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A Basic Approach to Evaluate Methane Partial Oxidation Catalysts

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The partial oxidation of methane to formaldehyde by molecular oxygen on silica and silica-supported oxide catalysts has been investigated at a pressure of 1.7 bar in the temperature range 520–650°C by using a batch reactor with external recycle. The effects of reactor diameter, recycle flow rate, catalyst weight, and methane-to-oxygen ratio on the catalyst activity have been outlined. By performing several blank tests with an empty and a quartz-filled reactor, it has been demonstrated that the gas-phase reaction does not affect the catalytic pathways. Reasons for controversial results reported previously are discussed. They lie in the lack of an adequate experimental approach and in the generally adopted rule to evaluate the catalytic activity at differential conditions in order to push the HCHO selectivity to high values. The approach presented here allows to evaluate the catalytic activity by performing tests at quasi-zero conversion per pass but at a finite extent of conversion. The need to express the catalytic activity as space time yield (*STY*) to HCHO ($g \cdot kg_{cat}^{-1} \cdot h^{-1}$) is presented. The reactivities of various commercial SiO_2 samples obtained by precipitation, sol–gel, and pyrolysis methods have been determined. The fact that the nature and source of silica has a marked effect on *STY*, previously observed for reaction at 520°C, has been confirmed for operation at 550–650°C. Highest *STY*s are found with precipitated silica samples. In fact, at 650°C with such precipitated SiO_2 a *STY* to HCHO of 303 $g \cdot kg_{cat}^{-1} \cdot h^{-1}$ has been obtained. Incorporation of molybdena depresses the *STY* value for the precipitated silica but enhances the *STY* of bare fumed silica. In contrast, addition of vanadia to either precipitated or fumed silicas leads to higher *STY* values.

INTRODUCTION

Amongst the different routes proposed during the last decade in order to selectively convert methane (via "one step" process) to higher hydrocarbons or more valuable liquid oxygenates, the direct partial oxidation to formaldehyde has been recognised as one of the most challenging since it could potentially substitute the conventional "three step" industrial process (*1*). However, notwithstanding the great research effort focused on this topic, the various approaches proposed and the results up to now available from the literature (*2–18*) appear to be scattered either in terms of selectivity or yield to HCHO, sometimes ambiguous and not greatly encouraging. The reasons for such discrepancies lie in the lack both of a general approach for evaluating and comparing the different catalytic systems and of research efforts aimed at the characterization of the proposed catalysts in an effort to elucidate the factors controlling their reactivities. The use of N_2O instead of molecular O_2 has been suggested in order to enhance the reaction rate and the selectivity to HCHO (*5*). SiO_2 (*6*) and silica-supported MoO_3 (*2*, *8*), V_2O_5 (*3*, *9*), and heteropolyacids catalysts (*5*) have been the subject of several kinetic studies aimed essentially at disclosure of the reaction mechanism. Several attempts have been devoted to evaluation of the factors controlling the

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reactivity of the SiO_2 surface (*6*, 18), the influence of the metal oxide loading (*7*, *8*, *19*, *20*), and activation treatments on the performance of the supported oxide catalysts. In this respect, we have recently discussed (*21*) how the preparation method, the Na content, and the mechanical and thermal pretreatments govern the reactivity of the SiO_2 surface in methane partial oxidation to formaldehyde.

Several authors have seriously questioned the catalytic nature of the title reaction (*6*, *12*, *22*). In particular, Kastanas *et al.* (*6*) inferred that formaldehyde formation occurs via gas-phase reactions involving the generation of $CH_3^{\cdot}$ radicals on the silica surface. Baldwin *et al.* (*22*) posed serious doubts on the need to use solid catalysts stating that the yields of HCHO obtained from the catalytic reaction are lower than those obtained from the purely homogeneous gas-phase reaction, while Hargreaves *et al.* (*12*) in claiming a high yield to HCHO at 750°C on MgO catalyst at very low oxygen conversion stated their inability to distinguish whether the oxidation of the radical to formaldehyde occurs in the gas phase or at the surface. Moreover, the oxidation reaction involves a very complex pathway since the desired partial oxidation product HCHO can itself be oxidized to carbon oxides more easily than CH_4 itself. Our belief is that the adoption of both adequately designed reactor systems and appropriate operating conditions are fundamental to the attainment of reliable data unaffected by experimental artifacts. Though kinetic considerations suggest operation at fractional conversion levels approaching zero, the reaction implies a peculiar quasi-exponential relationship between conversion and selectivity that could led to very erratic assessments if the experimental data are not accurately obtained and presented. Therefore, this paper is aimed at the presentation of an original experimental approach, based on a "particular" batch reactor, for evaluating the activity of methane partial oxidation catalysts and at describing how results obtained using this approach reveal several fundamental aspects dealing with the reactivity of various bare SiO_2 supports and silica-supported MoO_3 or V_2O_5 catalysts. Finally, the formulation of a generally applicable strategy for future research activity in this field is pointed out.

EXPERIMENTAL

Catalysts

Three different SiO_2 samples (Si4-5P, AKZO product, $S.A._{BET} = 395\ m^2 \cdot g^{-1}$; 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 a sample of TiO_2 (GVA-500, Corning Glass product, $S.A._{BET} = 45\ m^2 \cdot g^{-1}$) have been used as supports. Silica Si4-5P was obtained by precipitation method (therefore these sample will be termed "precipitated SiO_2"), while Cab-O-Sil M5 and 250 MP samples were prepared by pyrolytic ("fumed or pyrolytic SiO_2") and sol–gel ("silica gel") process, respectively. 2.0% MoO_3 and 2.0 and 5.0% V_2O_5 loaded catalysts have been prepared by incipient wetness impregnation of SiO_2 and TiO_2 supports 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 pressed 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 measurement at −196°C. MoO_3 and V_2O_5 loadings were determined by atomic absorption spectroscopy (AAS).

Apparatus and Procedure

Methane partial oxidation experiments have been performed in the *T* range 520–650°C using a specifically designed "batch reactor" (*23*), schematically presented in Fig. 1. The reactor is 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

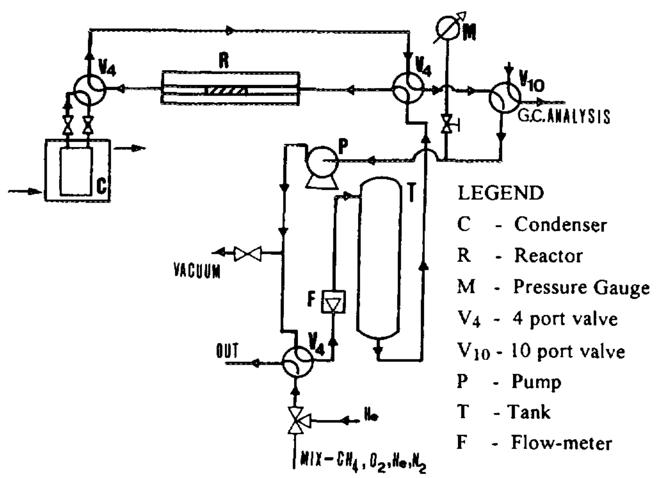

FIG. 1. Schematic diagram of the batch reactor.

their further oxidation. Two quartz and one stainless steel tube reactors, measuring 4, 10, and 4 mm in diameter (i.d.), respectively, and 100 mm in length, have been used. The catalyst bed was sandwiched between two quartz wool plugs. 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 with 0.05–2.0 g of catalyst sample. However, all the runs, unless otherwise stated, have been carried out with 0.05 g of catalyst (particle size, 16–25 mesh) by using the 4-mm-i.d. quartz reactor and with 1.0 g of catalyst (particle size, 16–25 mesh) by using the 10-mm-i.d. quartz reactor at 1.7 bar and 520°C with a recycle flow rate (*RFR*) of 1000 $N \cdot cm^3 \cdot min^{-1}$. In all experiments 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. Each run lasted 1–5 h depending on the activity of the investigated samples. The "standard" reaction mixture consisted of 18.2 mmol of CH_4, 9.1 mmol of O_2 as oxidant ($CH_4 : O_2 = 2 : 1$), 9.1 mmol of N_2 as standard for GC analysis and 54.6 mmol of He as diluent. Several experiments have been made with $CH_4 : O_2$ ratios of 8 : 1 and 15 : 1 by increasing in the reaction mixture the amount of CH_4 and decreasing the He content. All the gaseous products were analysed on-line by automatic sampling with a Hewlett–Packard 5890 A gas chromatograph equipped with a two-column analysis system and thermal conductivity detector, while HCHO was cumulatively determined by GC at the end of the run on the condensed mixture. Carbon and oxygen mass balances were generally better than 98–99% in all the runs.

RESULTS AND DISCUSSION

Blank Tests

The contribution of the gas-phase reaction to catalytic methane coupling has been the subject of a controversy still not settled (*24*). This issue has been underestimated for the methane partial oxidation to HCHO though it could seriously affect the reliability of the data. In order to evaluate the potential effect of the gas-phase reactions on our batch reactor experiments, several blank tests with empty and quartz or SiC filled reactors in the *T* range 520–650°C and at flow rate of 1000 $N \cdot cm^3 \cdot min^{-1}$ have been performed. Table 1 summarizes the results as percentage CH_4 converted per hour (i.e.,

TABLE 1

Partial Oxidation of Methane in the Absence of Catalyst[a]

Test	T_R (°C)	Hourly CH_4 conversion (mol%)	Product selectivity (%)				
			C_2H_6	C_2H_4	HCHO	CO	CO_2
Empty quartz reactor (i.d. = 10 mm)	520	—	—	—	—	—	—
	550	0.03	—	—	—	—	—
	600	0.08	32	—	62	5	1
	650	0.30	23	6	49	21	1
	650[b]	0.97	30	9	31	29	1
Empty quartz reactor (i.d. = 4 mm)	600	0.04	—	—	90	—	10
Empty stainless steel reactor (i.d. = 4 mm)	600	0.13	—	—	—	—	100
Quartz reactor (i.d. = 10 mm) filled with quartz granules[c]	650	0.13	36	—	50	9	5
Quartz reactor (i.d. = 10 mm) filled with SiC granules[d]	650	0.50	1	—	19	5	75

[a] Reaction conditions: P_R, 1.7 bar; recycle flow rate, 1000 $N \cdot cm^3 \cdot min^{-1}$. Reaction mixture composition (mmol): CH_4, 18.2; O_2, 9.1; N_2, 9.1; and He, 54.6.

[b] Recycle flow rate, 150 $N \cdot cm^3 \cdot min^{-1}$.

[c] W, 8.3 g (16–25 mesh).

[d] W, 12.1 g (16–25 mesh).

hourly CH_4 conversion, mol%) and product selectivity. It can be noted that (i) the extent of the gas-phase reaction progressively increases with increasing T_R; (ii) the presence of quartz granules in the reactor induces the quenching of any radical species formed limiting the gas-phase reaction, while the higher CH_4 conversion and the great fraction of total oxidation product observed for SiC filled reactor could be associated with some impurities of that specific material; (iii) the methane conversion seems to be proportional to the geometric surface of the quartz reactor; (iv) the formation of HCHO is associated with the use of the quartz reactor; (v) at $T \geq 600$°C the quartz reactor along with the HCHO promotes the formation of a considerable amount of coupling products; (vi) by lowering the flow rate to 150 $N \cdot cm^3 \cdot min^{-1}$ a significant enhancement in the CH_4 conversion is detected as consequence of a longer residence time. However, since in all our catalytic experiments the hourly CH_4 conversion ranged between 3 and 10% with the 10-mm-i.d. reactor for experiments in the range 520–600°C and between 1 and 8% with the 4-mm-i.d. reactors for experiments in the range 550–650°C, on the basis of the above results we argue that in the T range investigated and by operating with a flow rate equal to or higher than 1000 $N\ cm^3 \cdot min^{-1}$ the contribution of the homogeneous gas-phase reaction or blank effect on the "wall" of the reactor can be completely neglected.

Characteristics of the "Batch Reactor" and Selection of the Operating Conditions

The influence of contact time (*6*) and $CH_4:O_2$ ratio (*8*, *16*, *25*) on the selectivity to HCHO (S_{HCHO}, %) has been evaluated for continuous flow reactor experiments. This topic has been emphasized since the achievement of high S_{HCHO} has been largely recognized as the more desirable goal. We

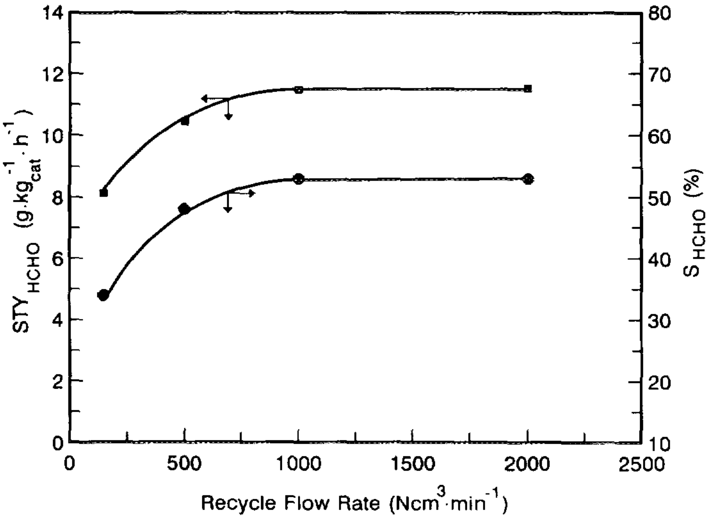

FIG. 2. Effect of the recycle flow rate (*RFR*) on the (■) space time yield to HCHO (STY_{HCHO}) and (●) selectivity to HCHO (S_{HCHO}) in the partial oxidation of methane over the bare Si4-5P catalyst at 520°C.

have already indicated (*21*) that the space time yield to HCHO (STY_{HCHO}, $g_{HCHO} \cdot kg_{cat}^{-1} \cdot h^{-1}$) is the more valid parameter to use in order to obtain a true reactivity scale. The batch reactor proposed here basically constitutes a unique tool to correctly address these matters and permits the formulation of a suitable experimental procedure for the evaluation of methane partial oxidation catalysts. The operating parameter of the batch reactor which to some extent could be related to the gas hourly space velocity in the continuous flow reactor is the *RFR*. In this respect, Fig. 2 depicts the influence of the *RFR* ranging between 150 and 2000 $N \cdot cm^3 \cdot min^{-1}$ on the S_{HCHO} and STY_{HCHO} achievable with bare Si4-5P SiO_2 catalyst at 520°C, while Fig. 3 shows the influence of the residence time on the hourly and per pass CH_4 conversions. It can be noted that an increase in the *RFR* from 150 to 1000 $N \cdot cm^3 \cdot min^{-1}$ yields a concomitant rise in both the S_{HCHO} and STY_{HCHO}, while RFRs higher than 1000 $N \cdot cm^3 \cdot min^{-1}$ do not further improve these parameters. Such higher *RFR*s, corresponding to residence times of 0.1–1.2 s, permit operation at CH_4 conversions per pass ranging between 0.1 and 1.1 mol% and at a finite value of hourly CH_4 conversion. The constant value of the hourly CH_4 conversion level obtained with variation in the residence time indicates that under these experimental conditions the reaction is unaffected by mass transfer limitations. The trends of S_{HCHO} and STY_{HCHO} with *RFR* reflect the kinetic and thermodynamic (i.e., thermal stability) controlling effects on the product selectivity. On the basis of the above results we decided to adopt for standard conditions the *RFR* of 1000 $N \cdot cm^3 \cdot min^{-1}$.

The influence of CH_4/O_2 ratio on the S_{HCHO} and STY_{HCHO} has been evaluated by performing a series of experiments at 520°C on bare Si4-5P SiO_2 sample with CH_4/O_2 ratio ranging between 2 : 1 and 15 : 1. The results, summarized in Table 2, signal that at CH_4/O_2 ratios higher than 2 : 1 only a moderate and progressive rise in the S_{HCHO} can be obtained, but this effect is counterbalanced by the decrease in the reaction rate, then a fairly constant figure of STY_{HCHO} has been found. These findings clearly show that the invoked positive effect of higher CH_4/O_2

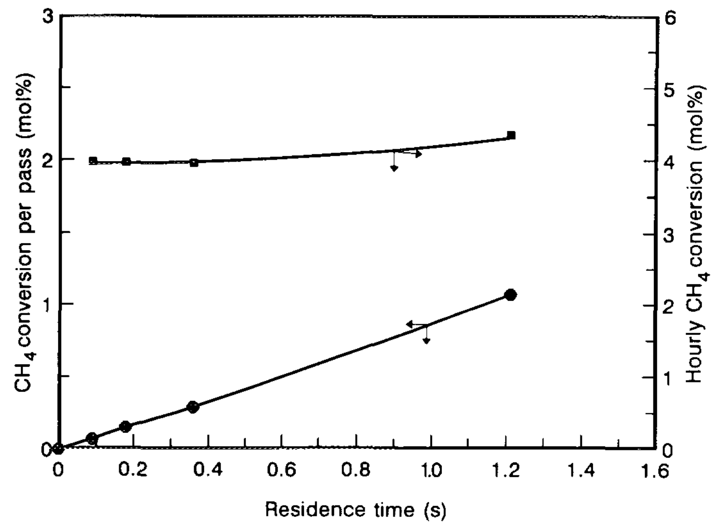

FIG. 3. Effect of the residence time on the (●) CH_4 conversion per pass and (■) hourly CH_4 conversion in the partial oxidation of methane over the bare Si4-5P catalyst at 520°C.

ratio on the title reaction is meaningless, since it exerts only a kinetic effect on the S_{HCHO} and sometimes could be the consequence of operations carried out in O_2-limiting conditions. Therefore we have adopted for standard conditions a CH_4/O_2 ratio of 2 : 1.

Besides, in order to evaluate the influence of the catalyst weight on the S_{HCHO} and STY_{HCHO} a series of experiments has been carried out at 520°C with 0.25–1.0 g of 5% V_2O_5/SiO_2 catalyst. The results, shown in Fig. 4, indicate that the hourly CH_4 conversion, as expected, increases regularly with the catalyst weight while the S_{HCHO} decreases, particularly on increasing the catalyst mass from 0.25 to 0.5 g, while the STY_{HCHO} is totally unaffected by the chosen catalyst weight. Furthermore, the serious limitation of the experimental approach based on continuous flow reactor regarding the decrease in the selectivity to HCHO with CH_4 conversion is completely overcome with the "batch reactor." Indeed, considering the results of a typical run on Si4-5P catalyst at 520°C, shown in Fig. 5, it is evident that the selectivity to HCHO remains constant while the CH_4 conversion rises with the reaction time. All the above findings document both the reliability and the versatility of our batch reactor in pursuing methane partial oxidation reaction and clearly highlight the need to compare the different catalytic systems in terms of STY_{HCHO}.

TABLE 2

Influence of CH_4/O_2 Ratio in the Partial Oxidation of Methane on Bare Si4-5P SiO_2 Catalyst

CH_4/O_2	Rate ($10^{-10} mol_{CH4} \cdot m^{-2} \cdot s^{-1}$)	Selectivity (%)			STY_{HCHO} ($g \cdot kg_{cat}^{-1} \cdot h^{-1}$)
		CO_2	CO	HCHO	
2	6.25	57	5	38	9.78
8	3.94	41	—	59	9.89
15	3.65	28	5	67	10.06

Note. Reaction conditions: W_{cat}, 1.0 g (16–25 mesh); P_R, 1.7 bar; T_R, 520°C; recycle flow rate, 1000 N · $cm^3 \cdot min^{-1}$. Reaction mixture composition: see Table 1.

Application of Batch Reactor Technique

In order to illustrate the use of the batch reactor technique we present an overview of results obtained in studies of methane partial oxidation on silica catalysts and on metal oxide systems using silica as the support material.

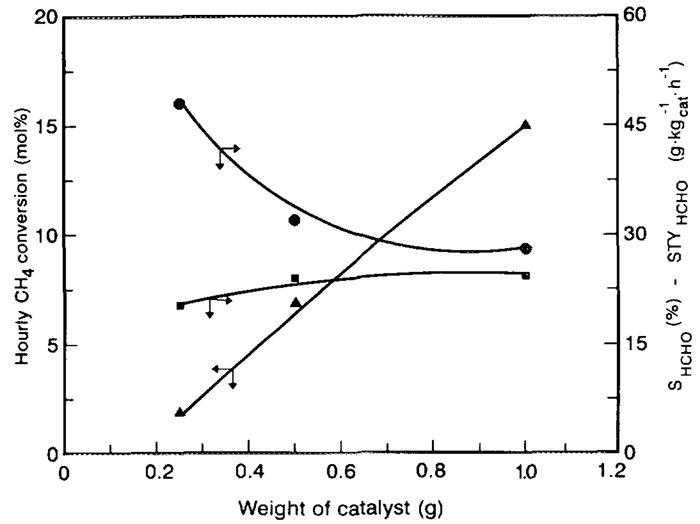

FIG. 4. Effect of the catalyst weight on the (▲) hourly CH_4 conversion, (■) space time yield to HCHO (STY_{HCHO}), and (●) selectivity to HCHO (S_{HCHO}) in the partial oxidation of methane over the 5.0% V_2O_5/SiO_2 catalyst at 520°C.

Activity of bare SiO_2 Catalysts. The issue of SiO_2 reactivity has been largely underestimated although it is fundamental in controlling the reactivity of silica supported oxide catalysts. Several authors have attempted to evaluate the reactivity of the bare SiO_2 (*5*, *6*, *18*, *21*), the data available from the literature, summarized in Table 3, appear to be scattered and controversial. This could be due either to the different silicas used or to the different operating conditions. Therefore, in order to gain basic insight into the

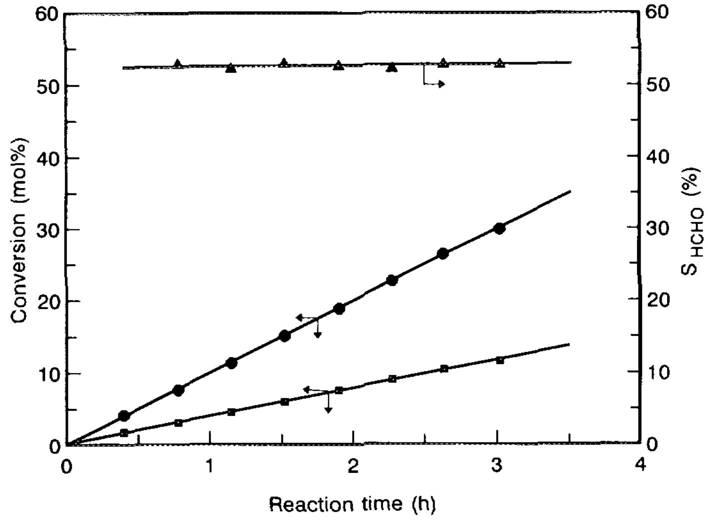

FIG. 5. Batch reactor test of the activity of the Si4-5P SiO_2 catalyst in the partial oxidation of methane at 520°C. (■) CH_4 and O_2 (●) conversion and (▲) selectivity to HCHO (S_{HCHO}) versus the reaction time.

TABLE 3

Activity and Formaldehyde Productivity of Various Commercial SiO_2 Samples in the Partial Oxidation of Methane (Data from the Literature)

Sample[a]	BET S.A. ($m^2 \cdot g^{-1}$)	T_R (°C)	P_R (bar)	Rate ($10^{-9}mol_{CH4} \cdot m^{-2} \cdot s^{-1}$)	STY_{HCHO} ($g \cdot kg_{cat}^{-1} \cdot h^{-1}$)	Reference
Silica gel (Grace Davison grade 400)	740	570	1.00	0.17	4.70	(*5*)
Silicic acid	274	620	3.80	0.95	13.20	(*6*)
Cab-O-Sil	191	620	3.08	1.44	8.90	(*6*)
Ludox gel	105	620	3.77	0.87	2.70	(*6*)
Cab-O-Sil M5	212	650	1.00	1.80	18.96	(*8*)
ID "Silica gel"	277	650	1.00	3.60	36.00	(*8*)
Cab-O-Sil	385	730	1.00	—	75.70	(*18*)
Silica gel (Grace 636)	480	630	1.00	—	25.80	(*18*)
Silica gel (Grace 636)	480	730	1.00	—	267.00	(*18*)
Si4-5P	381	520	1.70	0.63	9.78	(*21*)
Si4-5P (heat treated at 1000°C)	163	520	1.70	1.90	17.92	(*21*)
F5	676	520	1.70	0.55	13.51	(*21*)
HOI	150	520	1.70	0.50	3.28	(*21*)
GRADE 432	320	520	1.70	0.09	1.53	(*21*)
Cab-O-Sil M5	200	520	1.70	0.03	0.33	(*21*)

[a] Refer to reference for detailed nature of the silica.

factors controlling the activity of the SiO_2 in the partial oxidation of methane, we have previously selected and studied several typical commercial SiO_2 samples obtained either by "precipitation," "sol-gel," or "pyrolysis" methods. Their reactivities at 520°C expressed in terms of reaction rate, products selectivity and *STY* are also reported in Table 3 (*21*). On the basis of these data we concluded that precipitated SiO_2 is much more active than fumed SiO_2 in the title reaction. Indeed, the reaction rate on "precipitated" Si4-5P and F5 samples was more than 25 times higher than that observed on gel Grade 432 and fumed Cab-O-Sil M5 SiO_2 samples. Furthermore, the difference in reactivity of the various silicas becomes more evident when the *STY* is considered. It is remarkable that the productivity ratio on unit weight basis for Si4-5P or F5 and Cab-O-Sil M5 SiO_2 samples is 30–40 : 1.

As the contribution of the gas-phase reaction is negligible under our experimental conditions, we attempt to evaluate the reactivity of some differently prepared commercial SiO_2 samples in the T_R range 550–650°C. The main relevant results are listed in Table 4 in terms of reaction rate and STY_{HCHO}. These data fully confirm the reactivity scale already found at 520°C (*21*). Namely, the ratios of the STY_{HCHO} obtained with precipitated Si4-5P, gel 250 MP and M5 fumed silicas at 600 and 650°C are 35 : 5.5 : 1 and 15 : 3 : 1 respectively. In addition, Fig. 6 shows the influence of the reaction temperature both on STY_{HCHO} and S_{HCHO} in the partial oxidation of methane over the bare Si4-5P SiO_2 sample. A marked increase in the HCHO productivity with the temperature can be noted. Further, the slightly decrease observed in the selectivity to HCHO is taken to reflect the decomposition and/or oxidation of HCHO. This phenomenon becomes prevalent at higher temperatures even though we operate at quasi-zero conversion per pass. Such great differences in the reactivities of the bare commercial SiO_2

TABLE 4

Activity and Formaldehyde Productivity of Different SiO_2 Samples in the Partial Oxidation of Methane at High Temperatures

Sample	Preparation Method	BET S.A. ($m^2 \cdot g^{-1}$)	T_R (°C)	Rate ($10^{-10} mol_{CH4} \cdot m^{-2} \cdot s^{-1}$)	STY_{HCHO} ($g \cdot kg_{cat}^{-1} \cdot h^{-1}$)
Si4-5P	Precipitation	381	600	37.68	115.85
Si4-5P	Precipitation	381	650	116.24	303.84
250 MP	Sol–gel	180	600	12.92	18.58
250 MP	Sol–gel	180	650	44.38	60.11
M5	Pyrolysis	200	600	2.02	3.28
M5	Pyrolysis	200	650	12.64	20.76

samples certainly have relevant influence on the reactivities of the silica supported oxide systems and could be one of the reasons for the conflicting data reported previously. Further work in this area should address this topic in order to avoid misleading assessments about the promoting effect of the oxides on the activity of the SiO_2 surface. On the whole, it is noteworthy that the unpromoted precipitated SiO_2 exhibits a considerable STY_{HCHO} also at high temperatures. This is the result of both a significantly high activity and a noticeable selectivity to HCHO which is well preserved by the adopted experimental approach. In particular, the STY_{HCHO} of 303 g · kg_{cat}^{-1} h^{-1} obtained at 650°C is more than one order of magnitude higher than the STY_{HCHO}'s reported for other SiO_2 systems (*5*, *6*, *18*) (see Table 3) and appears to be in absolute the highest value of STY_{HCHO} yet reported for unsupported and silica supported oxide catalysts operating at atmospheric pressure and reaction temperature lower than 750°C (see infra Table 5). Finally, contrary to the claims of Baldwin *et al.* (*22*) the above reactivity data of the SiO_2 systems strengthen the concept of the catalytic nature of the partial oxida-

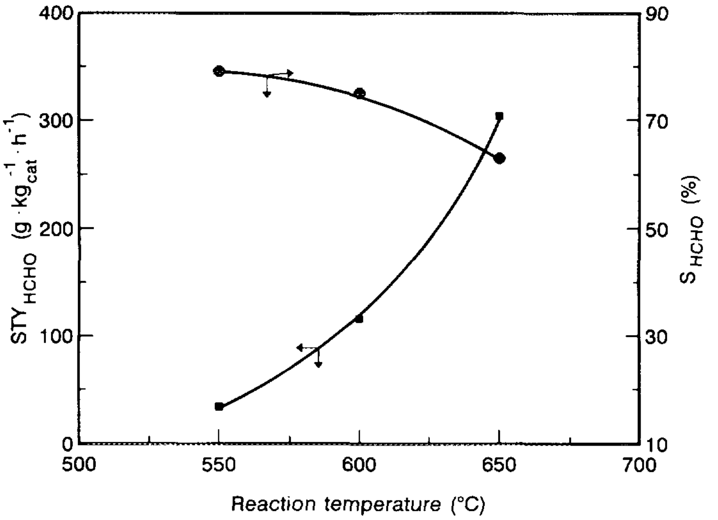

FIG. 6. Effect of the reaction temperature on the (■) space time yield to HCHO (STY_{HCHO}) and (●) selectivity to HCHO (S_{HCHO}) in the partial oxidation of methane over the bare Si4-5P catalyst.

TABLE 5

Formaldehyde Productivity in the Partial Oxidation of Methane on Oxide Catalysts (Selected Data from the Literature)

Catalyst	T_R (°C)	STY_{HCHO} ($g \cdot kg_{cat}^{-1} \cdot h^{-1}$)	Reference
	Oxidant : N_2O		
2.0% V_2O_5/SiO_2	500	5.40[a]	*(3)*
1.7% MoO_3/SiO_2	520	1.80[a]	*(2)*
20% HPMo/SiO_2	570	27.50	*(5)*
4.8% MoO_3/SiO_2	570	2.25	*(5)*
6.1% MoO_3/SiO_2	590	12.70	*(7)*
5.0% MoO_3/SiO_2	600	0.50	*(11)*
2.0% V_2O_5/SiO_2	600	22.80	*(20)*
10% MoO_3/2% Fe_2O_3/SiO_2	600	20.86	*(20)*
	Oxidant : O_2		
5.0% MoO_3/SiO_2	220	7.20[a,b]	*(26)*
2.0% MoO_3/SiO_2	520	2.10	*(27)*
B–P–O	580	4.80	*(28)*
9.0% B_2O_3/SiO_2	600	0.80	*(4)*
9.0% BeO-9.0% B_2O_3/SiO_2	600	24.00	*(4)*
2.3% V_2O_5/SiO_2	600	77.10[c,d]	*(9)*
No catalyst	625	15.00[e]	*(22)*
2.7% MoO_3/SiO_2	650	102.10[c]	*(8)*
Mo–Sn/SiO_2	700	80.00	*(10)*
MgO	750	270.20	*(12)*
Cu/Fe/ZnO	750	75.10	*(13)*

[a] HCHO + CH_3OH.

[b] Experimental performed under UV irradiation.

[c] Yield quoted is $g_{HCHO} \cdot liter_{cat}^{-1} \cdot h^{-1}$.

[d] Yield quoted on the basis of data reported in Ref. *(1)*.

[e] Yield quoted is $g_{HCHO} \cdot liter_r^{-1} \cdot h^{-1}$.

tion of methane to formaldehyde and then the need to use a catalyst to attain reliable and promising yields to HCHO.

Physicochemical characterization work is in progress and should enable us to understand the origin of the different reactivities experienced for the differently prepared commercial SiO_2 samples.

Activity of MoO_3/SiO_2 and V_2O_5/SiO_2 catalysts. In an attempt to give a measure of the conflicting data reported for the partial oxidation of methane to formaldehyde on solid oxide catalysts, a list of the more interesting results is presented in Table 5 in terms of STY_{HCHO}. For sake of comparison, also the best result reported for the gas-phase reaction has been included. The great variety of catalysts used, the vast differences in the experimental conditions, the different nature of the oxidant, the different experimental devices, the different aims of the authors along with the factors considered above help to explain some inconsistencies in the results outlined in Table 5. However, the majority of such results concern silica supported molybdena and vanadia catalysts. There is an unanimous consensus on the promoting effects of such oxides on the reactivity of the bare SiO_2 *(1–3, 7–9, 16, 20)*. Therefore, we have tried to evaluate the influence of the different SiO_2 supports on such promoting effect. From the direct comparison of reactivity at 520°C between 2.0% MoO_3 supported on "precipitated" Si4-5P or on "fumed" M5, reported in Table 6, it emerges that MoO_3 promotes the activity of the "fumed" M5 exactly by a factor

TABLE 6

Partial Oxidation of Methane on Molybdena Catalysts at 520°C

Catalyst	BET S.A. ($m^2 \cdot g^{-1}$)	Rate ($10^{-7} mol_{CH4} \cdot g_{cat}^{-1} \cdot s^{-1}$)	Selectivity (%)			STY_{HCHO} ($g \cdot kg_{cat}^{-1} \cdot h^{-1}$)
			CO_2	CO	HCHO	
SiO_2[a] (Si4-5P)	381	1.35	45	1	54	7.81
SiO_2 (M5)	200	0.05	31	5	64	0.33
MoO_3	2	0.01	n.d.[b]	n.d.[b]	n.d.[b]	—
2.0% MoO_3/SiO_2 (Si4-5P)	311	1.34	65	2	33	4.75
2.0% MoO_3/SiO_2 (M5)	198	0.23	14	6	80	2.08
2.0% MoO_3/TiO_2	50	0.78	100	—	—	—

[a] Tableted.

[b] n.d., not determined.

TABLE 7

Partial Oxidation of Methane on Vanadia Catalysts at 520°C

Catalyst	BET S.A. ($m^2 \cdot g^{-1}$)	Rate ($10^{-7} mol_{CH4} \cdot g_{cat}^{-1} \cdot s^{-1}$)	Selectivity (%)			STY_{HCHO} ($g \cdot kg_{cat}^{-1} \cdot h^{-1}$)
			CO_2	CO	HCHO	
SiO_2[a] (Si4-5P)	381	1.35	45	1	54	7.81
SiO_2 (M5)	200	0.05	31	5	64	0.33
V_2O_5	6	0.06	n.d.[b]	n.d.[b]	n.d.[b]	—
2.0% V_2O_5/SiO_2 (Si4-5P)	215	4.44	24	49	27	13.01
2.0% V_2O_5/SiO_2 (M5)	191	3.57	17	21	62	23.94
2.0% V_2O_5/TiO_2	48	7.28	70	30	—	—

[a] Tableted.

[b] n.d., not determined.

6, while it shows a significant poisoning effect on the "precipitated" silica likely masking its most reactive centres (*29*). Moreover, it is notable that the reactivity of the MoO_3/SiO_2 M5 catalyst is actually lower than that of "bare" precipitated Si4-5P or F5 sample. Finally, it is seen that silica free molybdenum based systems, such as MoO_3 or MoO_3/TiO_2 do not lead to any formation of formaldehyde. MoO_3 itself is essentially inactive, while MoO_3/TiO_2 although active is associated with the selective production of CO_2. On the other hand, the data reported in Table 7 clearly indicate that V_2O_5 enhances the reactivity of both precipitated Si4-5P and fumed "M5" silicas. Such promoting action results in a doubling of *STY* for the 2.0% V_2O_5/SiO_2 Si4-5P sample with respect to the bare Si4-5P silica, while for the fumed M5 systems the V_2O_5 promoted catalyst allows us to obtain a *STY* which is more than one order of magnitude higher than that of the bare silica. As observed for MoO_3 systems, bulk V_2O_5 is almost inactive and V_2O_5/TiO_2 exhibits a considerable activity toward the formation of CO_x. On the whole, such data indicate that the production of HCHO on unsupported and supported oxide catalysts is associated with the presence of the SiO_2 surface. In order to remove any doubt about the true catalytic nature of the studied reaction, the activity of the 2.0% V_2O_5/SiO_2 M5 catalyst has been measured at 600°C in the same sized quartz and stainless steel reactors. The almost identical results achieved with the two reactors, outlined in Table 8, lead to conclude that the wall of the quartz reactor does not

TABLE 8

Activity of the 2.0% V_2O_5/SiO_2 M5 Catalyst in the Partial Oxidation of Methane Measured by Different Reactors at 600°C

Reactor	Rate ($10^{-7} mol_{CH4} \cdot g_{cat}^{-1} \cdot s^{-1}$)	Selectivity (%)			STY_{HCHO} ($g \cdot kg_{cat}^{-1} \cdot h^{-1}$)
		CO_2	CO	HCHO	
Quartz (i.d. = 4 mm)	58.98	27	23	50	318
Stainless steel (i.d. = 4 mm)	60.31	27	22	51	329

play any role in the reaction pathway. Then, since the concept of surface initiated homogeneous–heterogeneous reaction cannot be invoked to explain the above results, it can be stated that the partial oxidation of methane to formaldehyde proceeds via a surface catalysed process which likely involves specific catalyst requirements (*18*, *21*, *29*). Furthermore, such data highlight the excellent performance of the 2.0% V_2O_5/SiO_2 M5 catalyst. In fact, it features a STY_{HCHO} of about 320 $g \cdot kg_{cat}^{-1} \cdot h^{-1}$ at 600°C which is about 100 and 3 times higher than those of the bare M5 and high active precipitated Si4-5P SiO_2 samples respectively and also higher than that of the precipitated Si4-5P SiO_2 at 650°C.

CONCLUDING REMARKS

Several important conclusions can be drawn from this study.

- A batch reactor with external recycle and a liquid condenser placed downstream of the reactor is a very reliable tool to evaluate the activity of methane partial oxidation catalysts in the temperature range 520–650°C.
- Gas-phase reaction is absolutely negligible in the range 500–650°C when operating at *RFR* equal or higher than 1000 $N \cdot cm^3 \cdot min^{-1}$ and with a catalyst mass ranging between 0.05 and 1.0 g as a function of the reactor size and reaction temperature level.
- The space time yields to HCHO (STY_{HCHO}, $g \cdot kg_{cat}^{-1} \cdot h^{-1}$) is the more valid parameter to estimate the activity of partial oxidation catalysts. Data analysis based on catalytic activity expressed as methane conversion and selectivity to HCHO could result in misleading conclusions.
- By increasing the CH_4/O_2 ratio in the range 2:1–15:1 only a slight increase in the S_{HCHO} has been observed, while the STY_{HCHO} remains unaffected.
- Unpromoted commercial SiO_2 supports constitute active catalysts for the title reaction. The reactivity of SiO_2 is mainly controlled by its preparation method. In particular, precipitated SiO_2 is significantly more active than gel and fumed silicas. At 650°C use of the precipitated SiO_2 system is associated with a STY_{HCHO} of about 300 $g \cdot kg_{cat}^{-1} \cdot h^{-1}$. Such figure is more than one order of magnitude higher than those reported for other SiO_2 systems. Future activities in this field should, for the sake of avoiding confusion, take into account the different reactivities of the various commercial SiO_2 samples.
- Addition of V_2O_5 enhances the activity of both precipitated Si4-5P and fumed M5 silicas by factors of 2 and 70, respectively. MoO_3 incorporation enhances the activity of the fumed silica by a factor 6, while it shows a significant poisoning effect on the activity of the precipitated silica.
- The partial oxidation of methane to formaldehyde on silica and silica-supported MoO_3 and V_2O_5 catalysts proceeds via a surface catalysed process and the formation of HCHO is associated with the presence of the SiO_2 surface.

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