Molecular mechanisms in partial oxidation of methane on $Ir/\alpha\text{-}Al_2O_3$: reactivity dependence on catalyst properties and transport phenomena limitations

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An in situ DRIFT and mass spectrometric study of catalytic partial oxidation of methane with $Ir/\alpha\text{-}Al_2O_3$ has enlightened relationships between the formation of surface metal carbonyl clusters and residence time and temperature conditions. Some cluster species produced during catalytic partial oxidation were also originated during CO_2 hydrogenation and CO_2 reforming experiments described in previous literature. An EXAFS analysis of the catalyst precursor, prepared through a solid–liquid reaction between $Ir_4(CO)_{12}$ clusters and the reactive surface sites of $\alpha\text{-}Al_2O_3$, is also included to discuss clusters structure produced at the surfaces.

Keywords: catalytic partial oxidation; iridium surface clusters; high-temperature–high-pressure spectroscopic study; DRIFT analysis; EXAFS analysis

1. Introduction

This work is part of an extensive research program devoted to the study of high-temperature–high-pressure chemistry of Rh, Ru, Ir surface clusters. The surface chemistry of an $Ir/\alpha\text{-}Al_2O_3$ material during the catalytic partial oxidation of methane is here examined.

The commercially available synthesis gas production processes reviewed in refs. [1–5] do not yet include catalytic partial oxidation (CPO). However, recently renewed attention of both academic and industrial research groups has been focused onto this reaction [6–15]. This attention was initially revealed in an article written by Ashcroft et al. [6], who claimed new reactivity features on a lanthanide ruthenium oxide catalyst. Few months later Lunsford et al. [7] pointed out that the reaction was not new since, starting from 1946, it had been investigated both on noble metals and on Ni based catalysts. Lunsford experimented the CPO reaction in a laboratory scale plug-flow reactor at residence times near 1 s on a Ni based catalyst. Monitoring with XPS the surface composition at different sections of the catalytic bed, he concluded that the CPO reaction (1) resulted from the combination of the fast total oxidation reaction (2) followed by the relatively slow steam and CO_2 reforming reactions (3), (4):

$$CH_4+\tfrac{1}{2}O_2 \rightleftharpoons CO+2H_2 \qquad H^\circ_{298K} = -38\,kJ/mol, \quad (1)$$

$$CH_4+2O_2 \rightleftharpoons CO_2+2H_2O \qquad H^\circ_{298K} = -811\,kJ/mol, \quad (2)$$

$$H_2O+CH_4 \rightleftharpoons CO+3H_2 \qquad H^\circ_{298K} = 206\,kJ/mol, \quad (3)$$

$$CO_2+CH_4 \rightleftharpoons 2CO+2H_2 \qquad H^\circ_{298K} = 247\,kJ/mol. \quad (4)$$

In 1991, by experimenting the reactivity of $CH_4/CO_2/O_2$ mixtures, Ashcroft et al. [8] touched another important point: the unique properties of the Rh, Ru, Ir metals to catalyze the CPO reactions in conditions under which the carbon formation reactions (5) and (6) deactivate most of the Ni based catalysts:

$$2CO \rightleftharpoons C+CO_2 \qquad \Delta H^\circ_{298K} = -172.54\,kJ/mol \quad (5)$$

$$CH_4 \rightleftharpoons C+2H_2 \qquad \Delta H^\circ_{298K} = 74.91\,kJ/mol \quad (6)$$

More recently, Hickman and Schmidt from the Minnesota University [9,10] and Choudhary et al. [11,12] from the National Chemical Laboratory of Pune reported new insight in CPO, indicating that extremely high conversions and selectivity towards syngas are achievable at very short residence time (τ) between 10^{-4} and 10^{-2} s. Under these reactivity conditions the rate of

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heat generation is much higher than the rate with which the heat is exchanged from the reaction zone. Then the laboratory reactors approach the limit of adiabatic operation leaving the autothermal temperature to approach the adiabatic temperature calculated by

$$\bar{C}_p(\bar{T} - T_0) + Q_E = \sum_{i=1}^{n}(-\Delta H_i)\bar{\chi}_i . \qquad (7)$$

In eq. (7) the term Q_E, accounting for the heat exchanged with the environment, is small compared with (a) the term $\bar{C}_p(\bar{T} - T_0)$ accounting for the sensible temperature raise from some gas temperature T_0 to the average reaction temperature $\bar{T}$, and (b) the term $\sum_{i=1}^{n}(-\Delta H_i)\bar{\chi}_i$, which represents the heat generated by the n reactions which participate in the chemical process, each at some average conversion $\bar{\chi}_i$.

This means that for τ values below 10^{-2} s and under stationary conditions, the reaction temperature ($\bar{T}$) is determined by the exothermicity of the reactions and by the temperature (T_0) at which the reactant gases are preheated. Under these conditions it is impossible to maintain a separate control over reaction temperature while varying the flow rates. Since we considered it very interesting to have indications on selectivity and conversion variations at fixed temperature while varying τ, we have studied the CPO reactions in a non-adiabatic reaction chamber equipped with a cooling cycle and which allowed diffuse reflectance Fourier transform spectroscopy (DRIFT) and mass spectrometry measurements. The results reported here concern reactivity features obtained with powdered polycrystalline Ir/α-Al_2O_3 samples (Ir 0.5 wt%), at temperatures between 450 and 750°C. The experimental findings indicate that selectivities and conversions are both varied at a given temperature depending on τ; in addition small surface Ir carbonyl clusters selectively originated at $\tau > 10^{-2}$ s, while at shorter residence times these species disappeared. Correspondingly different catalytic activities and selectivities were observed. These main experimental data are discussed considering that H_2, CO, CO_2 and H_2O are contemporaneously formed and selectivity and conversion variations are mainly affected by the occurrence of CO_2 reductive chemisorption which is favored at higher contact time values.

This work, being part of a research program devoted to the study of the surface chemistry of small Rh, Ru, Ir clusters during CO-hydrogenation, CO_2-hydrogenation, CO_2-reforming [16–18] and CPO of methane, include an EXAFS characterization of the Ir clusters species produced on the catalyst before the reaction.

2. Experimental

2.1. Sample preparation

The catalytic materials contained 0.5 wt% of Ir. This amount corresponds to less than a monolayer of clusters containing 4 Ir atoms such as $Ir_4(CO)_{12}$ or $[Ir_4(CO)_{11}]^-$ with a spherical volume of 1373 Å^3 (see also the results section). The Ir species were deposited at the surfaces through a solid–liquid organometallic reaction produced by dropping, under N_2 atmosphere, a THF solution of $Ir_4(CO)_{12}$ into a slurry of α-Al_2O_3 (Aldrich 99.999%, surface area ≈ 5 m^2/g) dispersed in the same solvent. After 24 h the powdered sample was filtered and dried under vacuum at room temperature.

2.2. Diffuse reflectance Fourier transform (DRIFT) spectroscopy and mass spectrometry experiments

The powdered Ir containing sample (20 mg) was deposited onto a porous fritted tungsten disk, inside an alumina heater surrounded by a water cooled dome with ZnSe windows transparent to the IR radiation. The reaction effluent flowed through the catalysts into an output line linked with a pressure reduction sampling system to a quadrupole mass spectrometer. A thin (0.5 mm of diameter) chromel–alumel thermocouple was inserted into the sample and used both to measure the catalyst temperature and to regulate the heating supply. Gaseous reactants ($CH_4/O_2/He = 2/1/11$ v/v mixtures) were flowed through the reaction chamber at flow rates between 25 and 250 ml/min. Thermal cycles were performed in flowing He, H_2, and $CH_4/O_2/He$ atmospheres by increasing the temperature at a rate of 50°C/min. During the cycles the temperature was adjusted each 100 K and stationary conditions were maintained for 10 min to collect the DRIFT spectra at a resolution of 2 cm^{-1}. During the cycles the output stream composition was monitored by mass spectrometry with selected peak monitoring.

2.3. EXAFS experiments

Two samples were studied: (a) freshly prepared Ir/α-Al_2O_3 catalyst and (b) crystalline $Ir_4(CO)_{12}$. The powdered materials were prepared as self-supported wafers which had a total absorption coefficient after jump (μx) close to 2.5. Sample homogeneity was controlled by using an optical microscope and radiographic methods. Measurements were performed in transmission mode at room temperature on the XAFS-I line installed at DCI storage ring at LURE (Orsay, France) operated at 1.85 GeV with a positron current of 280–320 mA. A channel-cut Si 331 monochromator was used, and transmitted photon flux was measured with two ionization chambers filled with air. The energy scale was calibrated with a copper foil assigning the value of 899.1 eV to the first maximum after jump. Spectra were collected between 11100 and 12100 eV, at the L_{III} edge of Ir, with a counting time of 2 s for each of the 500 examined points. The spectral data were collected three times for the $Ir_4(CO)_{12}$ sample and nine times for the Ir/α-Al_2O_3 sample.

3. Results and discussion

3.1. EXAFS characterization of the freshly prepared samples

The EXAFS data were analyzed according to standard methodology [19] with a program set written by A. Michalowicz [20]. The pre-edge region was subtracted with a straight line and the spectra were extracted by fitting the absorption coefficients with a cubic polynomial fit. Signals were normalized with the method proposed by Eisemberger and Lengeler [21]. The E_0 value was chosen at the inflection point of the jump (11206.7 eV); at this point the spectra were mediated and the standard deviations calculated. The EXAFS spectra of the two Ir/α-Al_2O_3 and $Ir_4(CO)_{12}$ samples are shown in fig. 1A. The EXAFS signals were multiplied by k^3 in the 2.33–13.04 A^{-1} range and have been Fourier-transformed after convolution over a Kaiser window. The Fourier transforms of the two samples are shown in fig. 1B; the first peak of the figure accounts for the Ir–C distance while the second contains information on Ir–O and Ir–Ir atom pairs and gains contributions from multiple scattering originated by the Ir–C–O group. The similarity between the two spectra indicates that clusters with structure similar to $Ir_4(CO)_{12}$ are originated on the freshly prepared Ir/α-Al_2O_3. This is further confirmed by a quantitative analysis performed by fitting the Fourier filtered first peak of the Ir/Al_2O_3 sample with a theoretical signal using a non-linear least-squares routine [22] (MINUIT subroutine of the CERN library) and minimization of the χ^2 function, thus following the recommendations of the International Workshop of Standards in XAFS [23]. The fitting was performed by applying the single-electron single scattering EXAFS theory using the equation

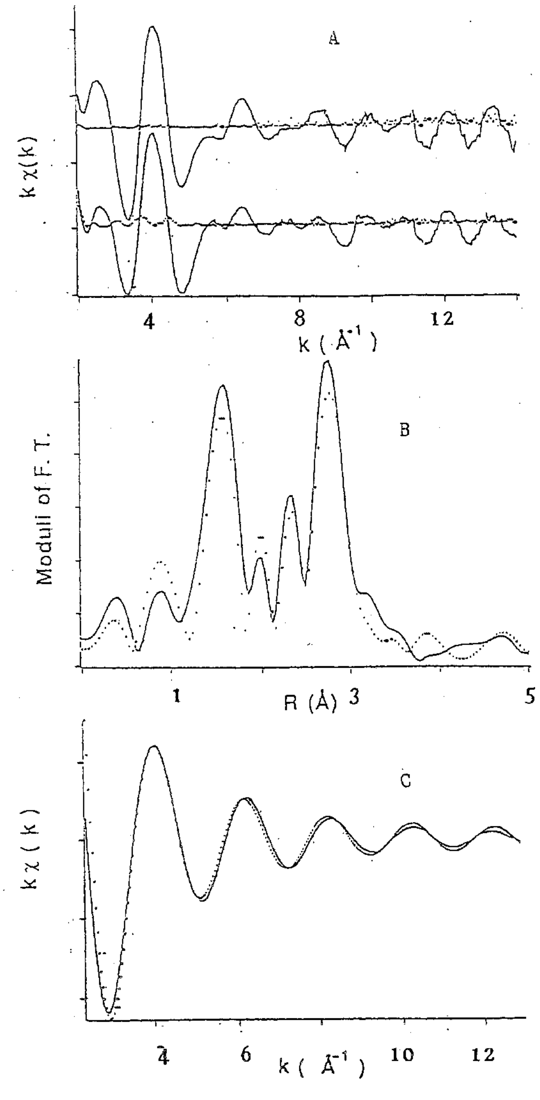

Fig. 1. (A) EXAFS spectra of the $Ir_4(CO)_{12}$ (above) and Ir/α-Al_2O_3 (below) samples, (B) moduli of the Fourier transforms ($Ir_4(CO)_{12}$ continuous line, Ir/α-Al_2O_3 dotted line), (C) filtered first peak of the of Ir/α-Al_2O_3 (dotted line), and its fitting (continuous line).

$$k\chi(k) = \sum_i \frac{N_i}{R_i^2} A_i(k) e^{-2\sigma_i^2/k^2} e^{-2R_i/\lambda(k)} \sin[2kR_i + \phi_i(k)], \tag{8}$$

where N_i is the number of atoms in the ith scattering shell at distance R_i from the absorbing atom, σ_i is a coefficient related to thermal and static disorder, $\lambda(k)$ is the electron mean free path, $A_i(k)$ and $\phi_i(k)$ are the amplitude and phase functions.

Experimental amplitude and phase functions for Ir–C atom pair deduced from the known crystallographic structure of $Ir_4(CO)_{12}$ were used [24,25]; $\lambda(k)$ was kept convoluted in the amplitude and phase function and an arbitrary value of 0.07 Å was chosen for σ. The results obtained, are summarized in table 1, which also contains the values used for $Ir_4(CO)_{12}$ and the errors estimated on the basis of standard deviations using an interval of confidence equal to 1. Fig. 1C shows the overlapping of the filtered first peak of the Ir/α-Al_2O_3 with its fitting. Gates et al., studying with EXAFS small Ir surface clusters produced on MgO with an analogous procedure, also discriminated between bridged and linear CO groups [26]. This analysis could not be performed with our data, since we could find only four independent points ($N_{ind} = 2\Delta R \Delta k/\pi$) and this, according to the Nyquist theorem [27], allows for variation of only three parameters during the fitting.

Previously we reported a vibrational analysis of the

Table 1
Results obtained with the analysis of the EXAFS signals

Sample	N^a (CO/Ir)	R(Ir–C) (Å)	σ^b (Å)
$Ir_4(CO)_{12}$	3	1.87	0.07
Ir/α-Al_2O_3	2.70 ± 0.14	1.873 ± 0.008	0.0796 ± 0.0091

[a] Number of carbonyl groups coordinated by each Ir atom.
[b] Debye–Waller factor.

IR and laser-Raman bands of the CO groups of the Ir clusters which suggested the reaction between the $Ir_4(CO)_{12}$ clusters and the α-Al_2O_3 surface originates $[HIr_4(CO)_{11}]^-$ species. The EXAFS analysis also sustains this assignment indicating that each Ir atom is linked to 2.70 ± 0.14 carbon atoms with an Ir–C average distance of 1.873 ± 0.008 Å. For comparison, the crystal structure of $[P(CH_2C_6H_5)(C_6H_5)_3][HIr_4(CO)_{11}]$ [24,25], indicates an average Ir to terminal carbon distance of 1.84 Å, and Ir to bridging carbon distances of 1.98 and 2.18 Å.

We consider that the high temperature IR spectra discussed below also indicate that the small Ir clusters have not been aggregated into large clusters with metallic like properties during the reactivity experiments. Further EXAFS studies are in progress to study the Ir clusters transformation under reaction conditions.

3.2. DRIFT and mass spectrometric experiments

The experiments performed in the reaction chamber equipped for DRIFT and mass spectrometry consist of three steps represented in the following scheme:

$$A \xrightarrow[298-773-298\,K]{He} B \xrightarrow[298-773-298\,K]{H_2} C \xrightarrow[298-1023-298\,K]{\substack{CH_4+O_2 \\ (5\times10^{-1}\geq\tau\geq5\times10^{-3})}} D$$

The first two heating cycles (heating rate 60 K/min, flow rate 60 ml/min), respectively in He and H_2 flows, produced surface chemistry reactions which were previously reported and discussed [17]. These two heating cycles were performed to condition the samples at high temperature and to produce nude Ir clusters at the beginning of the CPO experiments.

The third thermal cycle was performed in flowing $CH_4 + O_2 + He$ stream ($CH_4/O_2/He = 2/1/11$ v/v, flow rate 67 ml/min, $P_{tot} = 0.11$ Mpa) at two different flow rates and contact times between 5×10^{-1} and 5×10^{-3} s. Fig. 2 shows the spectral variations with temperature in the carbonyl stretching zone, produced at $\tau \geq 0.02$ s. IR absorption bands were detected at temperatures higher than 673 K. The corresponding partial pressure variations of reaction products detected in the ionization chamber of the quadrupole mass spectrometer, are plotted in fig. 3A. This figure shows that partial pressure of the CO_2 increases up to 773 K and remains constant at higher temperatures, while the partial pressures of CO and H_2 are increased up to 1023 K. A CH_4 conversion of 34% and selectivities towards CO and CO_2 respectively of 65 and 35% were measured at 1023 K; while the ratio H_2/CO was 3.2 v/v.

The analyses of the IR band sharpness, position and multiplicity suggest that small carbonyl surface clusters are originated during the reactions. The comparison between these signals with the ones recorded at the same high temperatures, during CO_2 hydrogenation [17] and CO_2 reforming [18] experiments, strongly suggest that the same or similar surface species originated in the three high temperature reaction environments. Figs. 4A, 4B, 4C show the carbonyl stretching bands detected at 973 K by feeding the reaction chambers respectively with $CO_2 + H_2$, $CO_2 + CH_4$ and $CH_4 + O_2$ mixtures. The signals were treated with the same Fourier self-deconvolution procedure to remove the Lorentzian broadening function [29]. We consider that the fact that the same or very similar signals are produced during the three experiments indicates that carbonyl species are formed through reductive chemisorption of CO_2. We already demonstrated that this reaction is possible during CO_2 hydrogenation and CO_2 reforming. In a recent work [18] we also demonstrated that CO_2 reductive chemisorption also produces, by breaking one of the two C–O bonds, surface oxidic species which are able to activate the methane oxidation [16–18]. We point out that the same carbonyl clusters cannot be achieved during CO hydrogenation, a reaction which has also been studied with the same procedure [17]; in fact in this last case much broader bands shifted at different wavelengths have been originated (fig. 4D).

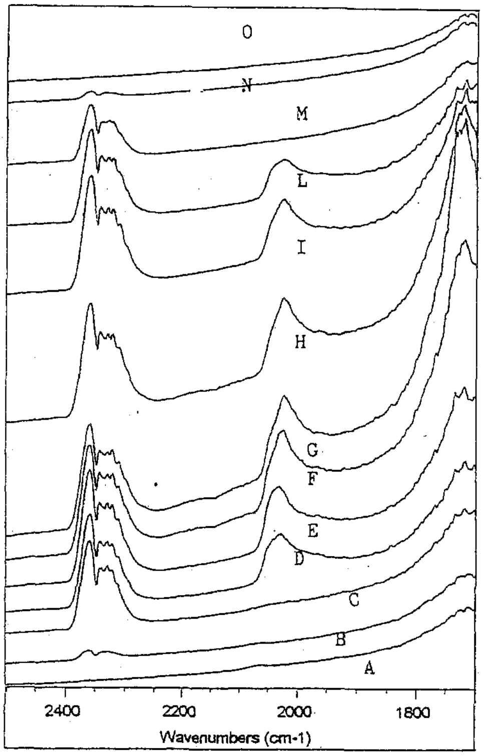

Fig. 2. Carbonyl stretching band variations, produced during a thermal cycle between 298 and 1023 K in flowing $CH_4/O_2/He = 2/1/11$ v/v. Heating cycle: (A) 473 K, (B) 573 K, (C) 673 K, (D) 773 K, (E) 873 K, (F) 973 K, (G) 1023 K. Cooling cycle: (H) 973 K, (I) 873 K, (L) 773 K, (M) 673 K, (N) 573 K, (O) 473 K.

When the CPO reaction was performed on a freshly prepared sample, at shorter contact times ($\tau \leq 2 \times 10^{-3}$ s) no carbonyl bands were observed and selectivities towards CO and H_2 decreased as well as reactant conversions. In addition the selectivity towards CO_2 increased at increasing temperatures remaining the

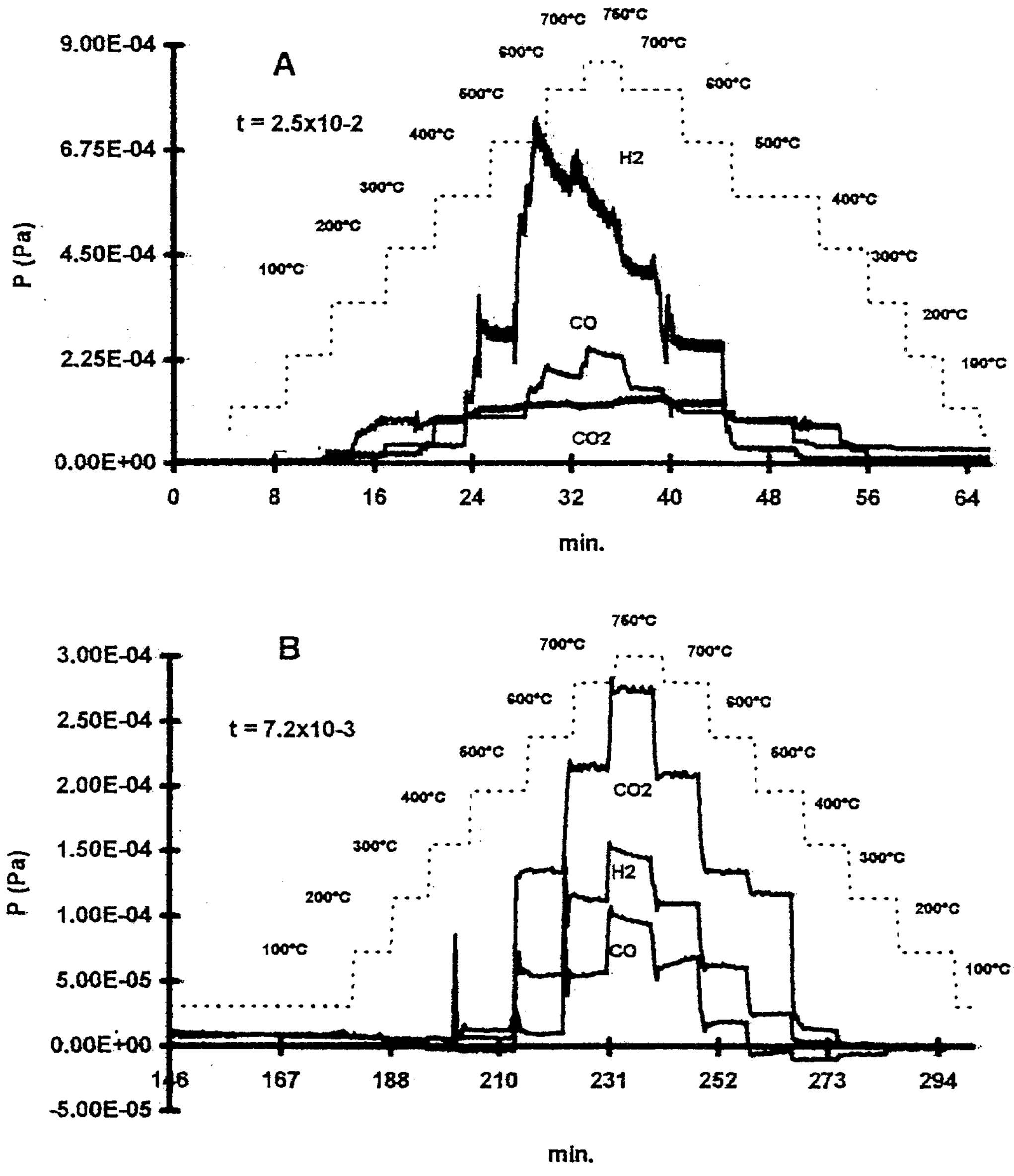

Fig. 3. Variation of the reaction products partial pressure measured in the "closed source" ionization chamber of the quadrupole mass spectrometer during the thermal cycles performed at: (A) $\tau = 1.8 \times 10^{-2}$ s, (B) $\tau = 7.2 \times 10^{-3}$ s.

highest in all the temperature range. At $\tau = 2 \times 10^{-3}$ s and 1023 K we measured a CH_4 conversion of 15% and selectivities towards CO and CO_2 respectively of 34 and 64%, while the H_2/CO ratio was 1.5 v/v. The differences between product selectivities measured at τ values different by an order of magnitude can be read from figs. 3A and 3B.

In order to discuss the variations with τ of (a) IR spectra of surface species, (b) reaction conversions and (c) reaction selectivities and to relate this study with previous work, we summarize the work of Schmidt et al. These authors hypothesize that the CPO reactions, occurring at contact time below 10^{-2} s, have high conversions of reactant and high selectivity towards CO and H_2 because only under these conditions the catalytic processes do not involve the intermediate formation of CO_2 and H_2O while CO and H_2 are directly achieved as primary reaction products. These authors propose that this is the result of a combination between (a) surface chemical properties of Rh, Ru, Ir [28] and (b) the reduction of the boundary layer limit (δ) at the surface of the catalyst particle and the enhancement of the mass transfer coefficient (k_m) which favors the migration of the primary reaction products outside of the reaction zone [9] (see eq. (9) where D_i is the diffusion coefficient of the rate limiting species i),

$$k_m \approx D_i/\delta\,. \qquad (9)$$

Typical experimental conditions reported in literature are the following: (a) ignition at 573–673 K and $P \approx 0.11$ Mpa, (b) reaction temperature in stationary conditions in the range between 1273 and 1373 K

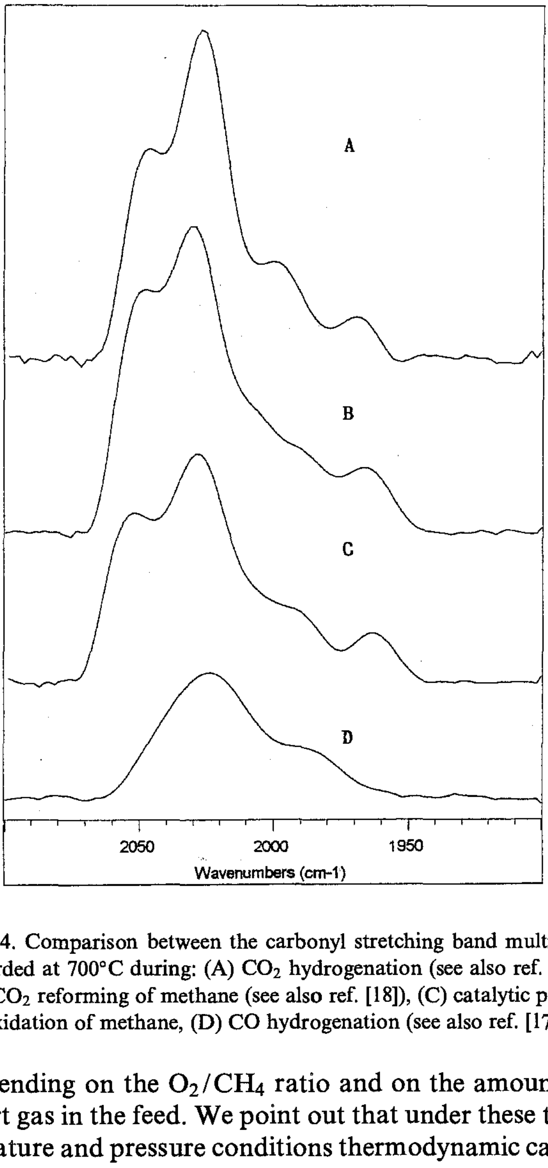

Fig. 4. Comparison between the carbonyl stretching band multiplets recorded at 700°C during: (A) CO_2 hydrogenation (see also ref. [17]), (B) CO_2 reforming of methane (see also ref. [18]), (C) catalytic partial oxidation of methane, (D) CO hydrogenation (see also ref. [17]).

depending on the O_2/CH_4 ratio and on the amount of inert gas in the feed. We point out that under these temperature and pressure conditions thermodynamic calculations indicate that conversion of the reactant and selectivity towards CO and H_2 are above 95% and indeed it is very difficult to discriminate on the basis of the Schmidt results if the reaction selectivities and conversions are controlled by surface kinetic and/or mass transfer processes.

We believe that the results reported here could be useful in discussing the hypothesis by Schmidt and in general the phenomenon of short contact time CPO. The experimental results achieved at relatively low temperatures (1023 K $\geqslant T$) in a water cooled non-adiabatic reaction chamber indicate that CO_2 is produced together with CO also at very short τ and that, by further reduction of the τ values from $\tau = 2 \times 10^{-2}$ s to $\tau = 2 \times 10^{-3}$ s the selectivity towards CO_2 is not diminished but increased. This seems to discharge the hypothesis of a mass transfer controlled CPO with a high selectivity towards CO and H_2. Indeed the increase in CO_2 selectivity produced with the reduction of τ suggests that CO_2 is also a primary reaction product and that the reaction that follows the CO_2 formation, namely the one in which CO_2 is reductively chemisorbed originating the Ir carbonyl clusters, results unfavored at low τ values. We conclude that, on Ir/α-Al_2O_3, the high conversions and selectivities towards CO and H_2, observed in laboratory scale PFR reactors at $\tau \approx 10^{-2}$ s cannot be achieved by removing reaction heat and decreasing reaction temperature below 1023 K. There should be other reasons why CPO could occur so efficiently at very short τ. Further experiments on Rh and Ru based catalysts are in progress.

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