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NOTES

A Temperature-Programmed Reaction Method for Catalyst Testing in the Partial Oxidation of Methane to Formaldehyde

During the last years a large variety of unpromoted and promoted oxide catalysts has been claimed to be effective in the partial oxidation of methane (MPO) to formaldehyde (*1, 2*). This reaction proceeds via a very complex network (*2, 3*) and requires medium–high temperatures ($550 < T_R < 650$°C) to attain detectable rates (*2*). The unique features of the SiO_2 surface in catalysing the formation of partial oxidation products have been largely documented (*4–7*), while the roles played by MoO_3, V_2O_5, Nb_2O_5, WO_3, Cr_2O_3, and other oxides on the reactivity of the SiO_2 (*1, 2, 8–13*) and the nature of the active centers (*1, 2, 6, 9, 11–13*) are still topics of debate. A number of papers have particularly addressed the importance of the reaction system (*1, 2, 6, 14*) and the contribution of the gas phase and/or wall reaction (*2, 10, 12, 15*) in getting valid and comparable reactivity data. Indeed, since the constraints of the conversion-selectivity relationship (*1, 8*), suitable reactor device must exploit a differential methane conversion level per pass as to ensure high selectivity to HCHO providing also finite conversion values for a reliable kinetic analysis of the data (*6, 12, 14*).

In this note we present the potentiality of the temperature-programmed reaction (TPR) method (*16*) in evaluating the activity of the MPO catalysts. A preliminary comparative analysis of the catalytic performances of bare SiO_2 and various silica supported oxide (MoO_3, V_2O_5, Nb_2O_5) catalysts is reported.

4 wt% MoO_3/SiO_2, 5 wt% V_2O_5/SiO_2, and 2 wt% Nb_2O_5/SiO_2 catalysts were prepared by incipient wetness impregnation of a precipitated SiO_2 support (Grade Si 4-5P, Akzo Product; BET S.A., 395 $m^2 \cdot g^{-1}$) (*12*). Ammonium heptamolybdate and ammonium metavanadate in ammonia solution (pH ≈ 11) and niobium chloride in HCl solution (pH ≈ 1) were used as oxide precursors. After impregnation, all the catalysts were dried at 90°C for 24 h and then calcined in air atmosphere at 600°C for 16 h.

TPR measurements were performed in a conventional flow apparatus by using a linear quartz microreactor (i.d., 4 mm; length, 200 mm) connected *on line* with a Thermolab (Fisons Instruments) Quadrupole Mass Spectrometer for continuous analysis of the reaction mixture (transit time < 0.5 s). The tests were run in the T range 200–650°C by adopting a heating rate (β) of 15°C $\cdot$ min^{-1} and a $He/CH_4/O_2$ reaction mixture in the molar ratio 7/2/1 flowing at 50 STPml $\cdot$ min^{-1} over 0.05 g of catalyst (F/W, 16.7 ml $\cdot$ $s^{-1} \cdot g^{-1}$). Before the tests, catalyst samples were further conditioned *in situ* at 600°C for 1 h under a 15% O_2/He flow. Mass spectra were recorded in multiple ion monitoring (MIM) mode using the SEM amplifier operating at 1200 V (total pressure, 2×10^{-9} bar) and an ionization potential of −70 V. TPR spectra have been obtained by acquiring the signals relative to the following *m/z* values: 2 (H_2), 4 (He), 15 (CH_3), 17 (OH), 28 (CO), 29 (CHO), 30 (HCHO), 32 (O_2), and 44 (CO_2). Then, CH_4 consumption has been detected by CH_3 signal, while HCHO formation has been revealed by following CHO and HCHO masses. By using He as internal standard, CH_4 and O_2 conversion values were derived from the CH_3/He and O_2/He signal ratios, respectively. For the calcula-

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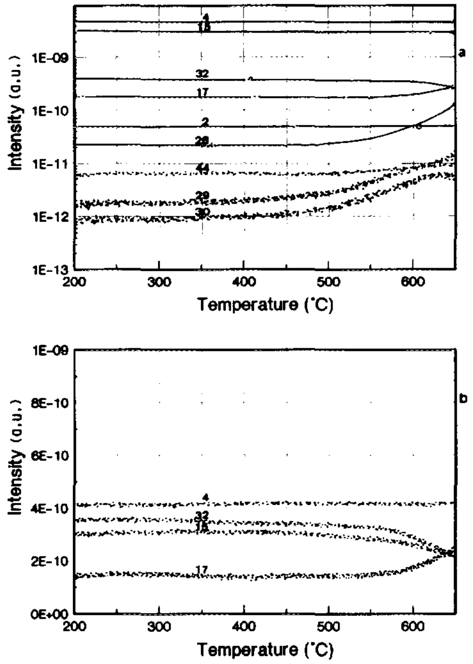

FIG. 1. Partial oxidation of methane over the 5% V_2O_5/SiO_2 catalyst. (a) TPR profiles of: $m/z = 2$, H_2; $m/z = 4$, He; $m/z = 15$, $CH_3(CH_4)$; $m/z = 17$, OH; $m/z = 28$, CO; $m/z = 29$, CHO; $m/z = 30$, HCHO; $m/z = 32$, O_2; $m/z = 44$, CO_2. (b) TPR profiles of He (m/z, 4), CH_4 (m/z, 15), O_2/(m/z, 32) and H_2O (m/z, 17) in a linear scale. ($m/z = 4$ and $m/z = 15$ have been multiplied by a factor of 0.1). Experimental conditions: β, 15°C · min^{-1}; W_{cat}, 0.05 g; reaction mixture flow, 50 ml · min^{-1} ($He/CH_4/O_2 = 7/2/1$).

tion of the relative abundance of HCHO, CO and CO_2 species the integral factors 0.93, 0.468, and 0.78 for m/z 28 (CO), 29 (CHO), and 44 (CO_2), respectively, have been used (*17*). The carbon mass-balance, estimated by the cross-check of the CH_4 conversion values calculated on the basis of the products formed with those obtained from the CH_3/He signal ratio, resulted within ±7%.

The complete TPR spectrum of the 5% V_2O_5/SiO_2 catalyst is shown in Fig. 1a. Further, in a linear scale the traces of He (m/z, 4), CH_4 (m/z, 15), O_2 (m/z, 32), and H_2O (m/z, 17) are displayed in Fig. 1b. It can be noted that the background partial pressure of the selected masses (m/z) keeps unchanged up to the temperature (T_o) at which the 5% V_2O_5/SiO_2 system begins to explicate its catalytic action which results in the formation of HCHO, CO, CO_2 and H_2O. Afterwards, a monotonically increase in the rate of product formation (Fig. 1a) and a concomitant decrease in the intensity of the signals related to CH_3 and O_2 species (Fig. 1b) have been observed. Such a trend has been experienced for all the investigated systems. However, in Fig. 2 a direct proof of the reactivity of unpromoted SiO_2 (Fig. 2a), 4% MoO_3/SiO_2 (Fig. 2b), 5% V_2O_5/SiO_2 (Fig. 2c), and 2% Nb_2O_5/SiO_2 (Fig. 2d) catalysts arises from the patterns related to the signals of CO, HCHO and CO_2. These patterns provide peculiar catalytic features allowing to establish both the onset temperature (T_o) at which the formation of each reaction product begins and the extent of product formed.

For the sake of comparison, the T_o's values for the different catalytic systems are listed in Table 1. Some important points emerge from these data:

(i) on the 5% V_2O_5/SiO_2 catalyst formaldehyde is detected at a T ($T_{o,HCHO} = 460°C$) lower than that found ($T_{o,HCHO} = 500°C$) for the bare silica, by contrast, $T_{o,HCHO}$ is markedly shifted to higher values on 4% MoO_3/SiO_2 ($T_{o,HCHO} = 580°C$) and 2% Nb_2O_5/SiO_2 ($T_{o,HCHO} = 560°C$) systems;

(ii) both $T_{o,CO}$ and T_{o,CO_2} values for the different systems are in the same sequence observed for $T_{o,HCHO}$;

(iii) the sequence of onset temperature of product formation for all the catalysts is

$$T_{o,HCHO} < T_{o,CO} < T_{o,CO_2}.$$

Points (i) and (ii) allow us to state that the reactivity of the SiO_2 is negatively affected by the addition of MoO_3 and Nb_2O_5, while V_2O_5 promotes the functionality of the SiO_2 surface towards the formation of partial oxidation products (HCHO, CO) (*12*). On the other hand, the sequence of onset temperatures provide some elements for envisioning the reaction pathway. Indeed, such sequence undoubtedly signals that the cata-

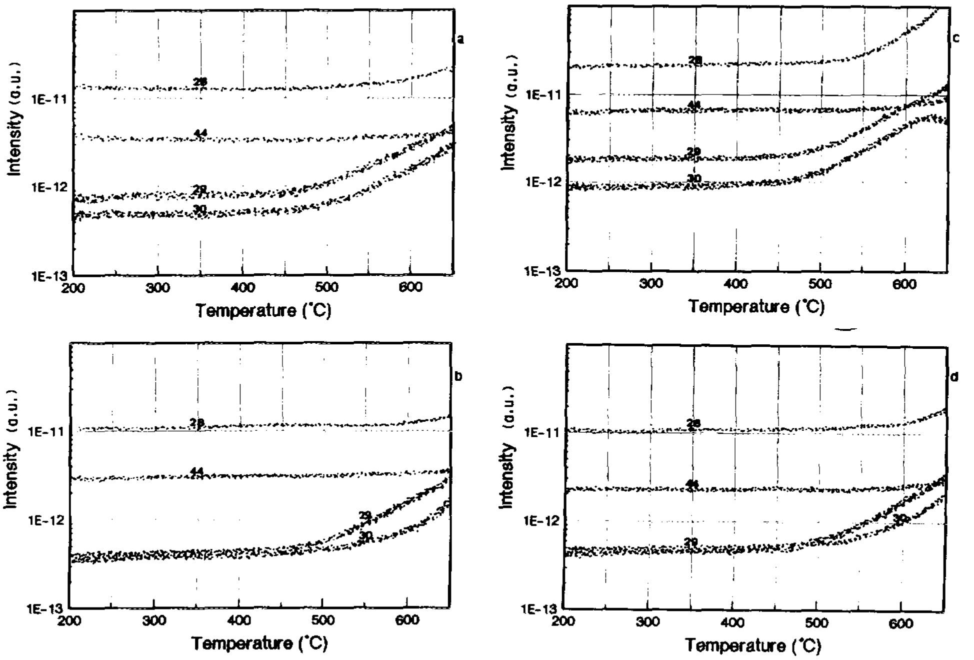

FIG. 2. Partial oxidation of methane over: (a) SiO_2; (b) 4% MoO_3/SiO_2; (c) 5% V_2O_5/SiO_2; and (d) 2% Nb_2O_5/SiO_2 catalysts. TPR profiles of HCHO (m/z = 29 and 30), CO (m/z = 28) and CO_2 (m/z = 44). Experimental conditions: see Fig. 1.

lytic action of MPO catalysts implies the primary formation of HCHO (*1, 2, 9, 18*). The formation of CO at T ($T_{o,CO}$) slightly higher than $T_{o,HCHO}$ (see Table 1) indicates that CO mainly arises from consecutive reactions (i.e., decomposition and/or oxidation) of formaldehyde on the catalyst surface (*3, 9, 18*). Moreover, the detection of carbon dioxide at T substantially higher (T_{o,CO_2}) than those found for either HCHO or CO production could be taken as a probatory evidence of the occurrence of a sequential reaction path (*2, 9, 18*),

$$CH_4 \rightarrow HCHO \rightarrow CO \rightarrow CO_2,$$

even if at higher reaction temperatures (>600°C) the contribution of a parallel reaction leading directly to CO_2 cannot be completely excluded. Such a hypothesis is sustained by the reaction pattern of the 4% MoO_3/SiO_2 catalyst. Indeed, the smaller difference between $T_{o,HCHO}$ and T_{o,CO_2} observed for this system probably reflects the occurrence of a parallel reaction accounting for the formation of carbon dioxide (*19*).

TABLE 1

Partial Oxidation of Methane on Silica-Supported Oxide Catalysts. Onset Temperature (T_o) of Product Formation

Catalyst	$T_{o,HCHO}$ (°C)	$T_{o,CO}$ (°C)	T_{o,CO_2} (°C)
SiO_2	500	540	630
4%MoO_3/SiO_2	580	600	620
5%V_2O_5/SiO_2	460	500	580
2%Nb_2O_5/SiO_2	560	610	>650

Further insight into the catalytic behaviour of the studied systems has been gained by a quantitative evaluation of the product amounts (A_{HCHO}, A_{CO}, and A_{o,CO_2}) formed between T_o and 650°C. Such integral area values (A), accounting for the capability of the studied systems in promoting the formation of the different products, have been

TABLE 2

Partial Oxidation of Methane on Silica-Supported Oxide Catalysts. Product Amount (A_X) and Product Selectivity (S^*_X, %)

Catalyst	A_{HCHO} (a.u.)	A_{CO} (a.u.)	A_{CO_2} (a.u.)	A_{tot}[a] (a.u.)	S^*_{HCHO}[b] (%)	S^*_{CO}[b] (%)	$S^*_{CO_2}$[b] (%)
SiO_2	5.1	6.5	0.2	11.8	42.8	56.0	1.1
4%MoO_3/SiO_2	2.2	1.8	0.5	4.5	50.3	42.3	7.4
5%V_2O_5/SiO_2	20.1	68.9	5.0	94.0	21.2	75.4	3.4
2%Nb_2O_5/SiO_2	3.5	2.8	0.	6.3	54.6	45.4	0.0

[a] $A_{tot} = A_{HCHO} + A_{CO} + A_{CO_2}$.
[b] $S^*_X = A_X/A_{tot}$.

summarized in Table 2. Notably, the values we found for the bare SiO_2, 4% MoO_3/SiO_2 and 5% V_2O_5/SiO_2 fully confirm the reactivity scale previously found under analogous reaction conditions by batch, flow and pulse reactors (*12*). In particular, the integrated area values of HCHO (A_{HCHO}), which can be taken as a measure of the catalyst capability in driving the MPO (*6–12*), reveal the strong promoting role of vanadia (A_{HCHO}, 20.1) on the reactivity of silica (A_{HCHO}, 5.1) along with a marked negative effect of molybdenum oxide (A_{HCHO}, 2.2) which likely depresses the peculiar catalytic functionality of the SiO_2 surface (*12*). Moreover, though oxide loading effects could be invoked (*1, 11*), the addition of niobium oxide (2 wt%) also yields a lowering in the activity of the SiO_2 support (Table 2). Hence, the values of the total product amount (A_{tot}) listed in Table 2, accounting for the overall catalytic activity of those systems ($A_{tot} = A_{HCHO} + A_{CO} + A_{CO2}$), well highlight the superior performance of the 5% vanadia-promoted silica catalyst (*12*) with respect either to the unpromoted SiO_2 or 4% MoO_3/SiO_2 and 2% Nb_2O_5/SiO_2 catalysts. In addition, taking into account the bare SiO_2 as reference system, it arises that the highest reactivity of the 5% V_2O_5/SiO_2 sample entails a lower integrated selectivity (S^*_X) to formaldehyde (S^*_{HCHO}) with a parallel increase in the selectivity to CO (S^*_{CO}). The opposite pattern, coming down from the constraints imposed by the conversion-selectivity relationship (*1, 8,*), can be observed for both 4% MoO_3/SiO_2 and 2% Nb_2O_5/SiO_2 catalysts. In fact, the higher selectivity to formaldehyde of these systems mostly arises from their worse capability in catalysing the title reaction. Finally, quantitative estimates of CH_4 and O_2 conversion

TABLE 3

Comparison of Activity Data for Silica and 5% V_2O_5/SiO_2 Catalysts Obtained by TPR and Batch Reactor Tests

Catalyst	CH_4 conv. (%)		O_2 conv. (%)		HCHO Sel. (%)		Y_{HCHO}[a]		Y_{HCHO}[a,b]	
	600°C	650°C	600°C	650°C	600°C	650°C	600°C	650°C	600°C	650°C
SiO_2	2.2	4.0	6.9	11.1	49	38	155	224	116	304
5%V_2O_5/SiO_2	4.4	13.1	9.9	36.7	31	20	201	386	318	793

[a] Productivity of HCHO: Y_{HCHO}, $g_{HCHO} \cdot kg_{cat}^{-1} \cdot h^{-1}$.
[b] Batch reactor; data from Ref. (*12*).

(%) and HCHO selectivity (%) at 600 and 650°C for SiO_2 and 5% V_2O_5/SiO_2 catalysts are reported in Table 3. The formaldehyde productivity values (Y_{HCHO}, $g_{HCHO} \cdot kg_{cat}^{-1} h^{-1}$), calculated from the above TPR conversion and selectivity data, are also compared in Table 3 with the formaldehyde productivity values previously obtained by batch reactor tests (*12*). The satisfactory agreement emerging between these two sets of data, further proving the positive role of vanadia on the reactivity of the silica in the MPO (*12*), undoubtedly confirms the validity of this TPR approach. On this account, the following order of reactivity can be drawn:

$$4\%MoO_3/SiO_2 \approx 2\%Nb_2O_5/SiO_2 < SiO_2 < 5\%V_2O_5/SiO_2.$$

Notwithstanding the slight difference in the Y_{HCHO} data obtained with TPR and batch reactor tests at 650°C, likely connected with some thermal effects in such nonsteady-state measurements and of the semiquantitative character of the QMS response, the proposed TPR method appears as a powerful tool for both investigating the reactivity of solid catalysts and accelerating the work of catalyst testing in the MPO.

In particular, the onset temperature of product formation (T_0) along with the product amount formed between T_0 and 650°C are suitable and reliable parameters for comparing the activity of the different MPO catalysts.

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