likely involving the activation of gas-phase O_2, while for highly loaded VPS catalysts the redox mechanism concurs to the overall reaction rate becoming even prevailing for VPS 20, VPS 50 and V samples ($R = 0.6$). The reactivity of the catalysts in the absence of gas-phase O_2 can be directly related to the capability of the solid to provide lattice oxygen allowing the formation of reaction products. From the above data (Table 3) it arises that the increase in the V_2O_5 loading implies the shift of the reaction pathway from concerted to redox mechanism with a remarkable decrease in the overall catalytic activity. In fact, the V_2O_5 loading rise from 5% (VPS 5) to 100% (V) results in a drop of the reaction rate of about three orders of magnitude per gram of oxide. Such an effect cannot be explained by invoking the different surface area of supported and bulk V_2O_5 catalysts. The active centers for oxygen activation on low and medium loaded V_2O_5/SiO_2 catalysts could be V ions with low coordination number stabilized on the silica surface [12]. Such active sites promote the formation of partially reduced very active surface oxygen species which participate in the reaction instead to undergo a deep reduction up to lattice ions [12]. Then, it can be argued that V_2O_5 loadings higher than 5% imply the formation of large surface vanadia clusters as crystals of bulk V_2O_5 causing a gradual decrease of low coordinated V centers and a concomitant enhancement in the amounts of 'extractable' lattice oxygen [16]. These structural modifications induce the shift of the reaction path from the concerted to the redox model.

Further insights into the different catalytic behaviour of medium and highly loaded VPS catalysts, bare PS and bulk V samples can be achieved by evaluating the product distribution presented in Tables 2 and 3 at comparable level of activity and taking into account the inverse relationship between activity and selectivity. Namely, it emerges that the selectivity to HCHO of V and highly loaded (> 10%) VPS catalysts is essentially lower than that of PS and VPS 5 samples. This finding allows to infer that the redox mechanism, which is prevailing for highly loaded VPS catalysts, leads mainly to the formation of CO_x while the concerted mechanism (bare PS and VPS 5 samples) implies the formation of HCHO as primary product [12].

3.3. MPS catalysts

The activity data of M and differently loaded MPS catalysts in the presence and in the absence of gas-phase oxygen, expressed in terms of reaction rate on unit oxide or catalyst weight basis and product distribution, are comparatively shown in Table 4.

It is evident that the addition of MoO_3 causes a decrease in the activity of the bare PS carrier, more enhanced at higher oxide loading, along with a slight improvement in the HCHO selectivity likely accounted for by the lower extent of methane conversion (Table 4).

Also for MPS catalysts the MoO_3 loading controls the extent of the reaction rate in the absence of gas-phase oxygen as evidenced by the plot of R against MoO_3 loading outlined in Fig. 2. It can be observed that for MPS 4 and MPS 7 samples the value of R ranges between 0.1 and 0.25. These results confirm that the lattice oxygen of MoO_3-based catalysts is rather 'inactive' up to 650°C [17] and then any interaction between CH_4 and the catalyst surface is hindered. Therefore, it can be concluded that on medium-loaded MPS catalysts the MPO proceeds according to the surface mechanism implying the activation of gas-phase O_2. Bulk M system at 650°C exhibits a very low activity both in presence and absence of gas-phase oxygen along with a slight HCHO selectivity, however its value of R is considerably higher than that of MPS catalysts. In fact, R displays a sudden increase for the bulk M system to a value (0.6) comparable with that of bulk V sample (Fig. 1). These findings infer that the

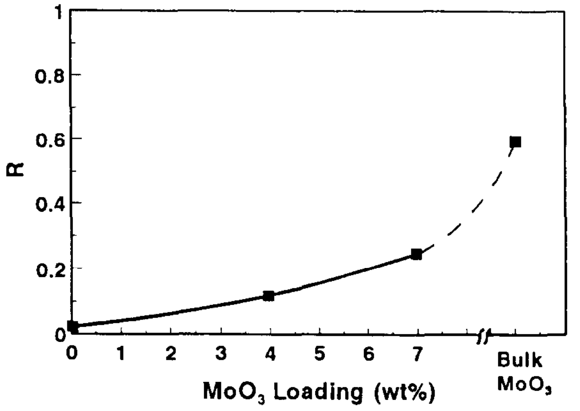

Fig. 2. Influence of the MoO_3 loading on the ratio (R, r_1/r_0) between the value of reaction rate in the absence (r_1) and presence (r_0) of gas-phase oxygen on the MPS catalysts at 650°C.

Table 4
Activity data of bulk and supported MoO_3 catalysts at 600 and 650°C in the presence and in the absence of gas-phase O_2

Catalyst	T_R	Reaction mixture	Reaction rate		Product distribution		
	(°C)		(μmol g_{ox}^{-1} s^{-1})	(μmol g_{cat}^{-1} s^{-1})	HCHO (%)	CO (%)	CO_2 (%)
PS	600	$CH_4 + O_2$	1.9	1.9	35	58	7
		CH_4	0.0	0.0			
	650	$CH_4 + O_2$	4.3	4.3	28	62	10
		CH_4	0.1	0.1	38	60	2
MPS 4	600	$CH_4 + O_2$	15.0	0.6	43	27	30
		CH_4	0.0	0.0			
	650	$CH_4 + O_2$	40.0	1.6	30	43	27
		CH_4	5.0	0.2	39	31	30
MPS 7	600	$CH_4 + O_2$	n.d.	n.d.			
		CH_4	n.d.	n.d.			
	650	$CH_4 + O_2$	17.1	1.2	38	44	28
		CH_4	4.3	0.3	41	34	25
M [a]	600	$CH_4 + O_2$	n.d.	n.d.			
		CH_4	n.d.	n.d.			
	650	$CH_4 + O_2$	0.05	0.05	16	70	14
		CH_4	0.03	0.03	16	72	12

[a] $W_{cat} = 0.30$ g.

Table 5
Density of reduced sites (ρ) and 'total' density of reduced sites (ρ_{tot}) of bulk and silica supported MoO_3 and V_2O_5 catalysts

Catalyst	T_R (°C)	ρ_{tot} (10^{16} r_s g_{cat}^{-1})	ρ (10^{16} r_s g_{cat}^{-1})
PS	600	1.35	1.35
	650	2.25	2.25
VPS 5	600	2.10	2.10
	650	6.90	3.90
VPS 10	600	8.90	4.30
	650	130.0	60.0
VPS 20	600	48.0	20.5
	650	249.0	133.0
VPS 50	600	70.0	31.0
	650	247.0	129.0
V	600	64.7	9.5
	650	127.0	11.5
MPS 4	600	0.80	0.80
	650	1.40	1.40
MPS 7	600	0.60	0.60
	650	1.00	1.00
M	600	n.d.	n.d.
	650	1.50	1.50

'redox mechanism', which is scarcely effective for supported MPS catalysts, becomes predominant for the bulk M system.

3.4. Density of reduced sites and oxygen pathway

In previous papers dealing with the factors controlling the reactivity of silica-based oxide catalysts in the MPO [12], we disclosed a direct relationship between catalytic activity and oxygen uptake under steady state reaction conditions pointing out that such property governs the catalytic behaviour of MPO catalysts. Then, in order to find out whether such a relationship is valid for any MPO catalyst, the density of reduced sites (ρ) of the studied catalysts has been evaluated and correlated with the catalytic activity. The values of ρ and ρ_{tot} at 600 and 650°C are listed in Table 5.

The above data indicate that: (i) both the total and irreversible oxygen uptake under steady-state reaction conditions increase with V_2O_5 loading reaching a maximum at loadings comprised between 20 (VPS 20) and 50% (VPS 50), thereafter they decrease for the bulk V system, (ii) the difference between ρ_{tot} and ρ for VPS catalysts becomes progressively more pronounced at higher V_2O_5 loadings and (iii) the addition of MoO_3 implies a decrease in density of reduced sites of the bare PS sample, without any difference in the values of ρ_{tot} and ρ. Then, the opposite effects exerted by MoO_3 and V_2O_5 on the activity of the bare PS carrier parallels the density of reduced sites of the catalysts [12]. In other words, V_2O_5, resulting an effective promoter of the activity of the bare PS, allows the stabilization of a higher density of reduced sites owing to its easier 'reducibility' under reaction conditions [17] whereas MoO_3, being essentially non-reducible under reaction conditions [12,17], depresses the activity of the underlying PS carrier because of a negative physical effect due to a partial coverage of the own active sites of the silica surface [12,17]. However, it is evident that the data reported in Table 5 do not fully account for the activity of differently loaded VPS catalysts in the MPO (Table 3) as the activity of VPS catalysts reaches the maximum on VPS 5 sample, while the density of reduced sites increases up to a loading of 20% (VPS 20) thereafter it levels off (VPS 50). In addition, the larger difference between ρ and ρ_{tot} (Table 5) for highly loaded VPS catalysts, which is related to the capability of such sys-

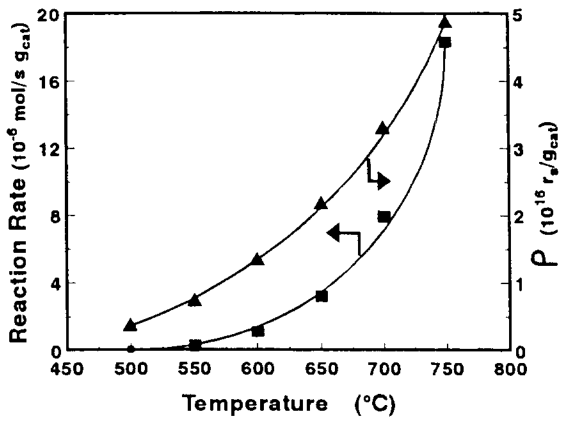

Fig. 3. Influence of the temperature on the reaction rate and density of reduced sites (ρ) of the bare PS sample.

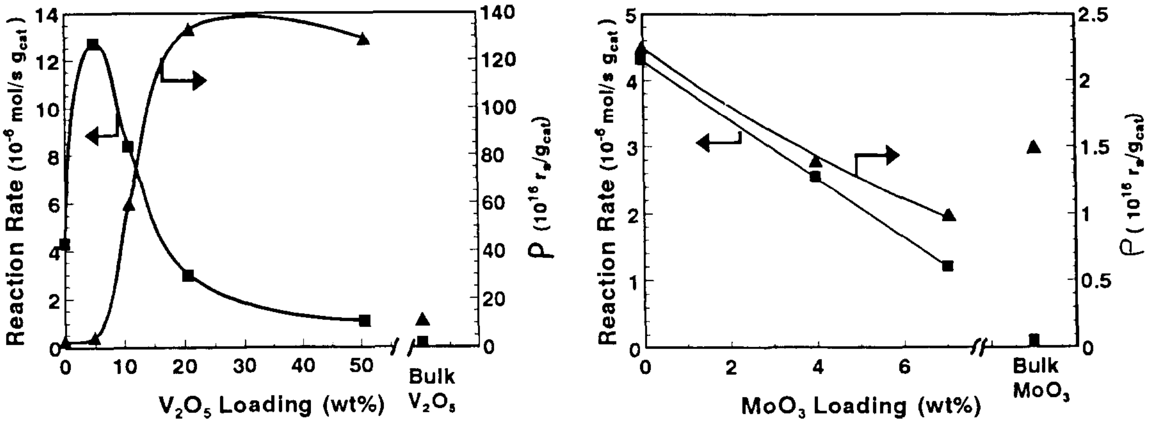

Fig. 4. Influence of the V_2O_5 and MoO_3 loading on the reaction rate and density of reduced sites (ρ) of VPS (left) and MPS (right) catalysts at 650°C.

tems to 'release' constitutional oxygen [16], allows to state that their higher reducibility is ineffective in the MPO. Evidently, on such highly loaded VPS catalysts the high density of reduced sites favours a rapid incorporation of the surface oxygen species into oxide lattice [15]. As the lattice oxygen is much less reactive than the surface oxygen species, the reaction rate of the MPO proceeding via redox mechanism is much lower than that observed when a concerted mechanism occurs.

For the bare PS sample, exhibiting a very low 'mobility' of lattice oxygen [17], the 'surface mechanism' well accounts for the formation of products. Then, the activity of this sample is controlled by the extent of the density of reduced sites as confirmed by the analogous trends of reaction rate and ρ with temperature shown in Fig. 3.

Whilst, assuming that the value of ρ is the density of reduced 'active' sites generated under steady-state reaction conditions, different trends of reaction rate and ρ with the oxide loading are found for VPS (a) and MPS (b) catalysts as shown in Fig. 4. Namely, taking into account the bare PS as reference system working in the MPO according to the surface mechanism, it arises that the addition of MoO_3 negatively affects both ρ and reaction rate and then their parallel decreasing trends with the oxide loading (Fig. 4b) indicate that also on the MPS systems the MPO mainly proceeds according to the 'surface mechanism'. A very low activity of the bulk M system at 650°C not accounted for by a corresponding decrease in ρ (Fig. 4b) signals a change in the reaction mechanism from the surface to the less effective redox model. The sudden growth in activity along with the moderate increase in ρ (Fig. 4a) observed for the VPS 5 catalyst suggest that at medium loading vanadia exerts a positive influence on the functionality of the PS support probably because of the stabilization of dispersed surface species enabling the formation of very active surface reduced sites. By contrast, the redox mechanism becomes predominant for highly loaded VPS catalysts and bulk V system as confirmed by the lack of a direct relationship between reaction rate and ρ (Fig. 4a).

4. Conclusions

On pure silica and low and medium loaded (≤ 5 wt%) V_2O_5/SiO_2 and MoO_3/SiO_2 catalysts the MPO proceeds via a concerted mechanism without participation of lattice oxygen. A direct relationship between density of reduced sites and activity proves the crucial role of gas-phase oxygen activation in the main reaction pathway.

On highly loaded (> 5 wt%) V_2O_5/SiO_2 and

MoO_3/SiO_2 catalysts as well as on bulk V_2O_5 and MoO_3 systems the two-step redox mechanism, involving the direct participation of lattice oxygen, is predominant. No relationship between density of reduced sites and catalytic activity is found indicating then that the interaction of gas-phase oxygen with the catalyst surface does not lead to the formation of active surface oxygen species, resulting instead in a quickly incorporation of O_2 into oxide lattice.

References

[1] B. Kartheuser, B.K. Hodnett, H. Zanthoff and M. Baerns, Catal. Lett., 21 (1993) 209.

[2] S.Y. Chen and D. Willcox, Ind. Eng. Chem. Res., 33 (1994) 832.

[3] R. Mauti and C.A. Mims, Catal. Lett., 21 (1993) 201.

[4] M.A. Bañares, I. Rodriguez-Ramos, A. Guerrero-Ruiz and J.L.G. Fierro, in L. Guczi, F. Solymosi and P. Tetenyi (Editors), Proc. 10th Int. Congr. Catalysis, Budapest, 1992, Vol. B, Akadêmiai Kiadó, Budapest, 1993, p. 1131.

[5] M.R. Smith and U.S. Ozkan, J. Catal., 142 (1993) 226.

[6] M.M. Koranne, J.G. Goodwin, Jr. and G. Marcelin, J. Catal., 148 (1994) 378.

[7] M.A. Bañares, N.D. Spencer, M.D. Jones and I.E. Wachs, J. Catal., 142 (1993) 406.

[8] M.A. Bañares, J.L.G. Fierro and J.B. Moffat, J. Catal., 142 (1993) 406.

[9] M.R. Smith and U.S. Ozkan, J. Catal., 141 (1993) 124.

[10] A. Parmaliana, F. Frusteri, D. Miceli, A. Mezzapica, M.S. Scurrell and N. Giordano, Appl. Catal., 78 (1991) L7.

[11] A. Parmaliana, F. Frusteri, A. Mezzapica, D. Miceli, M.S. Scurrell and N. Giordano, J. Catal., 143, (1993) 262.

[12] A. Parmaliana, V. Sokolovskii, D. Miceli, F. Arena and N. Giordano, J. Catal., 148 (1994) 514.

[13] D. Miceli, F. Arena, A. Parmaliana, M.S. Scurrell and V. Sokolovskii, Catal. Lett., 18 (1993) 283.

[14] A. Bielañski and J. Haber, Oxygen in Catalysis, Marcel Dekker, New York, 1991.

[15] V. Sokolovskii, Catal. Rev., Sci. Eng., 32 (1990) 1.

[16] G. Lischke, W. Hanke, H.-G. Jerschkewitz and G. Öhlmann, J. Catal, 91 (1985) 54.

[17] F. Arena, F. Frusteri, D. Miceli, A. Parmaliana and N. Giordano, Catal. Today, 21 (1994) 505.