

A combined mass spectrometric/gas chromatographic approach for the thermoanalytical characterization of supported heterogeneous catalysts

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Abstract

Quadrupole mass spectrometry has been applied to the investigation of the chemical reactivity of supported organometallic complexes as precursors of heterogeneous catalysts. The required high sensitivity to CO and CO₂, together with an improved versatility, is obtained by a combined mass spectrometric and gas chromatographic approach.

INTRODUCTION

In the last few years, growing interest has focussed on the utilization of transition metal carbonyl clusters as precursors of novel and more active supported heterogeneous catalysts [1–3]. These materials are prepared by deposition of the organometallic precursor on the inorganic support (silica, alumina, zeolites) via wet impregnation or in the vapor phase, eventually leading to metal particles of controlled topology. The nature of the surface species and, consequently, the final properties of the catalyst (texture, activity and selectivity) are mainly determined by the thermal treatments. These materials, being fine powders with negligible thermal conductivity, cannot be conveniently analyzed by conventional surface techniques operating under UHV conditions. Current applications of such techniques involve model, single-crystal studies, simulating the structures of the microcrystalline metallic phases on the surface of heterogeneous catalysts [4].

These catalysts are better investigated by thermoanalytical techniques, largely based on thermal desorption spectroscopy (TDS) [5]. Here, the desorption rates of surface species are measured as a function of the linearly programmed temperature. Depending on the reacting environment, these techniques are commonly referred to as temperature programmed decompo-

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sition (TPDE), temperature programmed reductive decomposition (TPRD) and temperature programmed oxidation (TPO).

Valuable information on the stability of the catalytic intermediates [6], as well as some predictions on the properties of the final metal catalyst [7], can be gained from an investigation of the nature and the evolution kinetics of the decomposition products, typically CO, CO₂, light hydrocarbons and/or oxygenated products.

However, the measurement of meaningful decomposition kinetics requires a very sophisticated analytical implementation. The product concentrations in the effluent gas stream have to be kept well below 0.5 mol%, in order to avoid readsorption of the evolving molecules from the gas phase, leading to distortions and shifts of the desorption peaks [8], and to ensure reaction conditions that avoid diffusional limitations in the surface processes [9].

Therefore, the highly sensitive detection of a wide range of products, particularly CO, CO₂, hydrocarbons and oxygenated products, is required.

In this paper, an unconventional quadrupole mass spectrometric/gas chromatographic design is proposed as the most effective analytical approach for the thermoanalytical characterization of supported heterogeneous catalysts.

EXPERIMENTAL

Supported samples were prepared via wet impregnation of the inorganic support (Silica Gel Davison 62, 80–100 mesh; γ -Al₂O₃ Cyanamid PHF-4, 60–80 mesh) with a solution of the organometallic precursor in a suitable solvent, i.e. *n*-octane for SiO₂, and CH₂Cl₂ for Al₂O₃. After impregnation, the catalyst samples were dried overnight in vacuo. Detailed information on the techniques of catalyst preparation and the spectroscopic characterization are reported elsewhere [6, 10].

The investigation of the kinetics of catalyst decomposition was carried out in a specially developed flow apparatus, entirely designed in our laboratories (Fig. 1). It can be divided into three main sections.

(i) Selection of the reacting gas (He, H₂(5%)/He, O₂(2%)/He) with electronic mass-flow control (Brooks mod. 5850TR). The 3-way valve (2) is used to pre-evacuate the system in the investigation of air-sensitive materials.

(ii) A glass, micro-flow reactor heated by a ceramic furnace and controlled by a microprocessor-based temperature programmer (Ascon mod. YM).

(iii) Analysis of the gaseous decomposition products, using:

(a) A gas chromatograph (Intersmat IGC12) for the analysis of CO, CO₂ and CH₄, interfaced to the flow system via a 10-port gas-sampling valve. A Ni catalytic converter of CO and CO₂ into methane is placed between the GC column and the flame ionization detector [11]. The

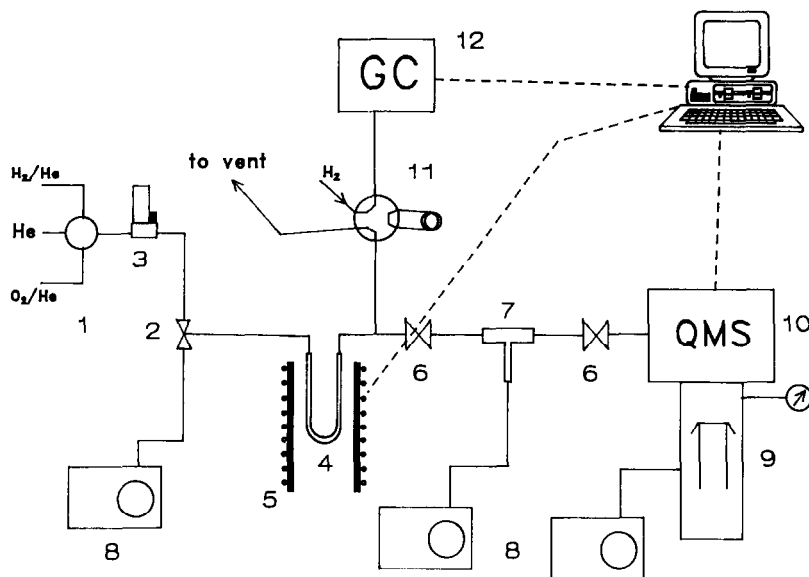


Fig. 1. Schematic diagram of the analytical setup: 1, gas selection; 2, 3-way valve; 3, mass-flow controller; 4, flow-through reactor; 5, heating furnace; 6, high vacuum valve; 7, jet separator; 8, rotary pump; 9, diffusion pump; 10, quadrupole mass spectrometer; 11, 10-port gas-sampling valve; 12, gas chromatograph.

integration of the GC peaks was done by an electronic HP 3396A integrator.

(b) A quadrupole mass spectrometer (Edwards EQ100F or VG Masstorr FX, 1–100 amu) evacuated by a combined rotary–diffusion pumping system. The quadrupole instrument is connected to the flow system through a differentially pumped jet separator.

(c) An IBM-compatible personal computer (Amstrad PC1640), interfaced with the GC integrator, the mass spectrometer and the temperature controller via serial RS232 interfaces.

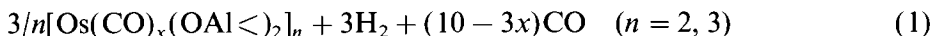
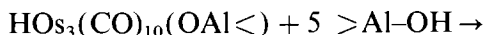
The use of two detectors in parallel required the correct balancing of the transfer lines between each detector and the flow reactor.

In a typical analysis, the powdered sample (10–300 mg) is heated in flowing gas from 25 to 500°C with a heating rate of 3°C min⁻¹. Analyses of the reaction products are made every 1 min (QMS) or 2.2 min (GC) in order to have a sufficient number of data points for the correct definition of the evolution profiles of the decomposition products.

RESULTS AND DISCUSSION

The analytical method described has been applied to a model Al₂O₃-supported osmium catalyst, where the active species is the trinuclear cluster HO₃(CO)₁₀(OAl<), covalently bound to the surface via Os–O–Al bonds.

On the basis of its chemical reactivity [6], we can predict that both CO and CO₂ will be evolved during its thermal decomposition in helium atmosphere. CO is formed via oxidative disruption of the trinuclear osmium structures and the formation of Os(II) species



CO₂ is produced, together with hydrogen, via a water gas shift reaction, involving the -OH groups of the alumina surface



Unfortunately, hydrogen evolution cannot be conveniently monitored by our system, because a low sensitivity for the detection of H₂ is the only drawback of a jet-separator interface. The evolution profiles of CO and CO₂ were therefore investigated under TPDE conditions in flowing helium, exploiting the parallel configuration of the two detectors (Figs. 2 and 3).

According to reactions (1) and (2), CO is evolved in a single peak at 178°C; the evolution of CO₂ is observed at 195°C. It is noteworthy that the peak positions are independent of the detector actually used, indicating the perfect balancing of the response time of the two detectors.

The GC detection of CO and CO₂ is totally satisfactory, with the complete absence of noise or baseline drifts (Fig. 2). The same cannot be said for the quadrupole mass analyzer (Fig. 3). The strong background

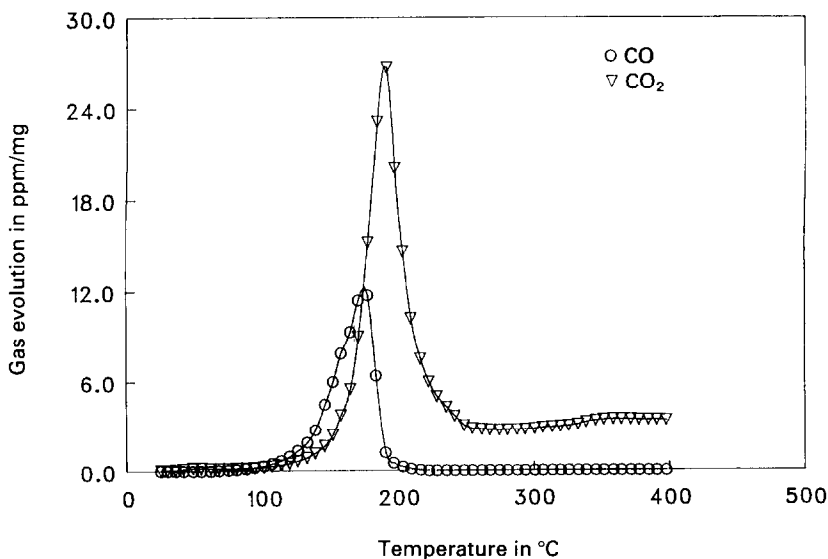


Fig. 2. Gas chromatographic analysis of the TPDE profiles in flowing helium of HOs₃(CO)₁₀(OAl)_x.

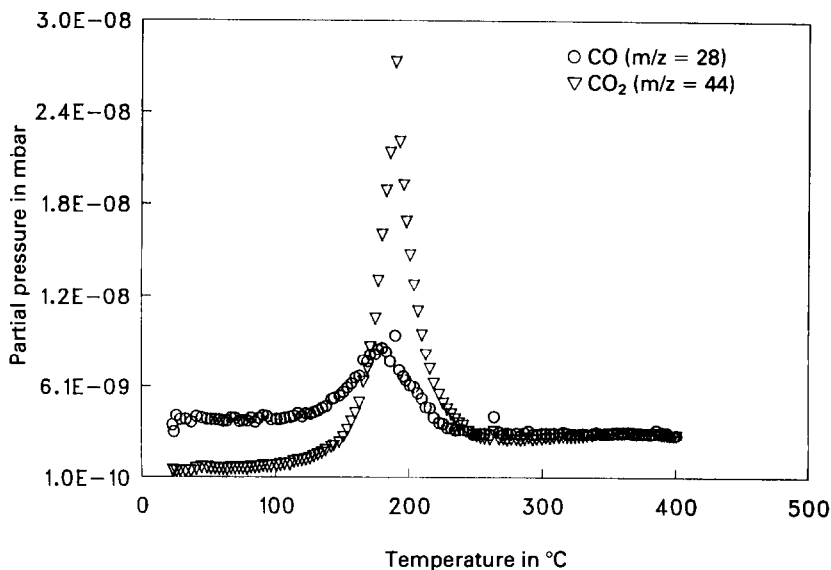


Fig. 3. Quadrupole mass spectrometric analysis of the TPDE profiles in flowing helium of $\text{HOs}_3(\text{CO})_{10}(\text{OAl})$.

signals at $m/z = 28$ and $m/z = 44$ are caused by the evolution of CO and CO_2 from the hot filament in the quadrupole analyzer [12].

Consequently, the main limitations of the low-resolution mass spectrometric detection of evolving gases, in particular the low sensitivity to CO and CO_2 , and the impossibility of quantifying light molecules with the same m/z ratio, for instance CO, N_2 and C_2H_4 at $m/z = 28$, can be overcome by the use of gas chromatography in parallel with quadrupole mass spectrometry. In this way, only very small amounts of sample (10–50 mg) are needed for the temperature programmed characterization of the catalyst. This is of primary importance in repetitive analyses of small batches of working catalysts.

The combined use of the two detectors is not always possible, particularly when spent catalysts or dirty samples have to be analyzed. Reforming catalysts in the petroleum industry are often characterized for their carbon content via temperature programmed oxidation (TPO). In this technique, carbon deposits are burned off in oxygen atmosphere, and CO_2 evolution is recorded as a function of increasing temperature.

A very simple gas analysis is thus required in TPO, because only carbon dioxide should be present in the evolving gas phase under proper conditions. This analysis is best done via gas chromatography alone. The use of the quadrupole mass spectrometer is, obviously, not recommended in the presence of the high partial pressures of oxygen required to ensure the complete combustion of carbon deposits to CO_2 .

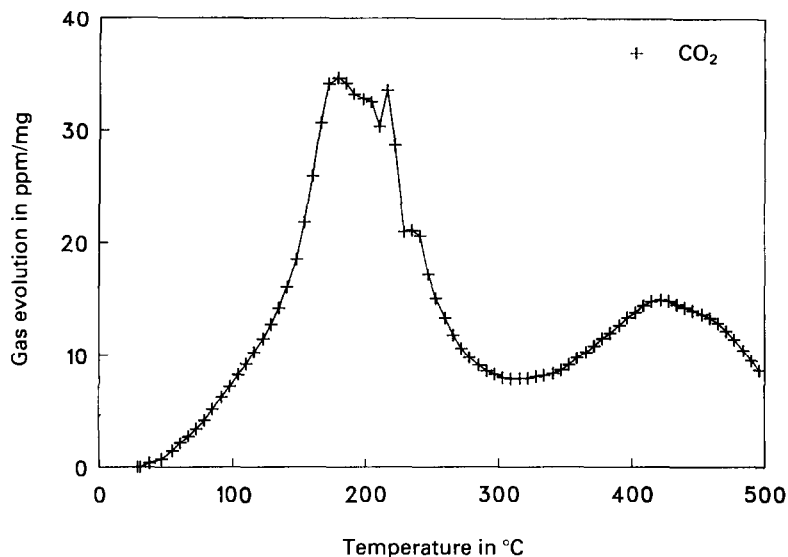


Fig. 4. TPO analysis in flowing O₂(2%)/He of a spent Pt/KL catalyst.

In Fig. 4, a Pt/KL zeolite catalyst has been tested under typical reforming conditions (methylcyclopentane conversion at 1 atm and 500°C for 5 h [13]) and then analyzed via TPO with only GC detection. Peaks of CO₂ evolution are observed around 190 and 410°C, indicating that both “soft” and “hard” coke are present on the surface. In addition, the integration of the evolution profile gives a total C/Pt ratio of about 20. In this way, information on the nature and amount of the carbonaceous residues can be straightforwardly obtained from the position and the integrated intensity of the CO₂ peaks [14].

A totally different situation arises when the contaminated sample has to be analyzed under inert (TPDE) or reducing (TPRD) conditions. The organic contaminants that remain adsorbed onto the surface of the porous support will be released during the temperature programmed analysis. These high molecular weight products, e.g. the impregnation solvents, are strongly retained on the GC stationary phase (generally Porapak_s [11]) used for the analysis of light gases. A fast GC analysis of such components is thus impossible.

The utilization of the quadrupole mass analyzer is therefore the only practical solution to this problem. A typical example is reported in Fig. 5. The surface osmium cluster HO₃(CO)₁₀(OSi_≤), covalently bound to the silica surface, has been prepared using *n*-octane as the impregnation solvent, which is strongly adsorbed on the porous support. The large desorption peak at *m/z* = 43 in TPDE is in fact caused by the evolution of adsorbed *n*-octane; it is noteworthy that the study of this catalytic system was totally impossible using the gas chromatographic detector.

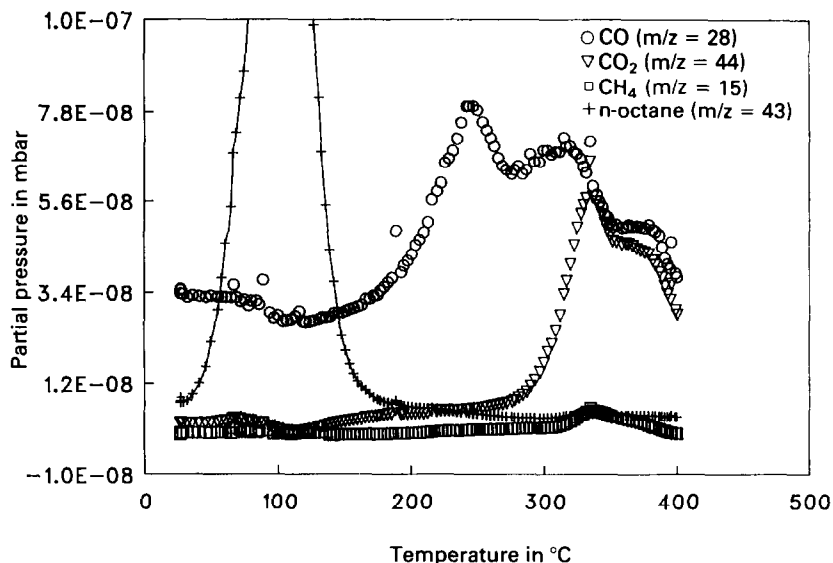


Fig. 5. TPDE analysis in flowing helium of $\text{HOs}_3(\text{CO})_{10}(\text{OSi}\leq)$ using the mass spectrometric detector.

Larger amounts of sample, in the 100–300 mg range, are thus required in order to have reasonable signal-to-noise ratios. In this way, useful, although qualitative, information on the reactivity of the system under test can be gained.

The analysis of the evolution profiles of CO indicates a totally different reactivity when compared with the analogous species on alumina (Figs. 5, and 2 and 3). In particular, the $[\text{Os}(\text{CO})_x(\text{OSi}\leq)_2]_n$ ($x = 2-3$) species formed at 200–240°C (reaction (1)) shows a much lower stability, being totally decarbonylated to metallic osmium in a second step at about 330–340°C.

In addition, it is possible here to demonstrate, although indirectly, the evolution of hydrogen during CO_2 formation (reaction (2)). In fact, a non-negligible evolution of methane at $m/z = 15$, paralleling that of carbon dioxide, is observed in helium atmosphere (Fig. 5). This feature can only be explained by the reduction of CO by the hydrogen formed in situ by the WGS reaction (reaction (2)).

This was confirmed by studying the reactivity of the starting $\text{HOs}_3(\text{CO})_{10}(\text{OSi}\leq)$ cluster under reducing TPRD conditions, using a $\text{H}_2(5\%)/\text{He}$ mixture (Fig. 6). The conversion of evolving CO to CH_4 starts at around 250°C, being complete at 330°C; in contrast, no CO_2 is evolved, because the water gas shift equilibrium (reaction (2)) is completely shifted to the left in the presence of a high partial pressure of hydrogen. At a temperature above 250°C, carbon monoxide is then reduced to methane

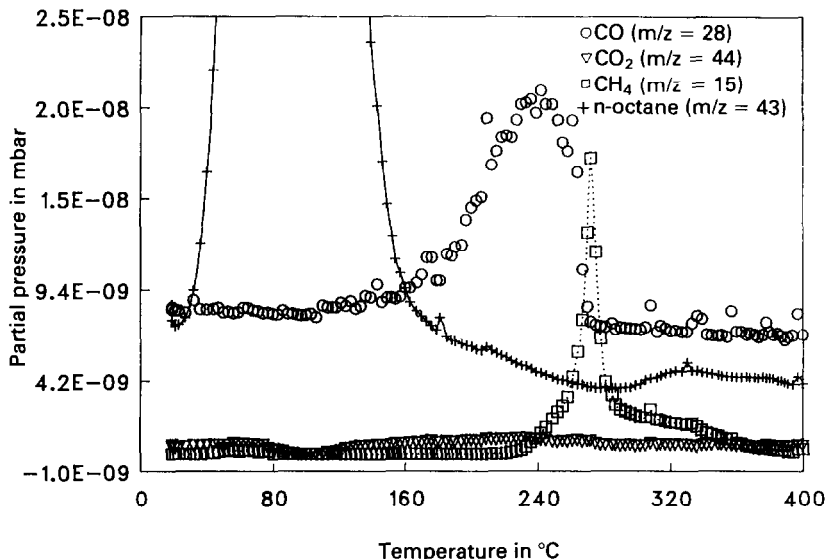


Fig. 6. TPRD analysis in flowing H_2/He of $\text{HOs}_3(\text{CO})_{10}(\text{OSi}\leq)$ using the mass spectrometric detector.

following the Fischer–Tropsch mechanism, with the parallel formation of water



In the TPRD profile of water at $m/z = 18$ (Fig. 7), a sharp evolution peak is observed at 275°C , corresponding exactly to the evolution of methane. The much larger peak around 100°C corresponds to the removal of physisorbed water weakly held at the surface.

CONCLUSIONS

The final properties of heterogeneous metal catalysts are markedly dependent on the complex transformation undergone by the precursor molecule in the activation process. TPDE and TPRD techniques are extremely useful for the characterization of surface reactions taking place during the thermal treatment of oxide-supported metal clusters.

The requirement of high sensitivity, high selectivity detection of CO and CO_2 has been solved by the combined use of quadrupole mass spectrometry and gas chromatography, coupled with a methanation converter. The two detectors can also be used separately. In this way, the use of oxidizing environments for TPO analyses is made possible, as well as the direct analysis of difficult samples, e.g. contaminated adsorbents or working industrial catalysts.

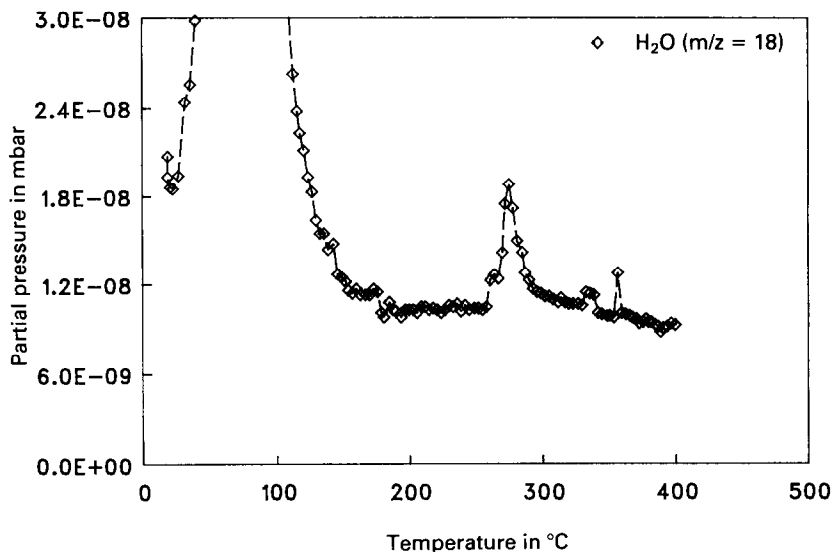


Fig. 7. Temperature programmed analysis of water evolution from $\text{HO}_3(\text{CO})_{10}(\text{OSi} \leq)$ under TPRD conditions of Fig. 6.

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