

SPECTROSCOPY OF SUPPORTED TRANSITION METAL OXIDE CATALYSTS UNDER WORKING CONDITIONS: POTENTIAL AND LIMITATIONS

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Researchers in the field of heterogeneous catalysis are nowadays working to develop spectroscopic cells that allow them to study supported metal oxides in catalytic action. This is the field of *in situ* spectroscopy. Here, a brief overview of the field is given by illustrating the strengths and weaknesses of diffuse reflectance spectroscopy, Raman spectroscopy, X-ray photoelectron spectroscopy and electron spin resonance for *in situ* characterization. The paper closes with case studies from our own work covering different fields of heterogeneous catalysis.

INTRODUCTION

Supported transition metal oxides constitute a very important class of heterogeneous catalysts, which are extensively used in chemical industries for the production of commodity chemicals and for the removal of noxious gases.^{1,2} Striking examples are Cr/SiO₂ and Cr/Ti/SiO₂ catalysts for the production of high-density polyethylene (HDPE) and linear low-density polyethylene (LLDPE);^{3,4} Cr/Al₂O₃ catalysts for the selective dehydrogenation of isobutane and propane to isobutene and propene, respectively;^{5,6} Re/Al₂O₃ and W/SiO₂ catalysts for olefin metathesis⁷ and V/W/TiO₂ catalysts for the selective reduction of NO_x with NH₃.^{8,9}

Identifying and quantifying oxidation states and coordination environments of transition metal ions (TMIs) is fundamental for understanding their chemistry and catalytic action. Various spectroscopic techniques are available to perform this task. Until recently most spectroscopic characterization studies were conducted under conditions often far away from real catalytic conditions. Indeed, knowing only the before-reaction part (hydrated and dehydrated catalysts) and after-reaction part (deactivated catalysts) of the catalytic event is not sufficient to identify the catalytic active site, and to develop relevant structure-activity/selectivity relationships.

Therefore, researchers are working to develop spectroscopic methods that allow them to study heterogeneous catalysts while they are in (re) action. This is the field of *in situ* spectroscopy, which in the strict sense refers to the study of a catalyst *at its working place* (e.g., in a stream of reactants at high temperatures). In this review paper, a brief overview of the field is given by using recent work from our own group and from the literature. We will limit ourselves to catalytic reactions in the gas phase. The following subjects will be discussed:

- (1) Design of *in situ* spectroscopic cells for catalyst characterization.
- (2) Possibilities and limitations of different spectroscopic techniques, namely *in situ* diffuse reflectance spectroscopy (DRS) in the UV-Vis-NIR region; *in situ* Raman spectroscopy (RS), X-ray photoelectron spectroscopy (XPS) with an *in situ* transfer line; and *in situ* electron spin resonance (ESR).

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(3) Case studies covering different fields of heterogeneous catalysis: the dehydrogenation of alkanes over supported chromium oxide catalysts;¹⁰ the selective oxidation of methanol to formaldehyde over supported vanadium oxide catalysts;^{11,12} and the direct conversion of methane to aromatics over W, Cr, V, W and Fe/H-ZSM-5 catalysts.¹³⁻¹⁶ It will be shown that structure activity relationships can be established on the basis of such *in situ* spectroscopic data.

DESIGN OF *IN SITU* SPECTROSCOPIC CELLS

In order to obtain relevant structure–activity relationships of heterogeneous catalysts, spectroscopic and catalytic measurements have to be done on the *same* catalyst at the *same* time under *optimal* spectroscopic and catalytic conditions. A scheme of an experimental set-up is given in Fig. 1. The catalyst is placed in a catalytic reactor, which allows measuring spectroscopic data at high temperatures in

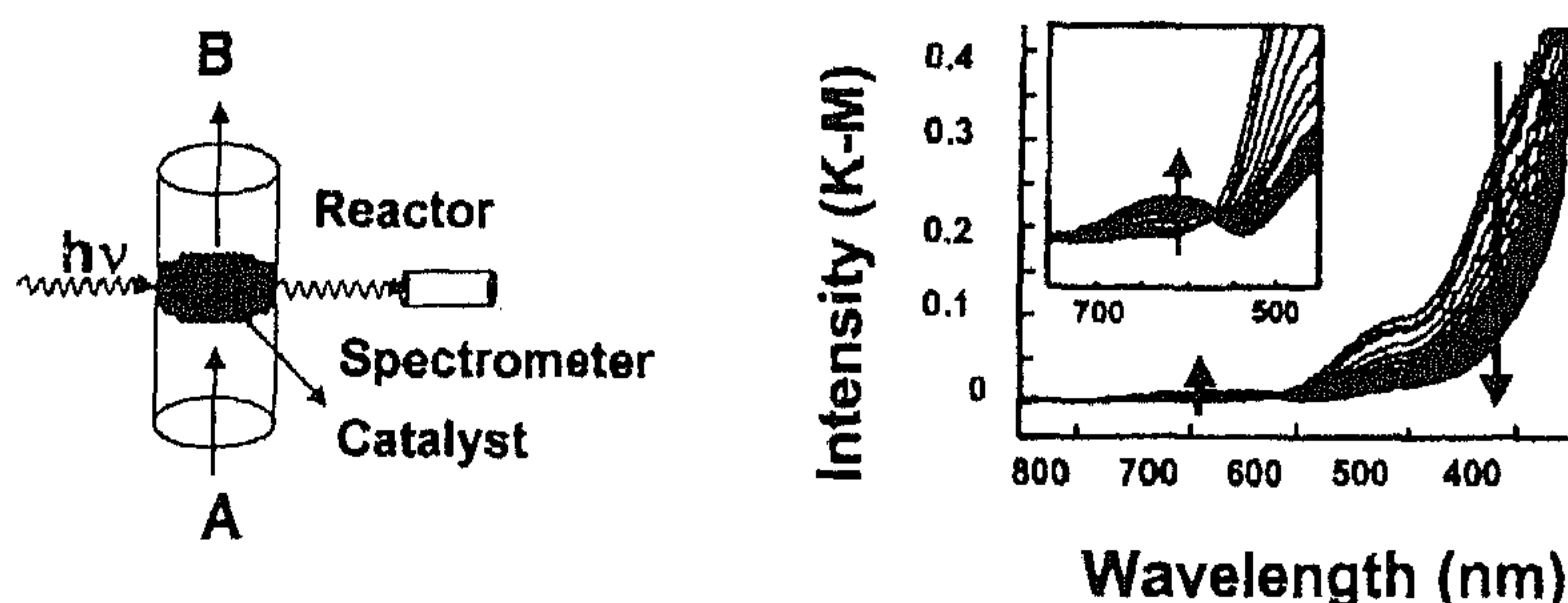


Fig. 1 – Scheme of an experimental set-up for *in situ* catalyst characterization, in combination with on line activity/selectivity measurements.

the presence of a reactant. The catalytic activity and selectivity of the catalyst can then be obtained *via* gas chromatography or mass spectrometry.

It is clear that the design of the *in situ* spectroscopic cell is here the crucial step. Indeed, one important problem is that the optimal conditions for performing spectroscopic and catalytic measurements are not identical. Table 1 summarizes the experimental conditions for obtaining well-resolved spectra of supported transition metal ions with DRS, RS, XPS and ESR. Generally speaking, high mea-

Table 1

Conditions for obtaining well-resolved DRS, RS, XPS and ESR spectra

DRS	RS	XPS	ESR
Room temperature Low metal loading Vacuum-low pressure	Room temperature Medium-high metal loading Vacuum-low pressure	Room temperature Medium-high metal loading Ultra high vacuum	Liquid N ₂ or He temperature Low metal loading Vacuum-low pressure

surement temperatures always give rise to less resolved spectra, which make analysis more difficult. Thus, a compromise has to be found between both types of measurements. This also implies that an *in situ* spectroscopic cell is catalytically less performant than a real reactor. For example, the *in situ* cell of Fig. 2 can reach conversions of about 10% for a dehydrogenation catalyst, which in a catalytic reactor would give a dehydrogenation activity of more than 40% under otherwise the same conditions.

Figs. 2–6 illustrate examples of spectroscopic cells available for studying heterogeneous catalysts in action. Fig. 2 is the commercial stainless steel reaction chamber of Harrick with quartz windows for diffuse reflectance measurements in the UV-Vis-NIR region.¹⁷ This cell can be used in combination with a Praying Mantis (PM) diffuse reflection attachment for studying catalysts up to 550°C under vacuum or in a gas flow up to 2–5 bar. Typically, 100 mg of granulated catalyst is placed in the reactor bed of 5–8 mm height and 5 mm diameter. The PM attachment replaces the integration sphere of the spectrophotometer. Its construction with two ellipsoidal mirrors is such that mainly the diffuse component of the reflected light is captured. One of the disadvantages is that only 8–10% of the reflected light is captured in comparison with the integration sphere, which results in a reduced sensitivity. In addition, the NIR region is not informative because of heat radiation of the catalyst.

Two different types of *in situ* Raman cells are given in Figs. 3 and 4. Fig. 3 shows a design – developed by the group of Israel Wachs at Lehigh University¹⁸ in which the catalyst is placed as a pressed wafer on top of a ceramic shaft. This shaft is placed in a quartz cell, which is surrounded by a

Fig. 2 – A, Scheme of a catalytic reactor and B, Praying mantis diffuse reflection attachment for *in situ* DRS measurements (Reprinted from Ref. (17), Copyright Elsevier Science Publishers, 1998).

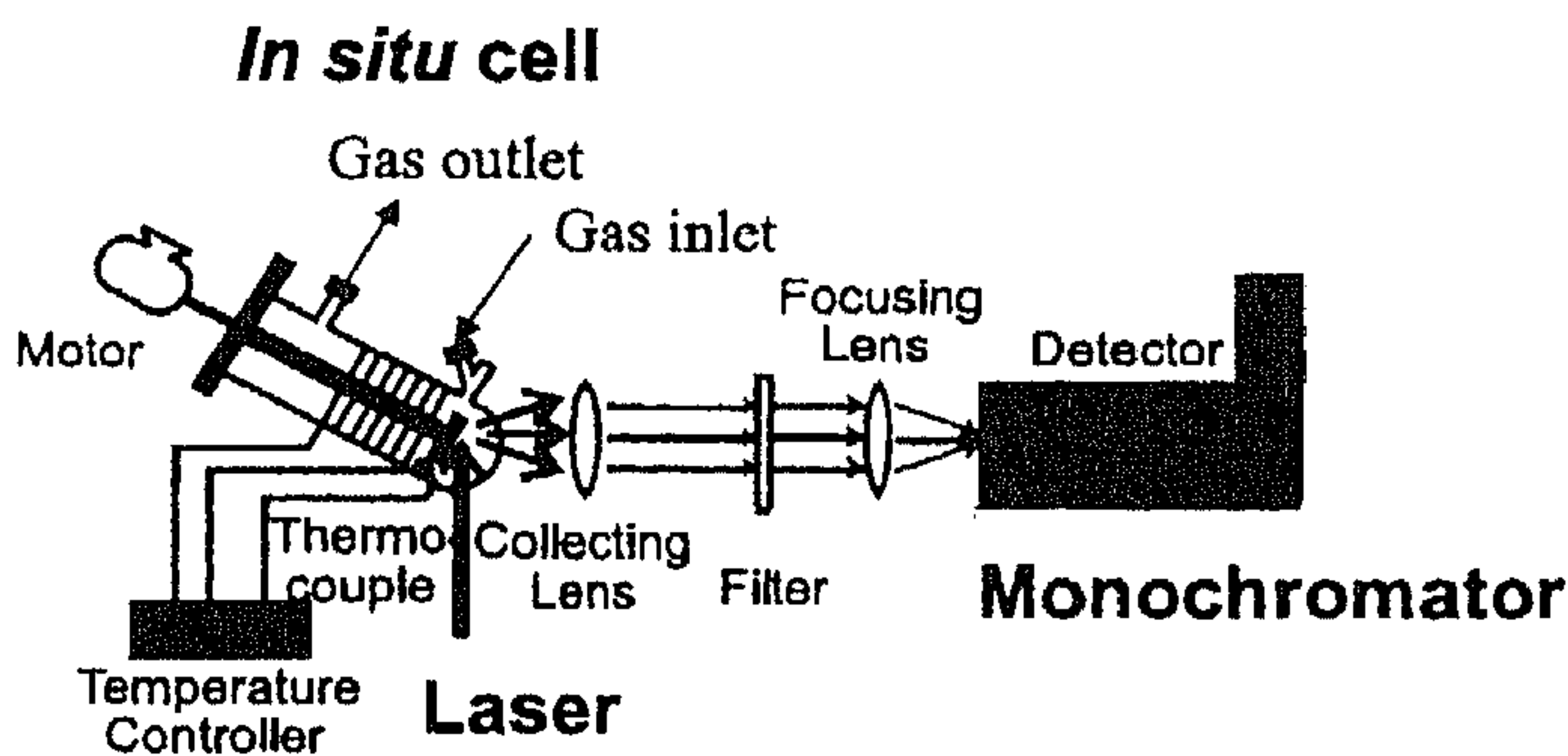
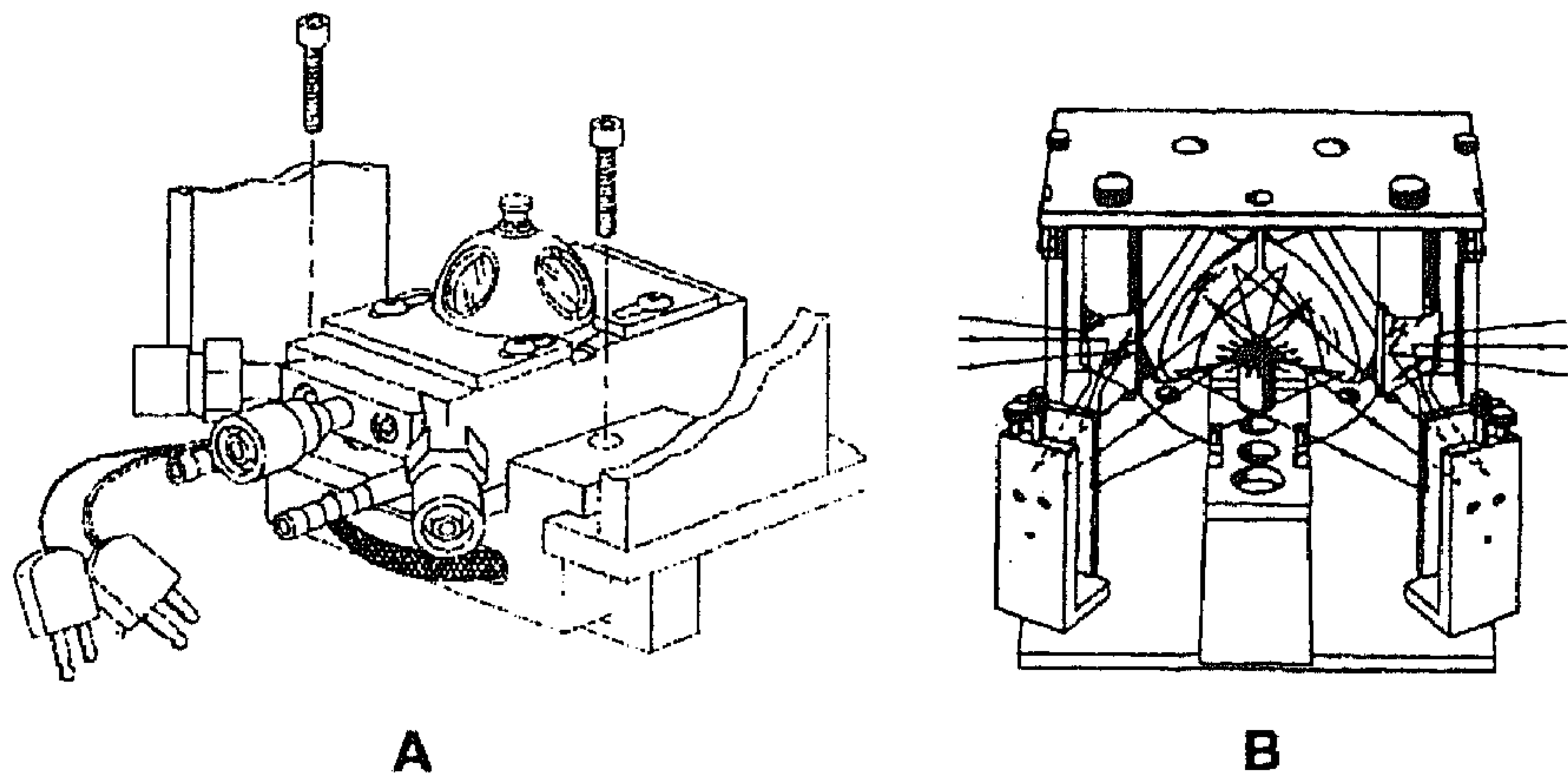


Fig. 3 – Spectroscopic cell for *in situ* RS measurements, as developed by the group of Israel Wachs.

Fig. 4 – Spectroscopic cell for *in situ* RS measurements, as developed by Gerhard Mestl (Reprinted from Ref. (19), Copyright American Chemical Society, 1997).

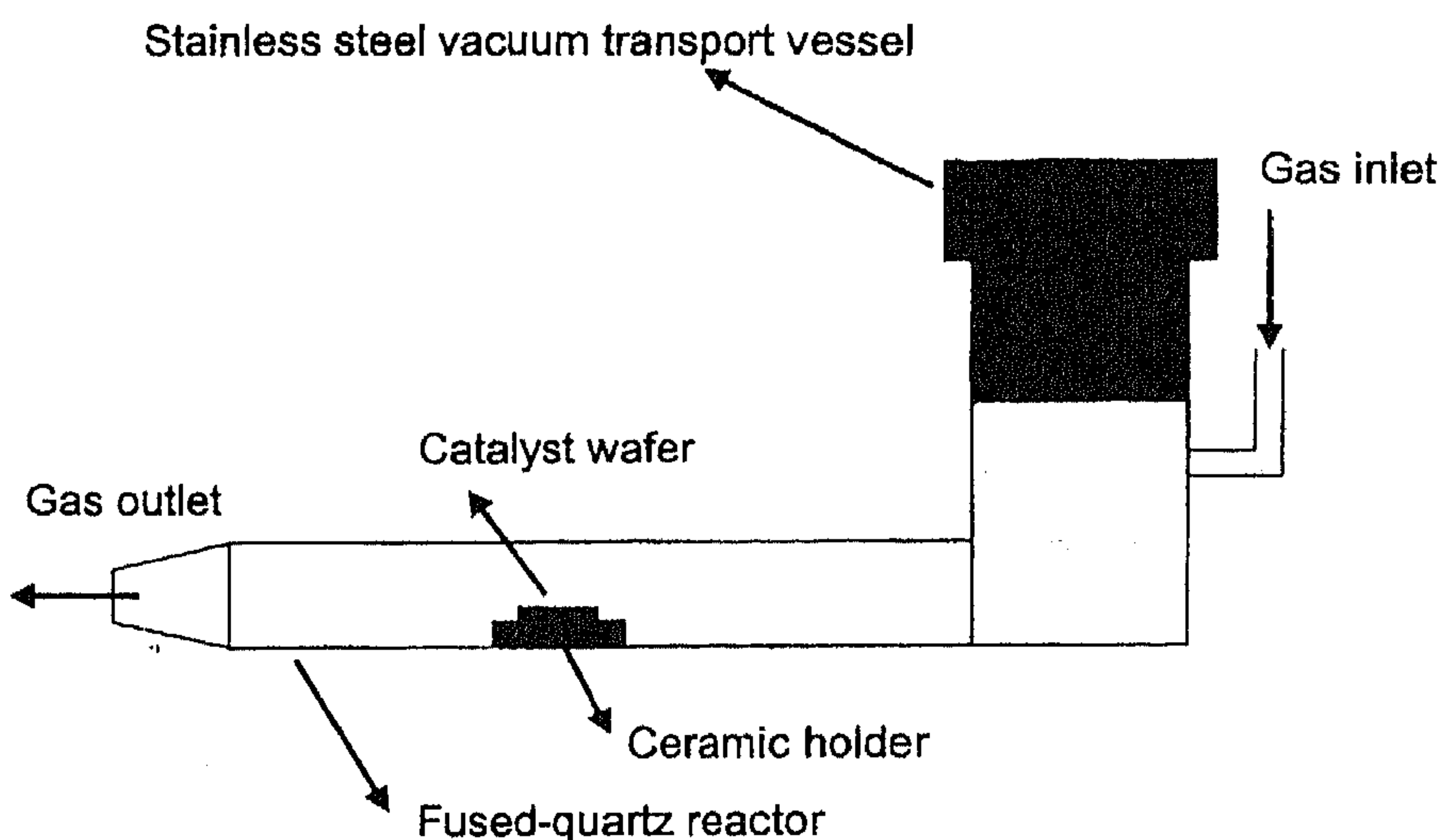
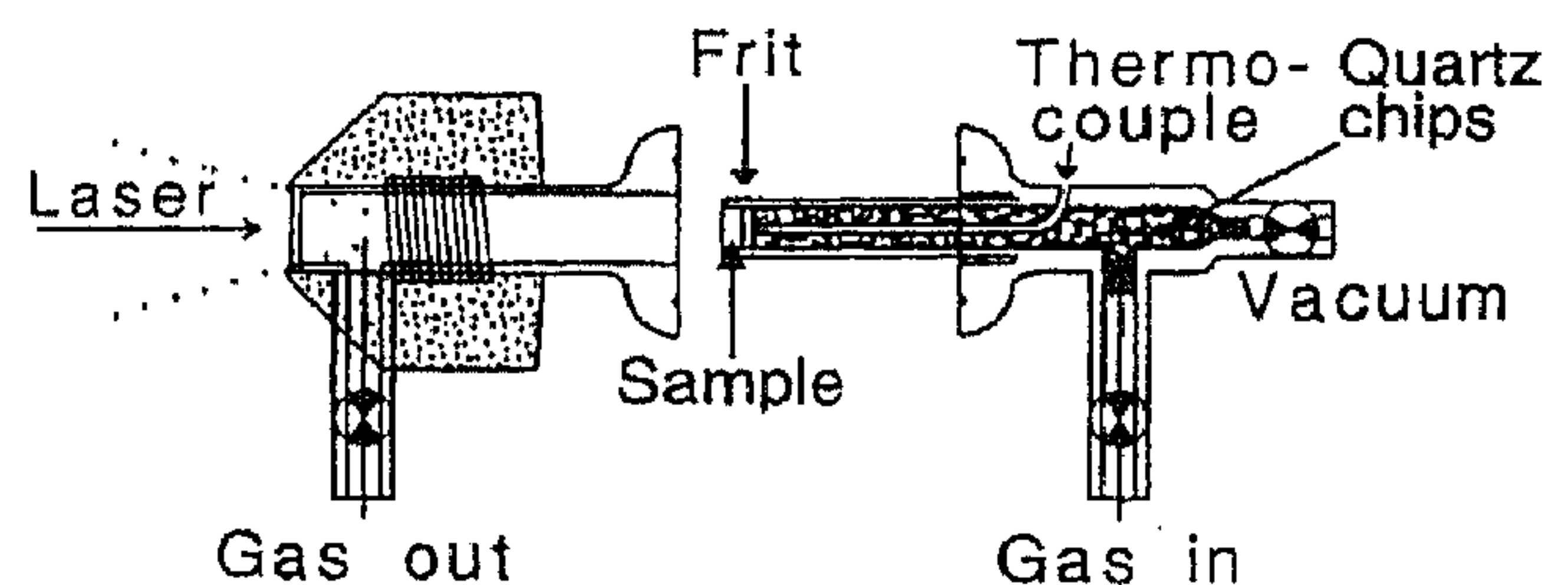


Fig. 5 – *In situ* transfer line for XPS measurements, as developed by the group of Jack Lunsford.

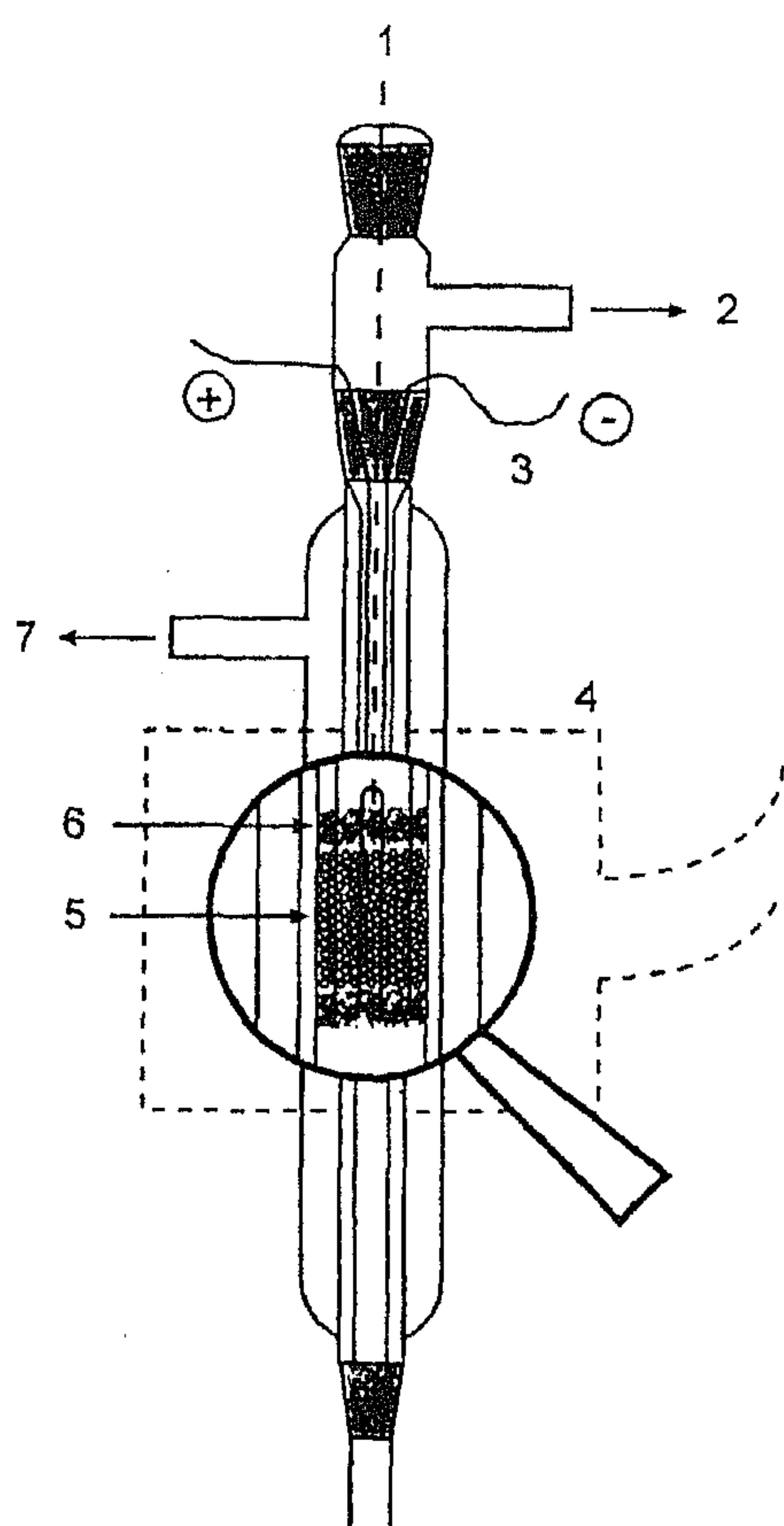


Fig. 6 – Spectroscopic cell for *in situ* ESR measurements, as developed by Angelika Brückner (Reprinted from Ref. (22), Copyright Elsevier Science Publishers, 1999): (1) thermocouple; (2) connection to gas dosing apparatus; (3) bifilar Pt-winding; (4) cavity; (5) catalyst; (6) quartz wool; (7) connection to isolation vacuum.

furnace, and which has a gas inlet and outlet. The scattered radiation from the catalyst sample is measured under an angle of 90° by the detector. A disadvantage of this system is the use of a pressed wafer because the reactant is not flowing through the catalyst bed. An advantage is that laser-induced catalyst heating or transformations can be avoided by spinning the ceramic shaft. In this respect, the *in situ* Raman cell of Fig. 4 – developed by Gerhard Mestl at Fritz Haber Institute¹⁹ can only be used when a low laser power is applied. Here, granulated catalyst powder is placed in a fixed bed quartz reactor. The amount of sample is only 50 mg, and the reactant is flowing through the catalyst bed. The working temperatures can be as high as 800°C , whereas the scattered radiation from the sample is measured under an angle of 180° by the detector. The latter implies the use of a high-performance filter.

An *in situ* transfer system for XPS measurements – as developed by the group of Jack Lunsford at Texas A&M University²⁰ is shown in Fig. 5. The catalyst in the form of a pressed wafer is placed on a ceramic holder, which can be treated at high temperature in the presence of a gas stream in a fused-quartz reactor with an O-ring sealed port. Thus, the gas is flowing over the pressed catalyst wafer. The treated catalyst can then be transferred with magnets to a stainless steel vacuum transport vessel. This vessel can be placed on the inlet system of the XPS spectrometer, which is evacuated, allowing the catalyst sample to be introduced into the UHV analysis chamber of the instrument without exposure to air.

An example of an *in situ* ESR cell is given in Fig. 6. This cell – designed by Angelika Brückner of the Institut für Angewandte Chemie^{21,22} – consists of two concentric quartz tubes. The outer quartz tube protects the spectrometer cavity against heating, whereas the inner quartz tube contains the catalyst sample as granulated powder. The cell design enables the reactant to flow through the catalyst bed. About 50–100 mg of catalyst is then heated via a platinum wire placed on the outer surface of the inner quartz tube.

POSSIBILITIES AND LIMITATIONS OF TECHNIQUES TO STUDY SUPPORTED TRANSITION METAL IONS IN CATALYTIC ACTION

Table 2 summarizes the strengths and weaknesses of DRS, RS, XPS and ESR for performing measurements at high temperatures in the presence of a reactant. All spectroscopic tools with the

Table 2

Strengths and weaknesses of DRS, RS, XPS and ESR for measurements at high temperature in the presence of a reactant

Characteristics	DRS	RS	XPS	ESR
Property measured?	d-d transition and CT-transitions	M-O and M=O vibrations	Binding energies	Zeeman and hyperfine interactions
Bulk technique?	Yes	Yes	No	Yes
Which oxidation states of TMI can be measured?	Both oxidized and reduced states	Oxidized states	Both oxidized and reduced states	Paramagnetic oxidation states
Quantitative?	Yes	No	Yes	Yes
Negative influence of temperature?	Yes	Not much – small shift to lower energy	Not applicable – applied at room temperature	Yes
Influence of the presence of reactants?	Yes – Organic molecules can absorb the UV region	Yes – Fluorescence induced by reactants/products	Not applicable – Only indirect effect via e.g. coke formation	Possible formation of organic radicals can be detected

exception of XPS are bulk techniques, and the *in situ* spectra are mostly less informative due to e.g. line broadening. DRS is the least expensive, and – in principle – the most versatile technique because both oxidized and reduced states of transition metal ions can be probed and quantified via their d-d transitions and charge transfer (CT)-transitions. RS and ESR are also very useful although the number of measurable oxidation states is more limited. Finally, the XPS technique – although widely used in catalyst research and capable of detecting all the oxidation states of transition metal ions at the surface of oxides – is rather expensive. In addition, the obtained information is not necessarily that of the active catalyst because an *in situ* transfer line is used and catalyst restructuring may occur in the UHV chamber.

CASE STUDIES

Alkane dehydrogenation over supported chromium oxide catalysts

An important route for the industrial production of alkenes is the catalytic dehydrogenation in the absence of oxygen at relatively high temperatures over a 13 wt% Cr/Al₂O₃ catalyst with some promoters.^{5,6} Recently, we have studied these catalysts as a function of the support composition (SiO₂:Al₂O₃ ratio of SiO₂.Al₂O₃ supports), Cr loading and reaction time by *in situ* DRS. The DRS technique allows to probe Cr⁶⁺, Cr³⁺ and Cr²⁺ in reaction conditions, while the reaction products (CO/CO₂, CH₄, C₂H₆, ...) are monitored by *on-line* gas chromatography.¹⁰

The catalytic performance of a 0.2 wt% Cr/Al₂O₃ catalyst in the *in situ* cell for n-butane dehydrogenation at 500°C is given in Fig. 7. Other supported chromium oxide catalysts had a similar activity and selectivity pattern, although their exact conversions/selectivities were different. It is also important to notice that the catalytic activity of the empty *in situ* cell at 500°C was below 0.1%. Fig. 7A shows that the catalytic activity of the 0.2 wt% Cr/Al₂O₃ catalyst reaches a maximum after 6 min on-stream, and decreases with increasing reaction time. In addition, the selectivity pattern of the reaction is quite complex (Fig. 7B). The catalytic reaction is characterized by an initial induction period, during

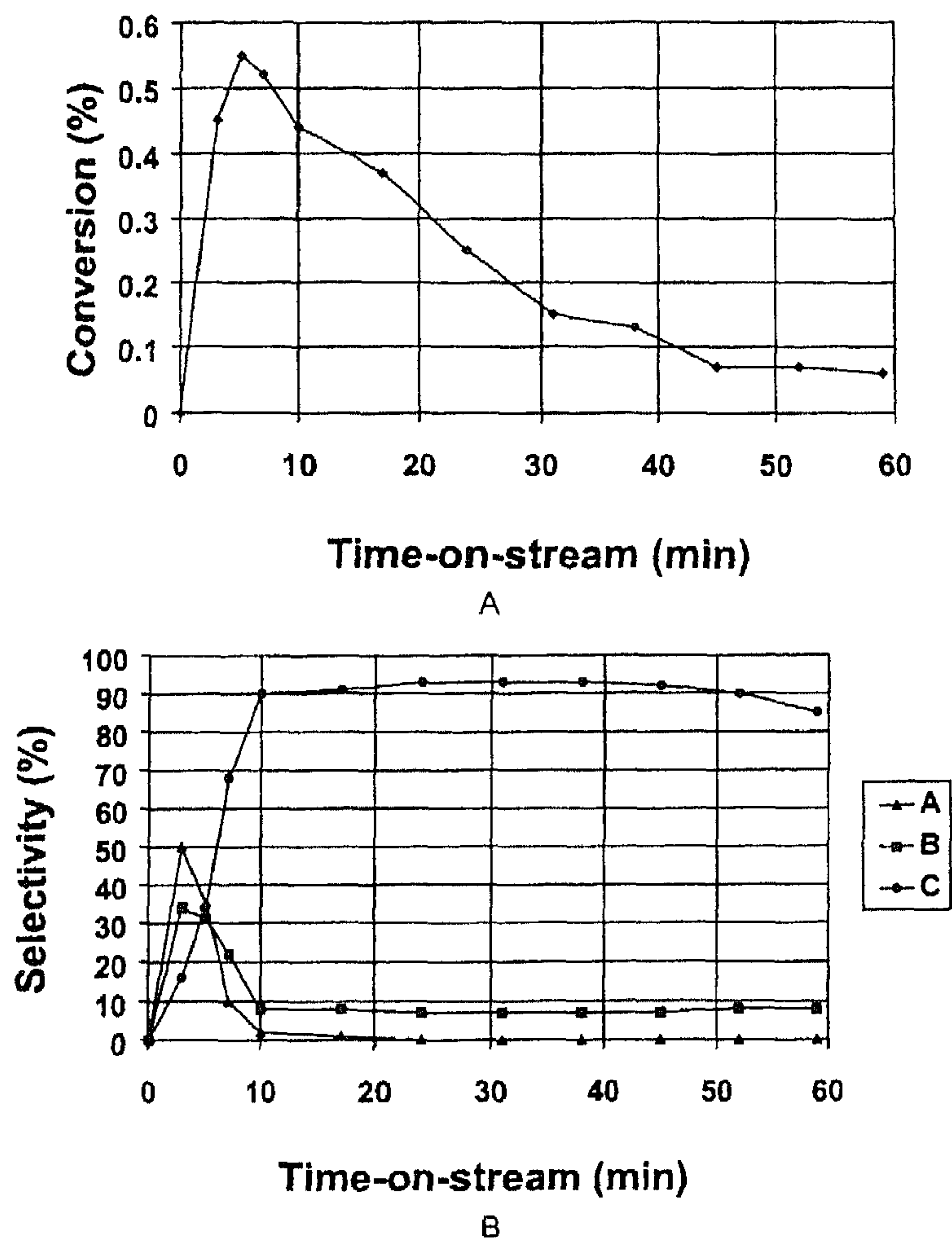


Fig. 7 – A, Conversion (%) vs. time on-stream (min) for *n*-butane dehydrogenation at 500°C over a 0.2 wt% Cr/Al₂O₃ catalyst in the *in situ* DRS cell. B, Selectivity (%) vs. time on-stream (min) for *n*-butane dehydrogenation at 500°C over a 0.2 wt% Cr/Al₂O₃ catalyst in the *in situ* DRS cell: (a) CO/CO₂; cracking products (C₁, C₂ and C₃) and (c) but-1-ene and but-2-ene (Reprinted from Ref. (10), Copyright Royal Chemical Society, 1998).

which CO/CO₂ and some cracking products are formed. The maximum selectivity towards these products is reached after 3 min on-stream, and is ca. 50 and 35% for CO/CO₂ and the cracking products (CH₄, C₂H₄, ...), respectively. After the initial induction period, but-1-ene and but-2-ene are produced selectively. The selectivity towards alkenes reaches a maximum of ca. 90% after 10 min, and decreases slightly with increasing time on-stream. The dependency of the dehydrogenation activity on Cr loading for Cr/Al₂O₃ catalysts is illustrated in Fig. 8. It is shown that the conversion towards alkenes increases almost linearly with increasing Cr loading.

In situ DRS spectra between 300 and 800 nm were monitored as a function of time on-stream at 500°C. The scan time was 1 min, and 60 different spectra were recorded during 60 min. An example of a set of *in situ* DRS spectra is given in Fig. 9. Fig. 9 shows a gradual decrease of the absorption maximum at ca. 360 nm with increasing reaction time at the expense of a new weak band with an absorption maximum at ca. 590 nm. Fig. 9 also shows the presence of an isobestic point at ca. 490 nm, suggesting the presence of two different Cr species, namely Cr⁶⁺ (360 nm) and Cr³⁺ (590 nm). Thus, Cr⁶⁺ is reduced to Cr³⁺ in the first minutes during *n*-butane dehydrogenation, which results in the formation of CO/CO₂. It is anticipated that these Cr³⁺ species are the active sites for alkane dehydrogenation.

Fig. 8 – Conversion (%) vs. Cr-loading (wt%) for n-butane dehydrogenation at 500°C over Cr/Al₂O₃ catalysts (Reprinted from Ref. (10), Copyright Royal Chemical Society, 1998).

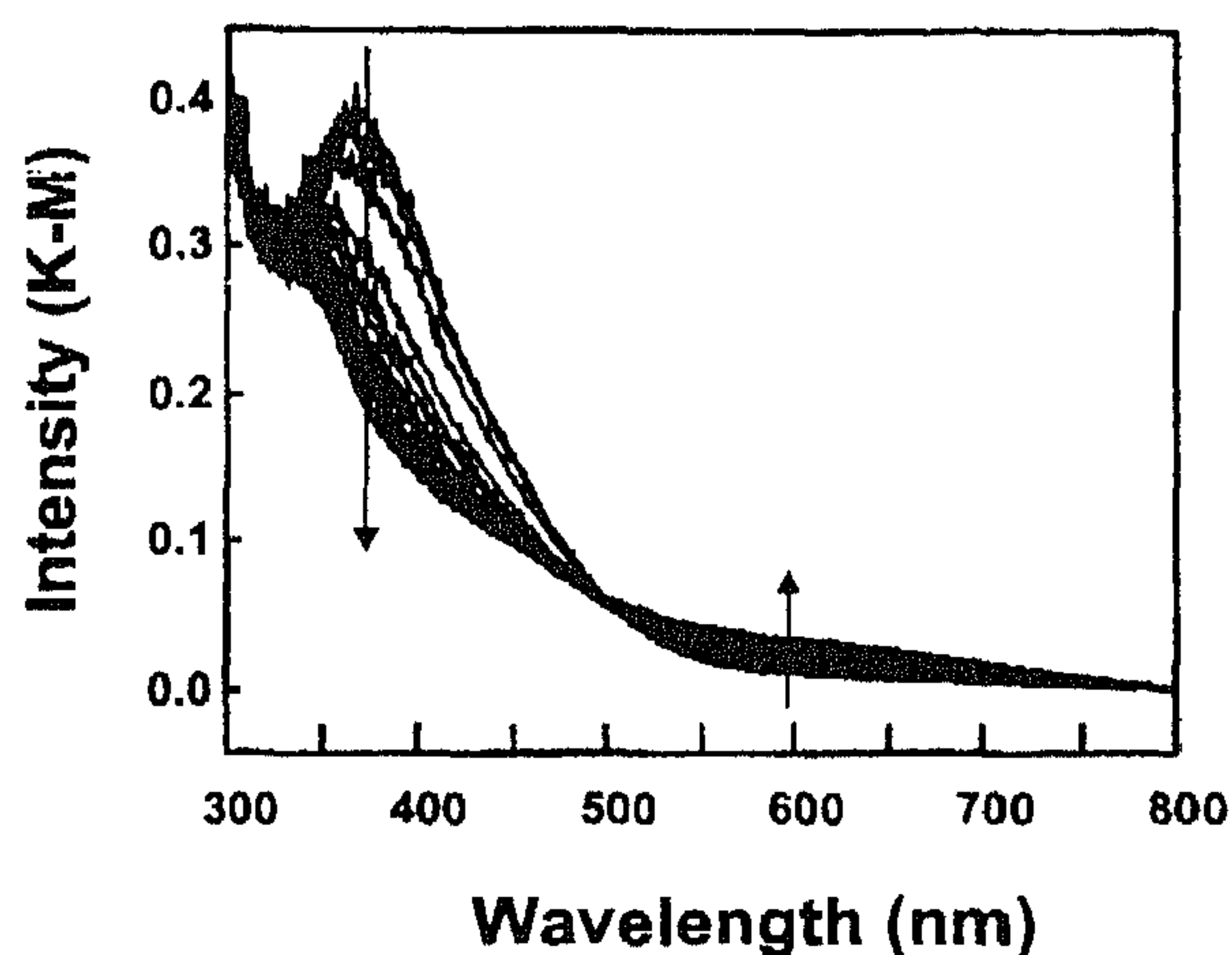
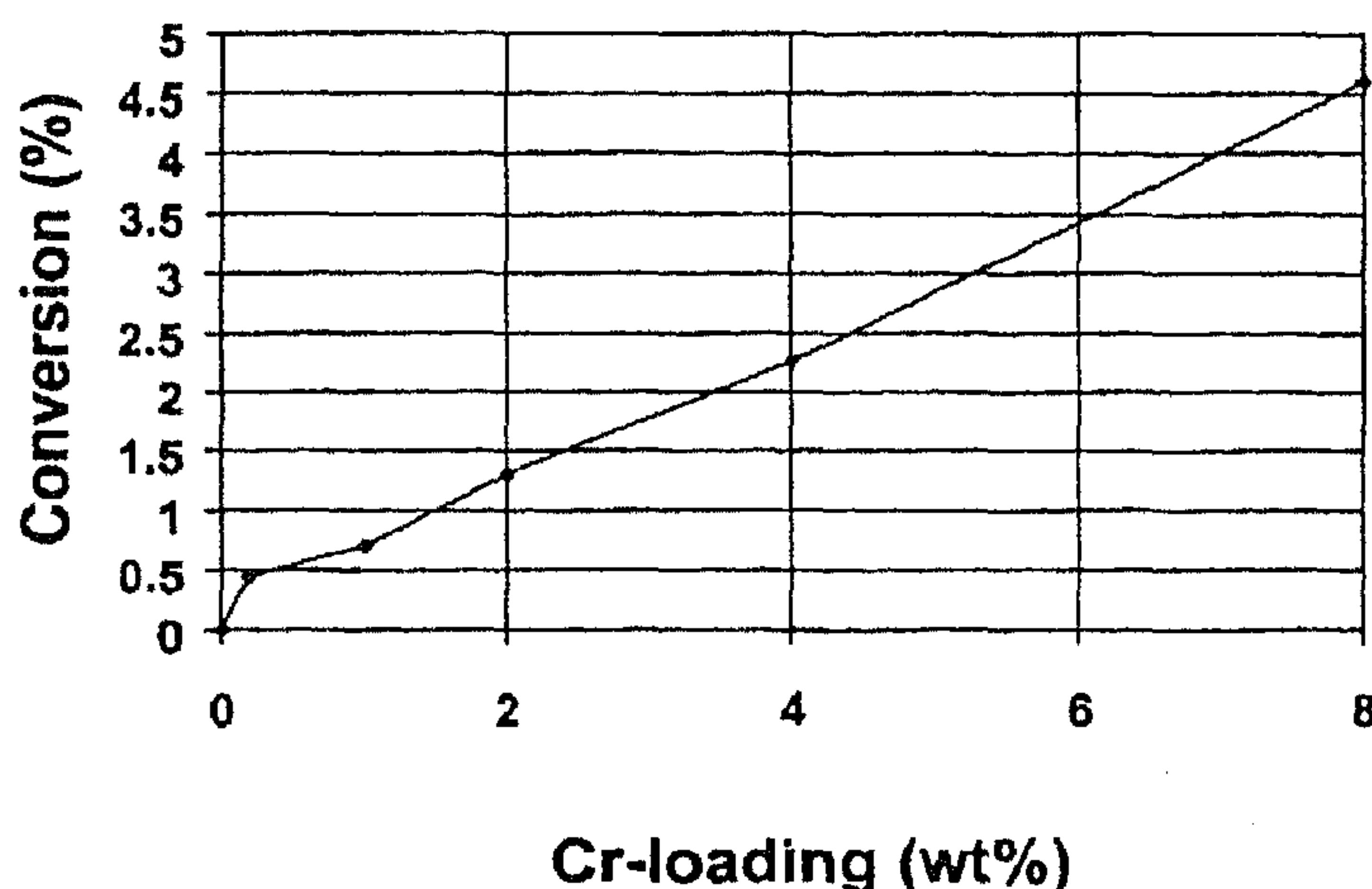


Fig. 9 – *In situ* UV-Vis DRS spectra of a 0.2 wt% Cr/Al₂O₃ catalyst treated at 500°C in n-butane as a function of time on-stream (Reprinted from Ref. (10), Copyright Royal Chemical Society, 1998).

Further evidence for this hypothesis comes from experiments in which the catalytic activity and the Cr²⁺:Cr³⁺ ratio was measured for 0.2 wt% Cr/SiO₂.Al₂O₃ catalysts as a function of the SiO₂:Al₂O₃ ratio. This is shown in Fig. 10. It is clear that the catalytic activity decreases from 0.44% for a Cr/Al₂O₃ catalyst, through 0.35% for a Cr/SiO₂.Al₂O₃ with 40 wt% SiO₂ catalyst to 0.18% for a Cr/SiO₂ catalyst. Thus, the dehydrogenation activity decreases with increasing SiO₂-content of the support. This sequence parallels the Cr²⁺:Cr³⁺ ratio on the support, as measured by quantitative DRS.²³ Thus, the dehydrogenation activity of the catalyst decreases with increasing Cr²⁺:Cr³⁺ ratio on the support.

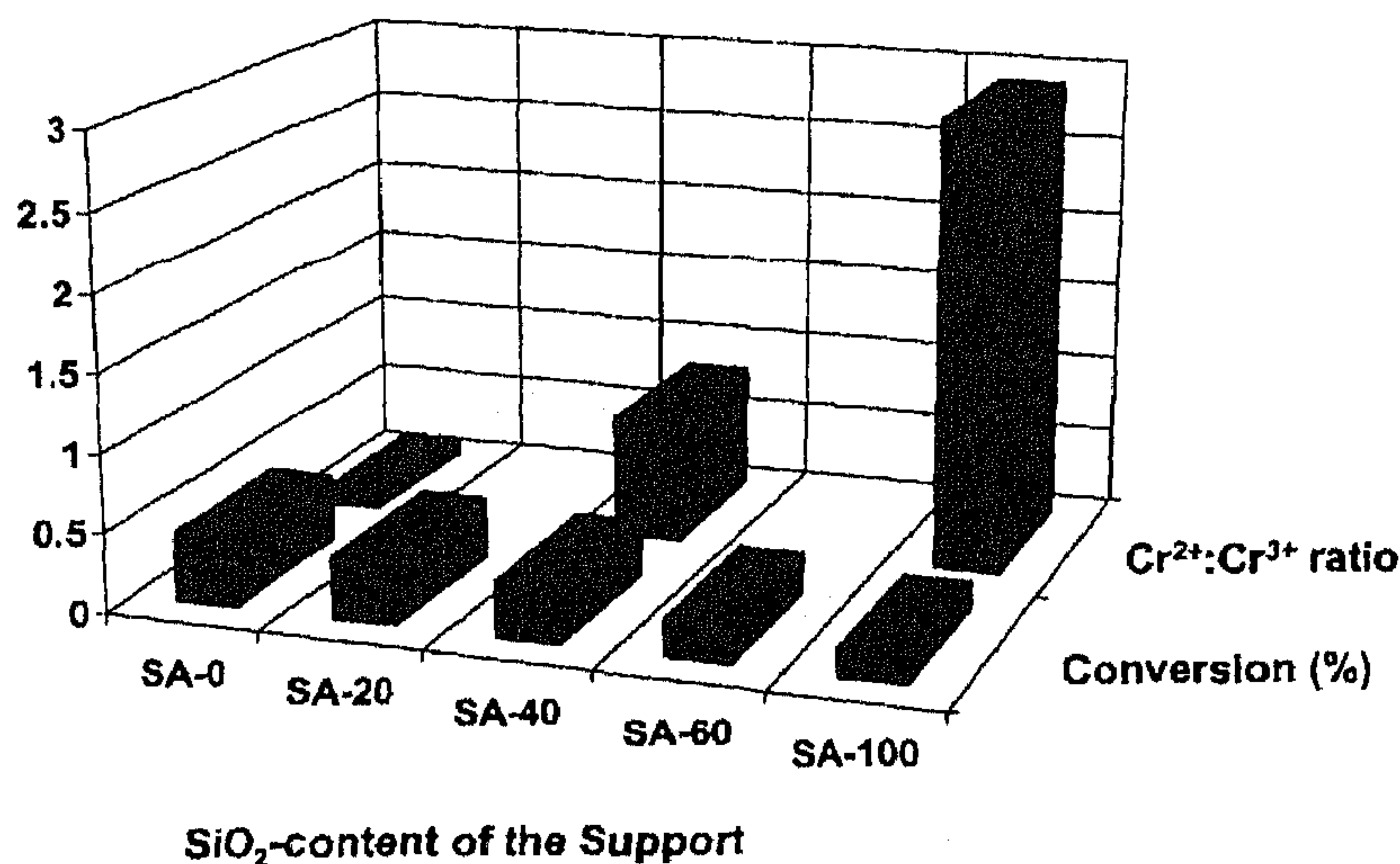


Fig. 10. – A, Conversion (%) and B, Cr²⁺:Cr³⁺ ratio as a function of the support composition for n-butane dehydrogenation at 500°C over 0.2 wt% Cr catalysts (Reprinted from Ref. (10), Copyright Royal Chemical Society, 1998).

Selective oxidation of methanol to formaldehyde over supported vanadium oxide catalysts

Supported vanadium oxide catalysts have been extensively studied by *in situ* RS and DRS for identifying the active site for the selective oxidation of methanol to formaldehyde.^{11,12} *In situ* Raman studies have revealed that the deposited vanadia phase consists of a two-dimensional surface vanadia overlayer (monomers, polymers,...) as well as V₂O₅ crystallites above monolayer coverage. The monolayer coverage, expressed as the number of V atoms per nm², together with the vibration frequency of the terminal V=O bond and the turnover frequencies (TOFs) for methanol oxidation at 230°C are summarized in Table 3.¹² The TOF, defined as the number of methanol molecules converted per surface vanadia site per second, is strongly dependent on the support, and the variation spans approximately three orders of magnitude at monolayer coverages (which corresponds with the same surface density of surface vanadia species). It was also shown that the TOFs were relatively independent of surface vanadia coverage, which indicates that the reaction rate is first order with respect to the surface vanadia sites. This suggests that methanol oxidation over the supported vanadia catalysts is a unimolecular

Table 3

Vibrations of the terminal V=O bonds, as measured by *in situ* RS, and the turnover frequencies (TOFs) for the supported vanadia catalysts at monolayer coverage¹²

Catalyst	Monolayer coverage (V atoms/nm ²)	V=O (cm ⁻¹)	TOF (s ⁻¹)
7 wt% V/Al ₂ O ₃	7.3	1026	6.8 × 10 ⁻²
2 wt% V/Nb ₂ O ₅	8.4	1033	4.0 × 10 ⁻¹
1.7 wt% V/TiO ₂	7.9	1030	1.1 × 10 ⁻⁶
1.1 wt% V/ZrO ₂	6.8	1030	1.7 × 10 ⁻⁶
0.8 wt% V/CeO ₂	5.7	1028	1.0 × 10 ⁻¹

reaction requiring only one surface vanadia site (the active site). The formaldehyde selectivities were 90–99% for the titania, zirconia, niobia and ceria supported vanadia catalysts, but only 50% for the alumina supported vanadia catalysts, and dimethylether was the major unselective product. The high dimethyl ether formation for the V/Al₂O₃ catalyst reflects the presence of surface acid sites.

During methanol oxidation, the surface vanadia species becomes partially reduced by the reaction environment. *In situ* RS during methanol oxidation revealed that the surface V⁵⁺ species retained its molecular structure, but that there was about 40–60% reduction of the V⁵⁺ Raman signal. The actual extent of reduction was probably less than 40–60% since the catalysts became slightly darker upon reduction and decreased the amount of scattered light to the detector. *In situ* DRS studies revealed the presence V⁴⁺ and the formation of surface methoxy (CH₃O-) groups upon reduction with methanol.

In order to develop structure reactivity relationships for supported vanadia catalysts *in situ* Raman studies, in combination with oxygen-18 labeling experiments and activity measurements, have been performed. The goal was to examine the role of terminal V=O bonds, bridging V–O–V bonds and bridging V–O-support bonds.¹¹ Oxygen-18 labeling of the terminal V=O bond during butane oxidation revealed that this bond is very stable and has an exchange time that is approximately 20 times longer than the characteristic reaction time. Consequently, these data suggest that the terminal V=O bonds do not contain the critical oxygen that affects the reactivity of supported vanadia catalysts during methanol oxidation. On the other hand, the surface concentration of bridging V–O–V bonds increases with surface vanadia coverage due to the increase in the ratio of polymerised to isolated surface vanadium species. The TOF for the oxidation of methanol to formaldehyde over V/TiO₂ is independent of the surface vanadia coverage indicating that the oxygen associated with the bridging functionality does not critically affect this reaction. Finally, the V–O-support has to be considered. The characteristics of this bond can

be altered by varying the specific oxide support, and the same holds for the TOFs of Table 3. Therefore, it is anticipated that the bridging V-O-support bond appears to be associated with the critical oxygen required for methanol oxidation since changing the specific oxide support dramatically affects the TOF. The general trend appears to be $\text{CeO}_2 > \text{ZrO}_2 \sim \text{TiO}_2 > \text{Nb}_2\text{O}_5 > \text{Al}_2\text{O}_3$, which inversely correlates with the Sanderson electronegativity values of the oxide support cations. This suggests that the bridging oxygens in V-O-support bonds that are more electronegative or basic, corresponding to oxide support cations with a lower electronegativity, are associated with the critical oxygen required for oxidation reactions over supported vanadium oxide catalysts.

Direct conversion of methane to aromatics over transition metal ion – containing H-ZSM-5 catalysts

The catalytic conversion of methane to desired commodity chemicals is a challenging approach for the utilization of natural gas resources. Several recent studies have demonstrated that methane can be converted to benzene, toluene and naphthalene in the absence of an oxidant, such as oxygen, over Fe/H-ZSM-5, V/H-ZSM-5, W/H-ZSM-5, Cr/H-ZSM-5 and Mo/H-ZSM-5 catalysts.^{13–16} This non-oxidative methane conversion is characterized by an induction period prior to the formation of aromatics. During this induction period the supported metal oxide is reduced and CO, CO₂, and H₂O are formed.

In order to identify the active phase for methane activation, XPS with an *in situ* transfer line has been used. As an example, the XPS spectra in the V 2p region of a 2 wt% V/H-ZSM-5 catalyst is given in Fig. 11. The calcined catalyst was slightly light yellow, and the corresponding XPS spectrum was characterized by a V 2p_{3/2} peak at 517.4 eV, which is typical for the presence of V⁵⁺. The intense peak at 523 eV is an O 1s X-ray satellite peak, which is overshadowed by the V 2p_{1/2} peak of V⁵⁺ located at around 525 eV. Treating the catalyst with methane at 750°C for 3.5 h resulted in a change in color to gray-blue. The resulting V 2p_{3/2} peak was located at 515.7 eV, which is typical for V₂O₃. The same peak position was observed for the catalyst treated for 10 h in methane; however, the peak intensity was

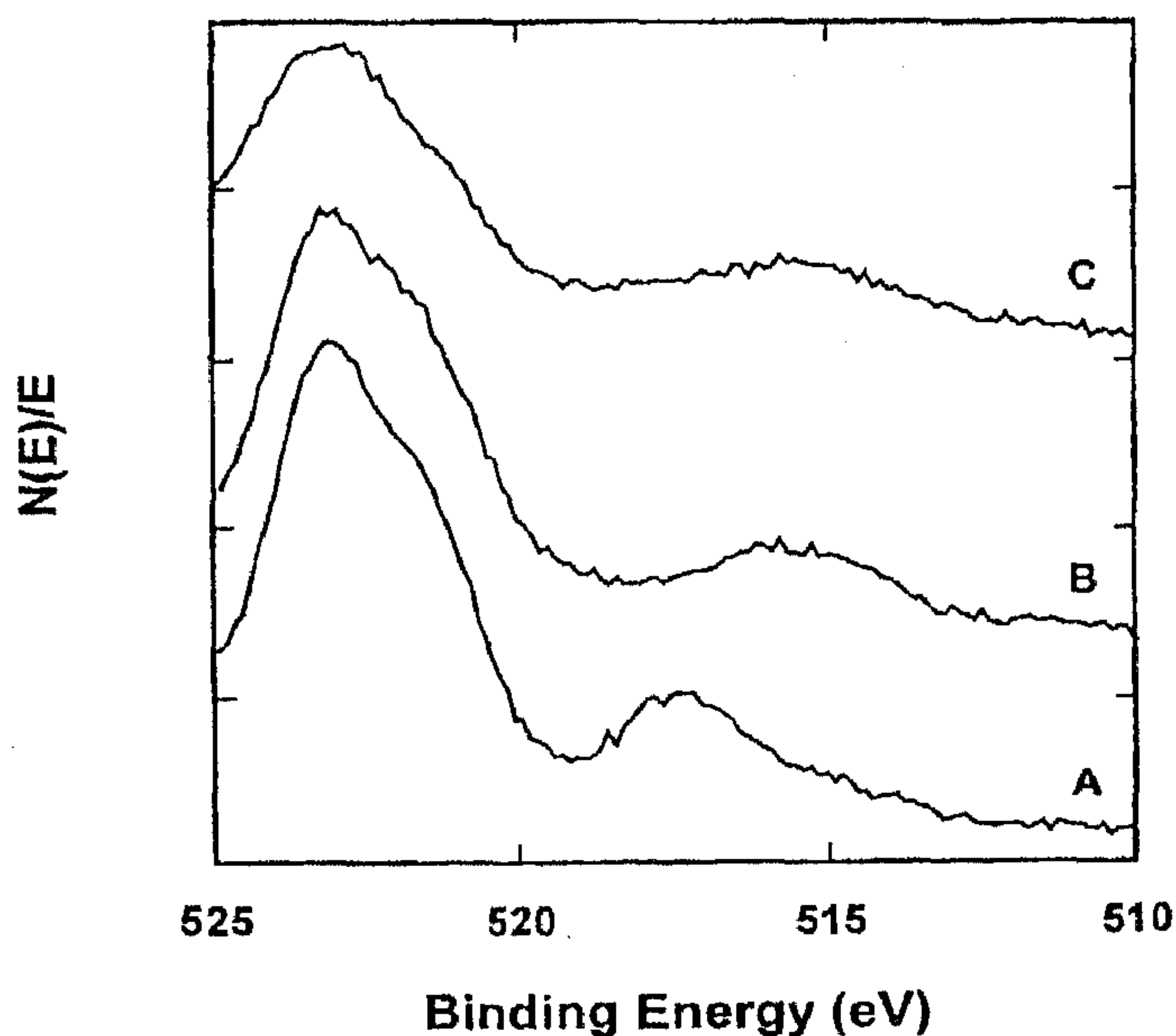


Fig. 11 – XPS spectra in the V 2p region of 2 wt% V/H-ZSM-5 catalysts: (A) after calcination at 500°C for 1 h; (B) after methane activation at 750°C for 3.5 h; and (C) after methane activation at 750°C for 10 h (Reprinted from Ref. (10), Copyright Academic Press, 1998).

less and the material was black. The corresponding C 1s region (spectrum not shown) showed an intense peak centered at around 283.2 eV, which is due to coke formation. Thus, the active V₂O₃ phase was partially covered by coke after 10 h on stream.

An overview of the active phases for the other transition metal ion-containing H-ZSM-5 catalysts is given in Table 4. It is clear that different active phases are able to activate methane at high tem-

Table 4

Survey of the catalytic active phase for methane activation as determined by XPS with in situ transfer (15)

Transition metal ion	Cr	V	Mo	Fe	W
Active phase	Cr ₂ O ₃	V ₂ O ₃	Mo ₂ C	Fe ₃ O ₄	WO ₂

peratures in the absence of oxygen. Thus, it appears that both suboxides (Fe₃O₄, V₂O₃, Cr₂O₃ and WO₂) and metal carbides (Mo₂C) are catalytically active.

CONCLUDING REMARKS AND LOOK INTO THE FUTURE

We have shown that the development and rigorous use of *in situ* spectroscopic techniques results in a fundamental understanding of several catalytic processes, for identifying the active site, and for the development of relevant structure activity relationships. Such studies require well-designed spectroscopic cells, which give rise to reasonable catalytic activities/selectivities. In this respect, further research has to be directed towards the use of optical fibers connected with a real (industrial) catalytic reactor, which enables the researcher to study a catalyst under real catalytic conditions. *In situ* DRS is the most complete and the least expensive spectroscopic technique to realize this objective, and will lead to the development of an expert system for the on line control of a catalytic reactor.

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