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Synthesis of methyl formate via two-step methane partial oxidation

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Abstract

Using a two reactor system the direct catalytic conversion of methane to methyl formate is achieved. The two-step reaction sequence consists of the partial oxidation of methane to HCHO at 600–700°C on a SiO_2-based catalyst and the dimerisation of HCHO to methyl formate at 130–170°C on amphoteric oxides such as TiO_2, ZrO_2 and Al_2O_3. By adopting a continuous flow recycle reactor mode methyl formate yield up to 12% has been attained. A preliminary analysis of the factors controlling activity and reaction pattern of oxide catalysts in the dimerisation of formaldehyde is given. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Methyl formate; Methane partial oxidation; Catalyst; Formaldehyde dimerisation; Oxide

1. Introduction

The direct conversion of natural gas to higher hydrocarbons, easily transportable fuels and chemicals is still one of the hottest and challenging research topics in catalysis. However, in spite of the efforts and resources devoted to this subject, due to the limited yield none of the catalytic processes proposed so far, such as oxidative coupling, partial oxidation to methanol or formaldehyde, thermal pyrolysis, electrophylic activation etc., is yet mature for industrial exploitation [1]. The lack of success of such direct catalytic methods for natural gas conversion has stimulated the interest toward indirect routes via syngas.

Recently, a renewed interest in the direct conversion of methane to oxygenates and higher hydrocarbons of higher added value [2–5] has been associated with the disclosure of more effective operating strategies and reactor configurations [6–9]. Indeed, Klier and his group have reported how the yield of CH_3OH and HCHO in the methane partial oxidation can be maximised by using a double bed reactor system, one for the abstraction of hydrogen from methane and the other for the formation and hydrolysis of the methoxide species [2]. Even a sequence of three catalysts for the synthesis of propanol from methane and air through a parallel/series reactor configuration involving the methane oxidative coupling to ethylene, the methane partial oxidation to syngas and the hydroformylation of ethylene, has been proposed [3]. In order to overcome the expensive cryogenic separation step for C_2H_4 recovering in the oxidative coupling of methane, Liu and Shen have studied the direct epoxidation of C_2H_4 in the dilute reaction stream realising the direct conversion of methane into ethylene oxide [4]. Exxon has also patented a method for producing a mixture of methanol and ethanol by contacting methane, water and an acidic aqueous solution of

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Fe^{3+} ions with a noble metal catalyst at 60°C and 30–60 bar [5]. Machocki has claimed that the use of a reactor–adsorber system with gas re-circulation gives a high yield of C_2H_4 in methane oxidative coupling [6]. A two-step reaction sequence has been adopted to convert methane into hydrogen and higher hydrocarbons in a Pd–Ag membrane reactor operating in a non-oxidative atmosphere [7]. In particular, methane was first activated at 300°C as a result of the dissociative deposition on a Ru catalyst, followed by rehydrogenation at 100–200°C to form higher hydrocarbons [7].

Aris et al. [8] vindicated the acquiring of C_2 yield values slightly higher than 50% in the oxidative coupling of methane on Sm_2O_3 catalyst by using a separate chemical reactor that simulated a counter-current chromatographic moving-bed.

Ethylene yield of up to 85% in the methane oxidative coupling was achieved in a gas recycle high-temperature electrocatalytic or catalytic reactor where the recycled gas passes through a molecular sieve trap in the recycle loop [9].

Then, a very promising alternative to the direct conversion of methane, which could open novel perspectives for the C_1 chemistry, is constituted by the methods based on the two-step transformation as well as by these approaches ensuring the protection of the highly reactive desired products by means of selective adsorption or easier separation via conversion into valuable chemicals (cross-coupling reactions, 'driven' consecutive reactions, oligomerisation reactions, etc). These strategies could allow the limitations of the one-step conversion mode in terms of yield, product separation and value of the final product to be overcome.

We have widely documented the excellent performance of silica based oxide catalysts in the partial oxidation of methane to formaldehyde [10–12]. Furthermore, the adoption of a continuous flow recycle reactor mode has allowed to reach HCHO yield values of 10–18% [13]. Thus, taking advantage of such excellent HCHO yield values and considering the importance of the HCHO as building block molecule for the production of a large series of basic and fine chemicals, a two-step process for the direct catalytic conversion of methane into methyl formate, by means of a dual bed reactor configuration involving the primary partial oxidation of methane to formaldehyde (MPO) and the subsequent dimerisation of formaldehyde (FD), has been devised and exploited [14].

This paper presents preliminary results on the synthesis of methyl formate via two-step methane partial oxidation which also provides insights about the performance of the catalysts employed in both MPO and FD reactions.

2. Experimental

2.1. Catalyst

A commercially precipitated SiO_2 sample has been used as catalyst for the MPO reaction, while commercial Al_2O_3, TiO_{2P}, TiO_{2T} and ZrO_{2VP} along with zirconia (ZrO_{2C}) and the related sulphated (3% $SO_4^{=}$/ZrO_2) samples prepared according to the procedure suggested by Scurrell [15] have been tested in FD reaction.

The list of oxide catalysts along with the relative supplier, commercial code and BET SA values are reported in Table 1.

2.2. Catalytic measurements

The schematic diagram of the two catalytic bed reactor apparatus used for the synthesis of methyl formate is shown in Fig. 1. The system consisted of: a set of mass flow controllers (MCF), feeding reactants (CH_4 and O_2), diluent (He) and internal standard (N_2) gases under controlled conditions; two continuous flow reactors, R_1 (l, 200 mm; i.d., 4 mm;) and R_2 (l, 200 mm; i.d., 12 mm) connected in series to attain the methane partial oxidation and formaldehyde dimerisation, respectively; and a recir-

Table 1
List of oxide catalysts

Sample	Commercial code	BET SA (m^2 g^{-1})
SiO_2	Si 4-5P Akzo	400
Al_2O_3	000-1.5E Akzo	190
TiO_{2T}	T805 Degussa	50
TiO_{2P}	P25 Degussa	50
ZrO_{2C}	Lab catalyst	19
3% $SO_4^{=}$/ZrO_{2C}	Lab catalyst	18
ZrO_{2VP}	VP Degussa	40

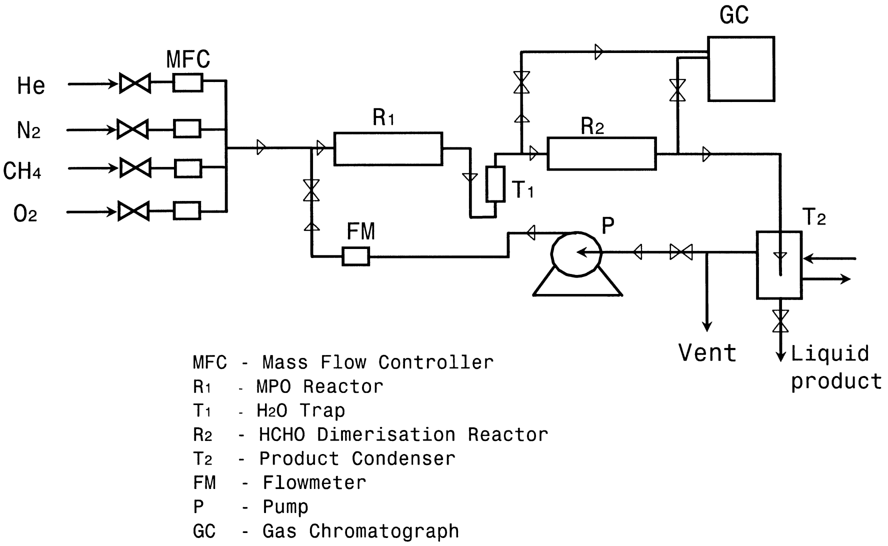

Fig. 1. Schematic diagram of the experimental apparatus for the synthesis of methyl formate via two-step methane partial oxidation.

culation pump (P) allowing experiments to be performed in continuous flow recycle mode (CFRR). A trap containing magnesium perchlorate, T_1, is placed between R_1 and R_2 reactors in order to remove H_2O from MPO reaction stream, while a cold water trap (−5°C) is inserted downstream of the R_2 reactor, T_2, in order to collect oxygenated products (formaldehyde and/or methyl formate).

All the experiments were performed at atmospheric pressure both in continuous flow (CFR) and continuous flow recycle reactor (CFRR) modes by adopting the conditions reported in Table 2.

The GC system used for the analysis of the reaction streams of R_1 and R_2 reactors and the method adopted for the calculation of the catalyst performance in both MPO and FD reactions along with the overall yield of the reaction system have been reported elsewhere [14].

2.3. Catalyst characterisation

Acidic and basic properties of oxide catalysts have been evaluated by TPD measurements of adsorbed NH_3 and CO_2, respectively.

NH_3–TPD tests in the range 100–640°C were performed using He as carrier gas flowing at 25 STP $cm^3\ min^{-1}$ and a heating rate (β) of 12°C min^{-1}. Catalyst samples (0.1 g) were treated in situ at 500°C for 16 h under He flow, then cooled to 150°C and saturated at this T in a 5% NH_3/He flow (25 STP $cm^3\ min^{-1}$) for 1 h. After saturation the catalyst was flushed at the same T for 1 h under the He carrier flow. NH_3–TPD spectra were acquired using a Quadrupole Mass Spectrometer (Thermolab, Fisons Instruments) connected on line with the reactor by a heated (180°C) inlet capillary system (transit time <0.5 s).

Table 2
Synthesis of methyl formate from methane and oxygen via two-step process: experimental parameters

MPO reaction	FD reaction
W_{cat}=0.2–1 g (40–70 mesh)	W_{cat}=0.2–10 g (40–70 mesh)
Feed composition (mol%): CH_4 (20), O_2 (10), N_2 (10), He (60)	Feed composition (mol%): He (61.5); N_2 (10.2) CH_4 (18.8); HCHO (0.37); CO_2 (0.30); CO (1); O_2(7.8)
Feed flow rate: 50 STP $cm^3\ min^{-1}$	Flow rate: 48.8 STP $cm^3\ min^{-1}$
Recycle flow rate: 1500 STP $cm^3\ min^{-1}$	

CO_2–TPD tests in the range 20–600°C were performed using He as carrier gas flowing at 50 STP $cm^3\,min^{-1}$ and β equal to 20°C min^{-1}. Catalyst samples (0.1 g), treated as described above, were cooled to 450°C and saturated in CO_2 flow (25 STP $cm^3\,min^{-1}$) cooling down from 450°C to room temperature and further for 30 min at room temperature. Thereafter, the sample was flushed in the He carrier flow until stabilisation of baseline. The CO_2–TPD spectra were acquired using a TCD connected to a DP 700 Data Processor (Carlo Erba Instruments).

3. Results and discussion

3.1. Methane partial oxidation on SiO_2 catalyst in a continuous flow recycle reactor

Several original attempts have been recently made for enhancing the yield in the direct catalytic conversion of methane into higher hydrocarbons or oxygenates [2–9]. However, since the higher reactivity of the reaction products with respect to CH_4 molecule, yield values to C_2 and CH_3OH and/or HCHO so far reported are limited to 20–25% and 2–3%, respectively. In particular, the recycle of the reaction mixture along with the separation or selective adsorption of the product resulted in significant improvements in the C_2 yield in methane oxidative coupling [6–9]. No similar approaches have been still reported in the literature for maximising the HCHO yield in MPO reaction. Therefore, considering the excellent intrinsic activity of silica based oxide catalysts in MPO [10–12], we have performed a series of continuous flow recycle reactor tests properly tuning the recycle ratio ($R=r_f/r_r$ where r_f and r_r refer to feed flow rate and recycle flow rate, respectively) and GHSV [13].

The catalytic system which allows the attainment of the highest HCHO yield values is the precipitated SiO_2 $_{Si4\text{-}5P}$ that gives a very high HCHO productivity (STY_{HCHO}=150–300 $g_{HCHO}\,g_{cat}^{-1}\,h^{-1}$) in the conventional continuous flow reactor system [10,11]. Then, the optimal recycle ratio as well as the influence of the reaction temperature, GHSV, feed composition and nature of the reactor material on the catalytic performance of the SiO_2 $_{Si4\text{-}5P}$ have been ascertained. The results presented in Tables 3 and 4 indicate that the nature of the reactor material is a determining factor for attaining very high HCHO yield since the use of a stainless steel AISI 316 reactor with respect to the quartz one implies a significant decrease in HCHO yield from 15.6 to 7.6% (see Table 3). The influence of the reaction temperature on the CH_4 conversion, HCHO yield and selectivity in the MPO on SiO_2 $_{Si4\text{-}5P}$ catalyst is outlined in Fig. 2. It is noteworthy to consider that HCHO yields up to 17.0% have been obtained in the MPO reaction on the SiO_2 $_{Si4\text{-}5P}$ catalyst operating in a continuous flow recycle mode. Such HCHO yield values are one order of magnitude higher than those so far vindicated for the direct conversion of methane to oxygenates in continuous running reaction systems [16].

3.2. Formaldehyde dimerisation on oxide catalysts

The dimerisation of formaldehyde to methyl formate on solid oxides was firstly disclosed by Ai as undesired side-reaction in the condensation of ketone

Table 3
Methane partial oxidation

T_R (°C)	Feed composition $CH_4/O_2/N_2$/He (mol%)	Flow rate ($cm^3\,min^{-1}$)	Reactor material	CH_4 conversion (mol%)	O_2 conversion (mol%)	Selectivity (mol%) HCHO	CO	CO_2	HCHO yield (mol%)
650	20/10/10/60	50	Quartz	30.5	82	51	28	21	15.6
650	20/10/10/60	50	AISI 316	27	85	28	6	66	7.6
650	16.5/25/8.5/50	20	AISI 316	55	70	23	2	75	12.6
675	16.5/25/8.5/50	20	AISI 316	66	85	21	2	77	13.9
700	16.5/25/8.5/50	20	AISI 316	72	95	19	2	79	13.7

W_{Cat}: 1 g.
Recycle flow rate: 1500 STP $cm^3\,min^{-1}$.

Table 4
Activity of SiO_2 $_{Si4\text{-}5P}$ catalyst in the methane partial oxidation reaction

T_R (°C)	W_{Cat} (g)	CH_4 conversion (mol%)	O_2 conversion (mol%)	Selectivity (mol%)				HCHO Yield (mol%)
				HCHO	CO	CO_2	C_2H_6	
650	0.47	18	50	64	24.5	11.5		11.5
650	1	28	78	60	27	13		16.8
670	1	31	88	55	27.6	17.3	0.1	17.0
690	1	32.7	94	52.5	26.3	21	0.2	17.2
650	2	30	86	45	33	22		13.5

Feed composition (mol%): CH_4 (20); O_2 (10); N_2 (10); He (60).
Feed flow rate: 50 STP cm^3 min^{-1}.
Recycle flow rate: 2500 STP cm^3 min^{-1}.
Quartz reactor.

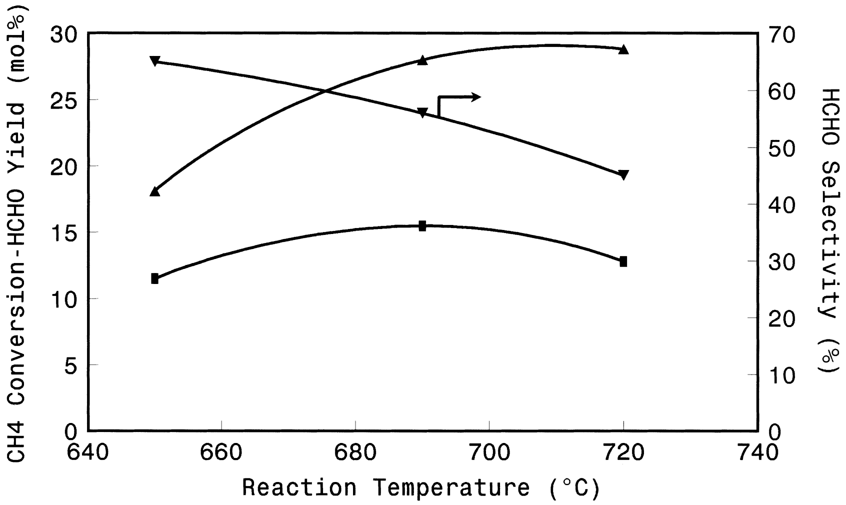

Fig. 2. Methane partial oxidation on SiO_2 $_{Si4\text{-}5P}$ catalyst in continuous flow recycle mode. Legend: (▲) CH_4 conversion; (▼) HCHO selectivity and (■) HCHO yield.

with formaldehyde [17]. In particular, Ai argued that formaldehyde dimerisation was enhanced over catalysts whose acid–base balance is less acidic than that of the systems catalysing more effectively the formation of methyl–vinyl ketone [17]. Indeed, it has been reported that pure oxides like ZrO_2, SnO_2, and TiO_2 and mixed oxides like F_2O_3–K_2O, SnO_2–MoO_3, SnO_2–V_2O_5 and SnO_2–Sb_2O_5 were found to be active in the formaldehyde dimerisation to methyl formate [17]. Then, in order to evaluate the suitability of several oxide systems for the FD reaction a series of experiments was performed in the range 130–170°C by feeding the FD reactor (R_2) with the outlet stream of the MPO reaction carried out in CFR mode.

The catalytic performance of such oxides has been evaluated both in presence (wet conditions) and in absence (dry conditions) of H_2O in the MPO stream.

The activity data of the studied systems in dry conditions are reported in Table 5 in terms of HCHO conversion and $HCOOCH_3$ selectivity. Such results show that ZrO_2 is the most effective system at any T attaining HCHO conversion values in the range 86–97% and a full selectivity (>98%) to $HCOOCH_3$. TiO_2 is also quite effective in the FD enabling conversion values slightly lower (72–91%) than those of ZrO_2 at a given T but with a lower selectivity especially at the highest investigated T (84% at 170°C). Doping of ZrO_2 $_C$ sample with $SO_4^=$ causes a lowering in activity

Table 5
Activity of various oxide catalysts in the HCHO dimerisation

Catalyst	T_R=130°C		T_R=150°C		T_R=170°C	
	HCHO conversion (%)	$HCOOCH_3$ selectivity (%)	HCHO conversion (%)	$HCOOCH_3$ selectivity (%)	HCHO conversion (%)	$HCOOCH_3$ selectivity (%)
$ZrO_{2\ A}$	86	100	87	99	93	92
Al_2O_3	39	99	50	92	63	71
SiO_2	12	100	18	98	22	94
$SO_4^{=}/ZrO_{2\ A}$	52	100	76	39	90	10
$ZrO_{2\ VP}$	87	99	94	98	97	94
$TiO_{2\ T805}$	72	98	83	96	87	84
$TiO_{2\ P25}$	83	98	89	96	91	84

at $T<170$°C but mainly a drop in the $HCOOCH_3$ selectivity at $T>130$°C. Al_2O_3 is less reactive than all the above systems reaching conversion values ranging between 39 (130°C) and 62% (170°C) and a good selectivity to $HCOOCH_3$ (92–99%) at 130°C–150°C which lowers to 71% at 170°C. The SiO_2 sample is the least active system with conversion values ranging between 12 (130°C) and 22% (170°C).

Although the mechanism of such reaction has not been elucidated in detail [17], it is evident that according to previous claims the presence of both acidic and basic sites is required in order to attain HCHO dimerisation. Namely, it can be hypothesised that two HCHO molecules are activated on two vicinal sites into a carbocation and a carbanion respectively according to the Tischenko mechanism:—

$$H_2C = O + A^+ \leftrightarrow H_2C^{(+)} — O_{ads} \tag{1}$$

$$H_2C = O + B^- \leftrightarrow H_2C — O^-_{(ads)} \tag{2}$$

The condensation of the above intermediates via the nucleophilic attack of the oxygen bearing a negative charge (2) to the carbon of the intermediate (1) leads to the formation of the methyl formate molecule. Then, in order to account for the different reactivity of the investigated oxides in the FD reaction (see Table 5) both their acidic and basic properties have been evaluated. The concentration of acidic and basic sites, expressed as NH_3 and CO_2 uptake respectively, of ZrO_2, TiO_2, Al_2O_3 and SiO_2 catalysts are reported in Table 6. All the systems display the presence of surface sites able to chemisorb NH_3 and CO_2 which can then explicate their action in HCHO activation. Although the lowest reactivity of SiO_2 is well accounted for by the lowest concentration of both acidic and basic sites (Table 6), it is evident that such data do not provide a quantitative relationship between activity and concentration of acid–base sites. Then, it is likely that some other factor controls the catalytic action of such amphoteric oxides in FD reaction. In particular, the lower activity of Al_2O_3 with respect to TiO_2 and ZrO_2 in spite of its larger concentration of acid–base sites can be explained by taking into account that a stronger adsorption of intermediates and/or diffusional restrictions could imply that reaction takes place at the external surface of catalysts being then not available at all sites for the reaction. In

Table 6
Acid–base properties of oxide catalysts

Catalyst	Surface acidity		Surface basicity		CO_2/NH_3
	($\mu mol_{NH_3 ads.}$ g^{-1})	($\mu mol_{NH_3 ads.}$ m^{-2})	($\mu mol_{CO_2 ads.}$ g^{-1})	($\mu mol_{CO_2 ads.}$ m^{-2})	
$ZrO_{2\ VP}$	239.3	5.99	54.8	1.37	0.23
Al_2O_3	288.5	1.51	146.6	0.77	0.51
$TiO_{2\ T}$	146.4	2.93	11.8	0.24	0.08
$SiO_{2\ Si4\text{-}5P}$	7.0	0.02	0.7	0.002	0.10

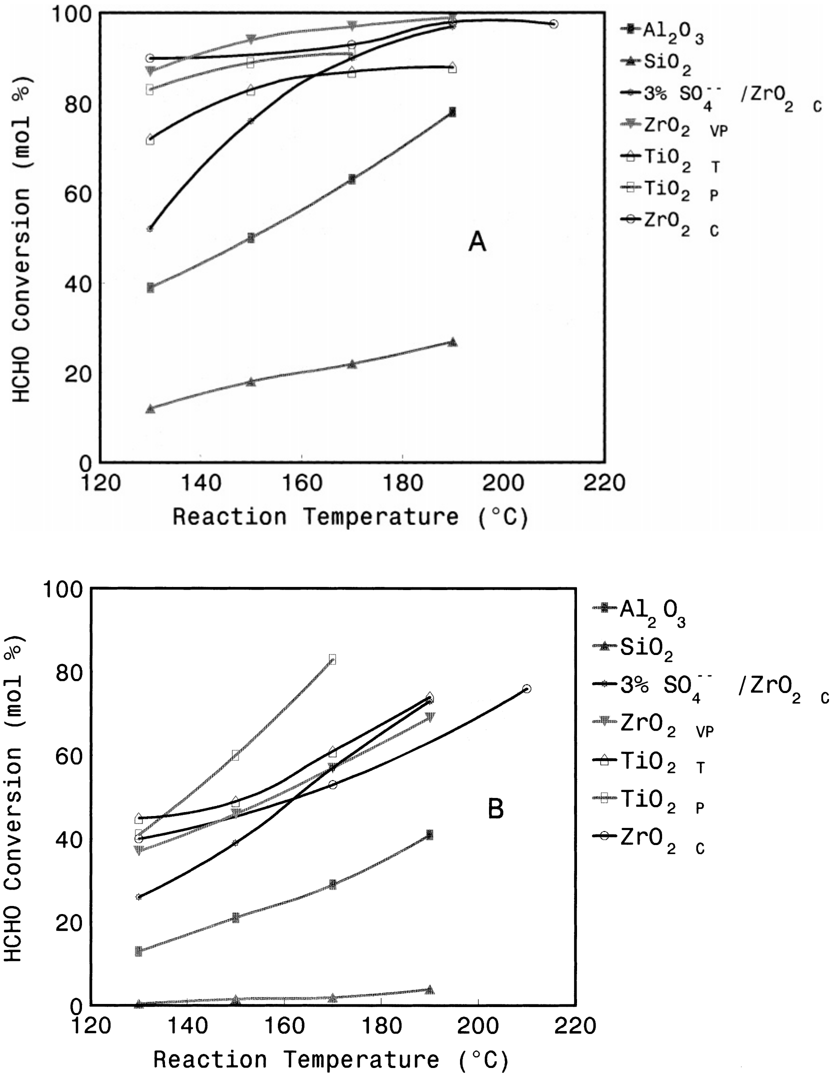

Fig. 3. Formaldehyde dimerisation on various oxide catalysts in dry (A) and wet (B) feed operations.

addition, the nature of acidic sites (Brönsted or Lewis) can also play a key role in the catalytic action of oxide catalysts in FD. Indeed, as shown in Fig. 3, the catalytic behaviour of ZrO_2, TiO_2, Al_2O_3 and SiO_2 in the presence and absence of H_2O is different both in terms of activity and $HCOOCH_3$ selectivity. Namely, the participation of Brönsted (B) and Lewis (L) sites in the FD should imply at a given *T* only a drop in selectivity, owing to the occurrence of the hydrolysis of $HCOOCH_3$ into HCOOH and CH_3OH, and no changes in activity. By contrast, a decrease both in the activity and selectivity occurs in the presence of water. However, considering the activity–selectivity data in absence of water the loss in efficiency is much more enhanced for Al_2O_3 and SiO_2 (Fig. 3). As water adsorption involves the transformation of L sites into B ones and taking into account that the latter systems exhibit a higher surface affinity for water than TiO_2 and ZrO_2, it is evident that L acid sites are much more effective than B ones in the FD reaction. However, further detailed studies on the nature and strength of acid–base sites are in progress.

3.3. Synthesis of methyl formate in a two bed reactor system

The collection of the reaction product is the most critical and expensive step in the methane partial oxidation to HCHO. In order to drive selectively the MPO reaction, many efforts have been addressed to maximise the HCHO selectivity, however the inverse relationship between conversion and selectivity implies that in continuous flow reactor configuration HCHO selectivity higher than 60% can be reached by operating at a CH_4 conversion lower than 2%. Our results, presented above, indicate that such limitations can be passed around by carrying out the reaction in continuous flow recycle reactor mode. However, the separation of the HCHO from the MPO reactor stream is a rather difficult operation since the low temperature required and its tendency to oligomerise. Then, taking into account such critical issues which severely limit the practical feasibility of the MPO reaction and attempting to fulfil the technical and economical needs to propose direct, simple and selective viable processes for the direct conversion of CH_4 into higher added value chemicals, we have devised a two catalytic reactor system which enables the direct conversion of CH_4 into $HCOOCH_3$ according to the following reaction sequence:

$$CH_4 + O_2 \rightarrow HCHO \rightarrow HCOOCH_3$$

the first step being the MPO reaction and the second the dimerisation of formaldehyde. SiO_2 $_{Si4\text{-}5P}$ has been used as catalyst for the MPO reaction, while ZrO_2 $_{VP}$ has been selected as FD catalyst.

The more relevant results of the synthesis of methyl formate via two-step methane partial oxidation in both continuous flow reactor and continuous flow recycle reactor modes in terms of conversion and selectivity of both MPO and FD reactions as well as overall yield to $HCOOCH_3$ are summarised in Table 7. Such results further confirm that CFRR is the most appropriate tool for performing methane partial oxidation reactions. In fact, this reaction mode along with an adequate selection of the catalysts for MPO and FD reaction and the appropriate tuning of the operating conditions for both steps allows the direct transformation of CH_4 into $HCOOCH_3$ with overall yield values up to 12%. It is worthwhile to underline that such yield values are the highest ones so far reported for the direct conversion of CH_4 into oxygenates.

This approach, beside to constitute an original strategy for the direct conversion of CH_4 into a C_2 oxygenated product of higher added value, can be considered as a reaction model for the proposition of novel consecutive two-step or cross-coupling reac-

Table 7
Synthesis of methyl formate via two-step methane partial oxidation

MPO reactor					FD reactor						
Catalyst: SiO_2		T_R=650°C			Catalyst: ZrO_2 $_{VP}$						
W_{Ca} (g)	CH_4 conversion (mol%)	Selectivity (mol%)			W_{Ca} (g)	T_R (°C)	HCHO Conv. (mol%)	Product distribution (mol%)			$HCOOCH_3$ Yield (mol%)
		HCHO	CO	CO_2				CH_3OH	HCOOH	$HCOOCH_3$	
Continuous flow reactor mode											
0.2	8.1	22	60	18	0.15	150	75	1	1	98	1.31
					0.3	150	94	1	1	98	1.64
					0.6	150	99	4	4	92	1.62
Continuous flow recycle reactor mode											
1	27.2	55	30	15	1	170	51.5	5.3	5.3	89.4	6.9
					3	170	88.4	8.4	8.4	83.2	11.0
					9	170	97.2	8.8	8.8	82.4	12.0

Feed composition (mol%): CH_4 (20); O_2 (10); N_2 (10); He (60).
Feed flow rate: 50 STP cm^3 min^{-1}.
Recycle flow rate: 1500 STP cm^3 min^{-1}.

tions for the synthesis of chemicals or fine chemicals using CH_4 as feedstock.

4. Conclusions

- The use of a particular precipitated SiO_2 catalyst and the adoption of the continuous flow recycle reactor mode led to HCHO yield up to 17% in the MPO reaction at 600–650°C.
- Acid-base bifunctional oxides, such as TiO_2, ZrO_2 and Al_2O_3, catalyse the dimerisation of HCHO into $HCOOCH_3$ at 130°C–170°C according to an intermolecular reaction pathway involving the activation of HCHO molecules on vicinal acid and base sites.
- High yield synthesis of methyl formate from methane and oxygen is achieved by a two-step catalytic reactor system involving the primary partial oxidation of methane to HCHO at 650°C and the subsequent dimerisation of HCHO to $HCOOCH_3$ at 130°C–170°C. The highest yield value attained is 12.0%.
- The adoption of a two catalytic reactor system with gas recycle, continuously fed with a reaction mixture of methane and O_2, makes it possible to achieve a high yield of $HCOOCH_3$. This strategy could be also exploited for other potential consecutive or cross-coupling reactions, by means of an appropriate choice of catalysts and operating conditions, which enable high-yield direct conversion of methane into hydrocarbons, fuels or oxygenates of higher added value.

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