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Mechanistic evidences of the synthesis of methyl formate from methane and air on oxide catalysts

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Abstract

The direct conversion of methane into methyl formate with high molar yields (>12%) by a two reactor system has been attained. The reaction sequence consists of the partial oxidation of methane to HCHO at 600–700°C (MPO) on a "precipitated" SiO_2 catalyst and the subsequent dimerization of HCHO to methyl formate (FD) at 130–170°C on various oxide systems (TiO_2, SiO_2, ZrO_2, $SO_4{}^{2-}/ZrO_2$). FTIR characterization of the oxide catalysts allowed to highlight the superior performance of amphoteric oxides like TiO_2 and ZrO_2 in the FD reaction arising from the presence of surface acid and base sites playing a synergetic role in the reaction pathway. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Methane; Partial oxidation; Formldehyde; Dimerization; Methyl formate; Oxide catalysts; Reaction mechanism; FTIR characterization; Acid–base sites

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1. Introduction

The direct catalytic conversion of natural gas to higher hydrocarbons, easily transportable fuels and chemicals of higher added value is currently one of the most hot and challenging research topics in catalysis. However, since the yield is limited, none of the catalytic processes proposed so far, such as oxidative coupling, partial oxidation to methanol or formaldehyde, electrophilic activation, etc. is yet mature for industrial exploitation.

A very promising alternative to the direct conversion of natural gas, 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 the approaches ensuring the protection of the highly reactive desired products by means of selective adsorption or easier separation via conversion into valuable chemicals. 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 (MPO) [1–3]. The adoption of a continuous flow recycle reactor mode has allowed to reach HCHO yield of 10–18% [4]. Thus, taking advantage of such excellent HCHO yield values and considering the potential of the HCHO as reagent 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, through a dual bed reactor system involving the primary partial

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oxidation of methane to formaldehyde (MPO) and its subsequent dimerization (FD) has been devised and exploited [5]. This approach well matches with both the need to convert the natural gas into a liquid product of high added value and the general sought to disclose novel, simple and effective routes for the synthesis of base and fine chemicals.

We have also ascertained that the MPO on silica-based catalysts proceeds according to a *surface redox mechanism* involving the cyclic activation of CH_4 and O_2 on the catalyst surface [1–4]. On the other hand, the FD reaction likely proceeds according to a Tischenko mechanism on oxide catalysts bearing acidic and basic sites [5,6]. However, the reaction pathway as well as the role of the nature (B or L), strength and relative concentration of acidic and basic sites on the catalytic action of such amphoteric oxides is still a matter of debate.

Therefore, in the framework of a research strategy aimed to attain high yield synthesis of methyl formate by partial oxidation of natural gas with air in a two-step catalytic reactor, this paper, on the basis of FTIR evidences, highlights the surface functionality and the working mechanism of several oxide systems (SiO_2, TiO_2, ZrO_2 and $SO_4{}^{2-}/ZrO_2$) in the FD reaction.

2. Experimental

Catalytic activity. Commercial SiO_2, TiO_2 and ZrO_2 along with a $SO_4{}^{2-}/ZrO_2$ sample, prepared according to the procedure suggested by Scurrell [7], were tested in the FD reaction at 130 and 170°C using a two catalytic bed reactor apparatus described elsewhere [5]. The FD reactor was fed by the gaseous mixture exiting from the MPO reactor, having the following percentage molar composition: He (61.5); N_2 (10.2); CH_4 (18.8); HCHO (0.37); CO_2 (0.30); CO (1); O_2 (7.8) and flowing at the total rate of 48.8 STP $cm^3\,min^{-1}$.

FTIR characterization. Surface acid–base properties of catalysts were investigated by FTIR spectroscopy (*Bruker IFS* 48) of adsorbed probe molecules (CO, CO_2, NH_3). Further insights into the surface reactivity of the studied oxides were obtained by FTIR analysis of adsorbed HCHO (Research Chemicals, 99%). All FTIR spectra are reported in absorbance after background subtraction.

3. Results and discussion

3.1. Catalytic tests

The catalytic performances of the various oxide samples in the FD, in terms of HCHO conversion and $HCOOCH_3$ selectivity, is compared in Table 1. ZrO_2 is the most effective system at any temperature attaining HCHO conversion values in the range 87–97% and a full selectivity (>94%) to $HCOOCH_3$. Doping ZrO_2 with 3 wt.% $SO_4{}^{2-}$ causes a marked drop in activity at 130°C (52%) and a dramatic loss in $HCOOCH_3$ selectivity at 170°C (10%). TiO_2 is slightly less effective than ZrO_2 enabling conversion values ranging between 83 and 91% and a lower selectivity in particular at 170°C (84%). Finally, SiO_2 was found to be the least active catalyst with conversion values ranging between 12 (130°C) and 22% (170°C) featuring however a full selectivity to $HCOOCH_3$.

3.2. FTIR studies

In order to shed light into the catalytic behaviour of the various systems, a study of the nature and

Table 1
Catalytic activity of various oxide catalysts in the FD reaction at 130 and 170°C

Catalyst	Commercial code	SA_{BET} ($m^2\,g^{-1}$)	$T_R = 130°C$		$T_R = 170°C$	
			HCHO conversion (%)	$HCOOCH_3$ selectivity (%)	HCHO conversion (%)	$HCOOCH_3$ selectivity (%)
SiO_2	Si4-5P Akzo	400	12	100	22	94
TiO_2 P25	P25 Degussa	50	83	98	91	84
ZrO_2 VP	VP Degussa	40	87	99	97	94
$SO_4{}^{2-}/ZrO_2$A	Lab Catalyst	18	52	100	90	10

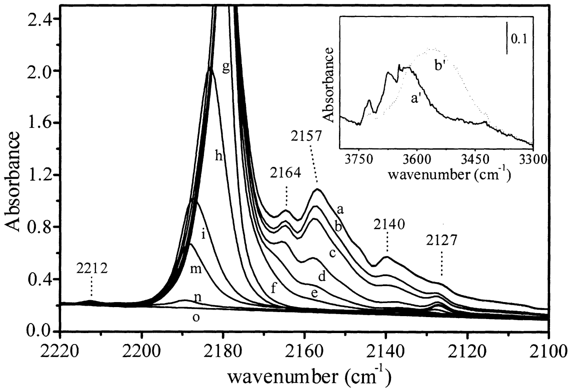

Fig. 1. IR spectra of CO adsorbed on TiO_2 pre-outgassed at 130°C for 45 min at progressively decreasing coverages from (a) 100 Torr to (o) after outgassing for 5 min at 77 K. In the inset the spectra in the ν_{OH} region before (full line, curve a′) and after admission of 100 Torr CO (dotted line, curve b′) are reported.

reactivity of surface sites by IR spectroscopy of different adsorbed molecules was carried out. Systematic experiments were performed on TiO_2 by adsorbing CO, CO_2, NH_3 and HCHO, while the adsorption of formaldehyde was studied on ZrO_2 and SiO_2, lying at the opposite ends of the reactivity scale.

The spectra of CO adsorbed at 77 K on the TiO_2 sample pre-outgassed at 130°C are reported in Fig. 1. At high CO coverage an intense peak at ca. 2180 cm^{-1} is observed (maximum out of scale in the figure). A very weak band at 2212 cm^{-1} and several components in the 2170–2100 cm^{-1} range are also detected (Fig. 1, curve a). The main peak can be assigned to CO molecules adsorbed on surface coordinatively unsatured (cus) five-coordinated Ti^{4+} ions on (0 1 0) faces [8], while the weaker component at 2164 cm^{-1} is due to CO stabilised onto ${Ti_{cus}}^{4+}$ centres of lower Lewis acidity, located on less energetic planes [9]. The very weak band at 2212 cm^{-1} should be ascribed to CO adsorbed on low coordinated Ti^{4+} ions of high Lewis acidity located on edges and corners [8], whereas the absorption at 2157 cm^{-1} is assigned to CO weakly hydrogen bonded to OH groups left on the surface after the activation of the sample [10]. These groups are actually perturbed by adsorbed CO, their vibrational pattern being shifted to lower frequency after admission of CO on the sample (inset Fig. 1, curves a′ and b′). Finally, the broad band at 2140 cm^{-1} is assignable to physically adsorbed CO in a liquid-like form, while the minor signal at 2127 cm^{-1} corresponds to the stretching of ^{13}CO molecules adsorbed on Ti^{4+} ions on (0 1 0) faces. By decreasing the CO coverage the components CO in liquid-like form and CO adsorbed on hydroxyls disappear, followed by the disappearance of 2165, 2180 and 2212 cm^{-1} bands in the order, as a consequence of the increasing strength of the Lewis acid character of the Ti^{4+} centres on which CO molecules are adsorbed (Fig. 1, curves b–o). The shift of the 2180 cm^{-1} band toward higher frequency by decreasing the CO coverage is due to the progressive fading of adsorbate–adsorbate interaction.

The intense band at 2180 cm^{-1} documents a high number of Ti^{4+} centres on surface (0 1 0) planes, indicating that an extensive dehydroxylation of such faces occurred even under mild thermal conditions. Noticeably, the removal of OH groups leaves a large amount of surface pairs of coordinatively unsaturated cations and anions. Thus, although CO monitors only Ti^{4+} centres, it could be inferred that Lewis acid–base Ti^{4+}–O^{2-} pairs are exposed in large amount on the TiO_2 (0 1 0) faces under FD reaction conditions (130–170°C). Then, direct evidences of the Lewis basic character of surface O^{2-} anions were obtained by adsorbing CO_2. The formation of several types of carbonate-like groups, besides the adsorption of CO_2 molecules in a linear form on Ti^{4+} cations (spectra not reported), has been recorded. Namely, spectral components assignable to bicarbonate species were also observed, indicating that residual OH groups behave as Brønsted basic centres. By contrast, no Brønsted acid sites were revealed by IR spectra of adsorbed ammonia, only features assignable to NH_3 molecules adsorbed on Ti^{4+} centres being found (spectra not reported).

The surface reaction paths of HCHO on TiO_2 were also investigated. The IR spectra after small doses of HCHO admission, reported in Fig. 2A, display bands at 1175, 1157, 1115 and 1065 cm^{-1} (Fig. 2A, curves a and b) typical of dioxymethylene species (hereafter referred to as D species) [11]. These are likely formed by reaction of HCHO molecules with surface Ti^{4+}–O^{2-} acid–base pairs, where the basic moiety (O^{2-}) carries out a nucleophilic attack to the carbon atom of the carbonyl group of an aldehyde molecule adsorbed on the neighbour Lewis acid centre (Ti^{4+} ion) via its oxygen atom. The absorption tail observed at higher frequency is due to the bonding mode of adsorbed

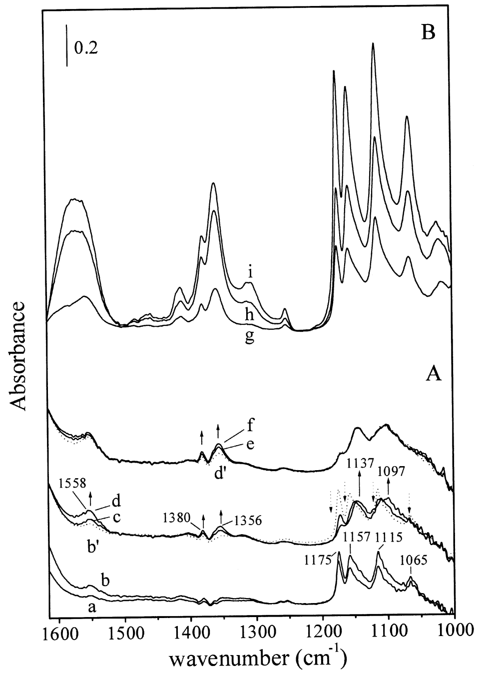

Fig. 2. IR spectra of formaldehyde adsorbed on TiO_2 pre-outgassed at 130°C for 45 min. Section A: curve a, immediately after the admission of 0.05 Torr HCHO; curves b–f, after 1, 5, 10, 20 and 30 min of contact. Dotted curves b′ and d′ are as full curves b and d, respectively. Section B: IR spectra of formaldehyde adsorbed under increasing HCHO vapour pressure: curve g, 0.2 Torr HCHO; curve h, 0.8 Torr HCHO and curve i, 1.5 Torr HCHO.

water molecules (maximum located at ca. 1630 cm^{-1}) admitted on the sample together with formaldehyde. By increasing the contact time, a progressive depletion of the D species peaks occurred, whereas new bands at 1558, 1380 and 1356 cm^{-1} and at 1137 and 1097 cm^{-1} appear and/or grew (Fig. 2A, curves b′, c and d). This behaviour can be interpreted in terms of a Cannizzaro-like disproportionation of D species giving formate (bands at 1558, 1380 and 1356 cm^{-1}) and methoxy (bands at 1137 and 1097 cm^{-1}) groups (hereafter referred to as F and M species, respectively) [11]. Noticeably, the bands due to F groups further increase in intensity even after the depletion of the D species and the growth of the absorptions due to M groups have reached their maximum (Fig. 2A, curves d′, e and f). This suggests that HCHO molecules can follow an alternative reaction path on the surface of TiO_2, being directly oxidised to formate species [11].

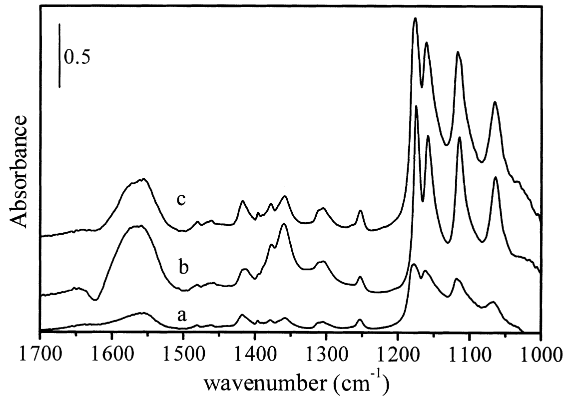

Fig. 3. IR spectra of HCHO (1.5 Torr) adsorbed on TiO_2 pre-outgassed for 45 min at: (a) room temperature; (b) 130°C; (c) 600°C.

The evolution of surface species as a function of the amount of adsorbed formaldehyde was further investigated (Fig. 2B). By increasing the amount of adsorbed HCHO the relative absorptions increase in intensity, and the bands due to F and M species (these bands observed as shoulders of the dioxymethylene peaks) appeared (Fig. 2B, curves g and h). The admission of further amounts of HCHO resulted in a limited increase in intensity of the bands due to F species, whereas the peaks due to D species significantly increased in intensity, completely covering up the absorptions due to M groups (Fig. 2B, curve i). Such spectral pattern did not further evolve by increasing the contact time of formaldehyde with the catalyst. It can be then inferred that a large fraction of Ti^{4+}–O^{2-} pairs is able to transform formaldehyde molecules into D species (Fig. 2B, high HCHO coverage), which decompose into F and M groups at temperatures close to those employed in the FD reaction [12].

The role of the hydroxyl groups towards HCHO molecules was ascertained by admitting HCHO on TiO_2 sample outgassed at RT. For the sake of completeness, the formaldehyde adsorption on a highly dehydroxylated TiO_2 sample, outgassed at 600°C, was also investigated [13,14]. The results are reported in Fig. 3, where the IR spectra of HCHO adsorbed on the TiO_2 sample pre-outgassed at RT, 130 and 600°C are compared. The adsorption of formaldehyde on the fully hydroxylated sample resulted in the appearance of bands due to F and D groups (Fig. 3, curve a),

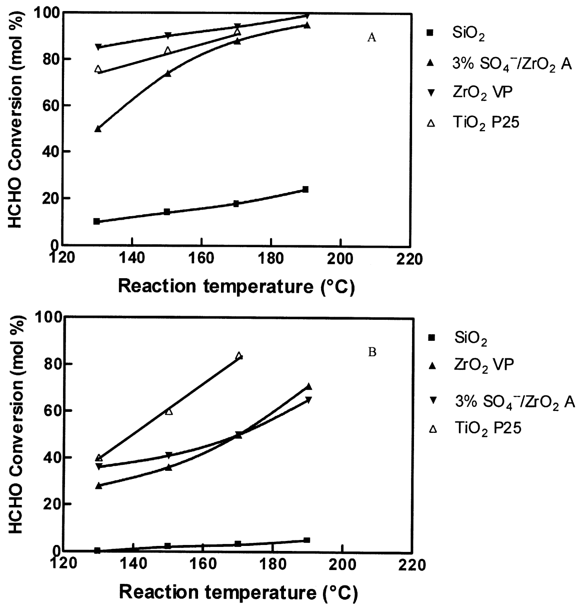

Fig. 4. Activity of various oxide catalysts in the FD reaction in the range 130–190°C under (A) dry and (B) wet stream conditions.

and at low HCHO coverage, also bands due to M species were detected (spectra not reported). This result clearly indicates that also hydroxyl groups can react with formaldehyde, likely playing the role of OH^- species in the homogeneous reaction of aldehydes in basic solutions. However, the overall intensity of the spectral profile appeared less intense with respect to the HCHO adsorption on TiO_2 pre-outgassed at 130°C (Fig. 3, curve b), and some differences in the relative intensity of the various components are also observed in the two cases. This behaviour suggests that surface hydroxyl groups are able to react with formaldehyde through a nucleophilic path, but in a lower extent with respect to the Ti^{4+}–O^{2-} acid–base pairs. In Fig. 4, the activity of the various oxides in the FD in the range 130–190°C under (A) dry and (B) wet mixture conditions is compared. The drop in the activity observed under wet conditions on all the oxide catalysts well accounts for the competitive reaction pathway of HCHO conversion on hydroxylated oxide surfaces. Furthermore, the differences in the relative intensity of the various spectral components could reflect the different relative population of sites able to promote the formation of D species or HCHO disproportionation on bare and hydroxylated oxide surfaces.

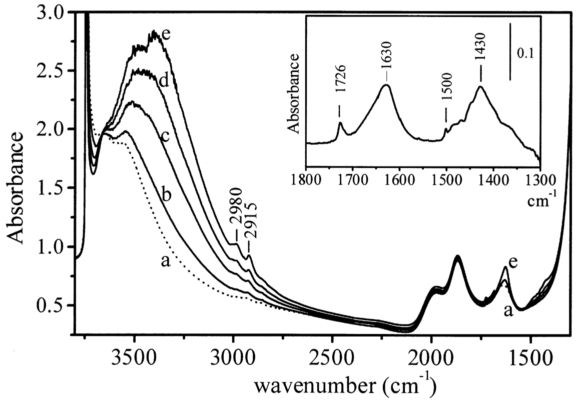

Fig. 5. IR spectra of HCHO adsorbed under increasing pressure on SiO_2 pre-outgassed at 130°C for 45 min: (a) 0.05 Torr HCHO; (b) 0.1 Torr HCHO; (c) 0.3 Torr HCHO; (d) 0.8 Torr HCHO; (e) 1.5 Torr HCHO.

The main role of Ti^{4+}–O^{2-} pairs in the reactivity toward formaldehyde was confirmed by adsorbing HCHO on TiO_2 sample outgassed at 600°C. In this case a spectral pattern very similar to that obtained for the sample outgassed at 130°C was observed, the overall spectral intensity resulting slightly lower owing to an incipient sintering of TiO_2 [15].

The same series of HCHO adsorption experiment was performed on the ZrO_2 catalyst. Notably, in this case the spectra were dominated by the bands due to F and M species even at high HCHO coverage, whereas the absorptions related with the D species appeared as minor features, accompanied by bands assignable to polyoxymethylene species (spectra not reported). Such a behaviour indicates that, at room temperature, the formation of F and M species is largely favoured on the surface of the ZrO_2 catalyst, with respect to TiO_2, likely as a consequence of a very fast disproportionation of D species. However, this reaction should easily occur on TiO_2 at higher temperature, and this could account for the similar catalytic performances of the two oxides in the range 130–170°C (Table 1).

By contrast, significant differences were observed in the case of formaldehyde adsorption on SiO_2 (Fig. 5). The admission of HCHO simply produced a progressive depletion of the 3740 cm^{-1} peak due to silanol groups, being transformed into a broad and complex adsorption at lower frequency, following a behaviour characteristic of hydroxyl groups engaged in H-bonding with adsorbed molecules. At lower frequency, essentially the growth of a band at 1630 cm^{-1} is observed, accompanied by the appearance of weak components at ca. 1730 and 1430 cm^{-1} and at 2980 and 2915 cm^{-1}. This spectral pattern is more clearly observable in the inset of Fig. 5, where the profile obtained by subtracting the spectrum of the SiO_2 sample before formaldehyde adsorption (Fig. 5, curve a) from that recorded in the presence of the maximum amount of HCHO (Fig. 5, curve e) is reported. The main band at 1630 cm^{-1} is due to water molecules admitted on the sample together with formaldehyde. The weak components at 1726, 1500 and 1430 cm^{-1} are assignable to molecular formaldehyde weakly interacting with silanol groups [16], while the weak bands at 2980 and 2195 cm^{-1} can be assigned to polyoxymethylene species [11]. The observed behaviour clearly indicates that silanol groups are not able to act as nucleophilic agents towards adsorbed aldehyde molecules, and this finding well matches with the poor catalytic activity exhibited by silica in the FD reaction.

Moreover, the synergetic role of the surface basicity in the reactivity towards HCHO molecules was also evidenced by the lower catalytic performance in the FD reaction exhibited by the $SO_4{}^{2-}/ZrO_2$ system (see Table 1). Indeed, in such a case the basic O^{2-} centres, involved in the formation of sulphate species, should not be available to react with aldehyde molecules accounting thus for a less effective action in FD reaction.

4. Conclusions

- The direct conversion of natural gas into methyl formate with high molar yields has been attained by a two-step catalytic reactor system.
- Amphoteric oxides, such as TiO_2 and ZrO_2, effectively catalyse the dimerization of HCHO–$HCOOCH_3$ in the range 130–170°C.
- FTIR spectroscopic studies indicate that the dimerization of HCHO proceeds via an intermolecular reaction path involving the activation and condensation of HCHO molecules on acid–base pairs.

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