Methanation of carbon dioxide over Ru/Titania at room temperature: explorations for a photoassisted catalytic reaction

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The methanation of CO_2 has been investigated over a special Ru/TiO_2 catalyst suggested by Thampi, Kiwi and Graetzel [4]. This paper deals with the analysis of the material and the investigation of the reported photoenhancement of the activity. The catalyst is characterised by in situ UV-VIS spectroscopy and by XPS. Conversion experiments at atmospheric pressure were carried out with and without UV light irradiation. The irradiation increases the conversion significantly. From various experiments it can be shown, however, that this effect is due to a thermal effect and does not involve an intrinsic photochemical step. Localised Ti^{3+} states sensitise the support to convert visible light into heat resulting in the observed increase in conversion.

Keywords: Carbon dioxide methanation; Ru/TiO_2 catalyst; *in-situ* UV-VIS spectroscopy; XPS

1. Introduction

The hydrogenation of CO_2 to methane over transition metal supported catalysts has been extensively investigated for upgrading of synthesis gas [1]. Efficient catalysts are Ni based systems on various oxide supports [2]. Efforts were also made for photomethanation of CO_2 from the atmosphere using sunlight as energy source. Several systems were investigated for homogeneous catalytic reduction of CO_2 in aqueous systems [3]. Recently, a heterogeneous catalytic system for the photoassisted reduction of atmospheric CO_2 with sunlight has been suggested by Graetzel and coworkers [4–6]. This system characterised by a critical preparation technique, is studied in order to elucidate

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the nature of the active ruthenium and to investigate the light effect on conversion.

The catalyst which was initially reported to contain partially oxidic Ru [4] was later described to consist of regular particles of "RuO_x made of metallic Ru" [6] which became particularly apparent after calcining the catalyst in hydrogen at 773 K. These particles which were ca. 1.5–5 nm in size are supported on the rutile part of industrial titania (DEGUSSA P 25), consisting of a mixture of the rutile and anatase modifications. Both selective dispersion and the nature as RuO_x were emphasised to be important for good catalyst operation.

It was stated in the literature [4–6] that this catalyst is suitable for heterogeneous photomethanation comparable to molecular Ru complexes together with metallic Ru colloids in homogeneous reaction [3]. The experiments in the literature on the present catalyst systems were carried out as batch type reactions with reaction times up to 24 hours. Under these conditions a photoenhancement effect of about 4 [6] at 318 K was reported with the "most ideal" catalyst (loading 3.8% Ru) investigated in this reference. In the present work the synthesis of the material was reproduced and a characterisation of the Ru and its interaction with the support is attempted. On this basis the nature of the reported plutoenhancement of catalytic activity is discussed. Conversion experiments are used as a relative measure of catalyst performance.

2. Experimental

Several catalyst samples were kindly donated by Graetzel (Lausanne). A variety of own preparations were characterised, in this communication we compare the results for the most active catalyst from Graetzel (cat. 1) with a reproducible preparation of our own catalyst family (cat. 2). The preparation procedure was the following:

A 3.8 molar solution of $RuCl_3$ in 0.1 N HCl was prepared and left to equilibrate overnight. 1 g TiO_2 (DEGUSSA PL 5) was added and the pH increased to 4.0 by means of a 1 M NaOH solution. This solution was left at 331 K overnight, then the residue was separated from the liquid and dried at 300 K in a dessiccator. Two calcining steps at 453 K for 6 hrs and 633 K for 12 hrs were followed by a cleaning procedure of 10 cycles consisting of digesting in distilled water followed by drying overnight at 383 K. Dark, grey-bluish, coloured, loose powders resulted from successful preparations.

The BET surface area of the catalyst was with 55 m^2/g before and after impregnation unchanged. Powder X-ray diffraction did not reveal any diffraction lines from the supported material nor did it indicate any change in the support pattern after catalyst preparation.

A quartz microreactor integrated in the diffuse reflectance attachment of a Perkin Elmer lambda 9 UV-VIS spectrometer was used. The reactor was operated as differential reactor with a platelet of 15 mg catalyst freely suspended in the gas stream or as integral reactor with ca. 850 mg powder catalyst suspended on quartz wool. Before catalytic testing the sample was reduced with a mixture of 20 ml/min high-purity H_2 and 20 ml/min He at 493 K for 1 h. Spectra were recorded either after reduction of the sample or after different catalytic runs with the sample in a He stream at room temperature. The sample was either heated up to ca. 700 K thermally or, was irradiated with UV light from a 150 W Xe lamp by focussing the light from a distance of 30 to 50 cm onto the whole area of the catalyst. Methane was detected by a FID. The gas flow was adjusted by mass flow controllers and purity was checked by on-line mass spectrometry. No significant amount of other hydrocarbons were detected in the product stream. Flow conditions were 1 ml/min CO_2 in 20 ml/min H_2 diluted by 20 ml/min He.

XPS data were obtained in a Leybold LHS 12 instrument using Mg K alpha excitation (80 W, Au 4f7/2 84.0 eV). Samples were prepared as loose powders and analysed after the pressure had reached 8×10^{-10} mbar. All samples were sensitive to irradiation damage by electrons from a flood gun or from Auger excitations. No changes were observed in XPS after one minute irradiation and after ca. 6 hrs irradiation which was used for adequate data collection. Fresh catalysts were activated in an attached high pressure reaction chamber by exposing them to hydrogen at 470 K and subsequently to CO_2/H_2 mixtures at 425 K for 12 hours. Higher treatment temperatures resulted in a loss of ruthenium coverage and were therefore avoided. The reference titania was heat treated in 700 mbar pure oxygen at 425 K for 12 hrs.

Charge compensation was first tried with a flood gun leading, however, to an irreversible line broadening indicative of electron beam damage of the samples. A slight misorientation of the samples giving rise to extra secondary electrons from the gold sample holder was found to remove almost all charging. Residual inconsistencies in alignment of the binding energy scales were removed by using the maximum of the O 1s line as internal standard placed at the lowest binding energy of 529.5 eV.

3. Results

In fig. 1 characteristic UV-VIS reflectance spectra are shown for the pure support (top) and the activated catalysts. There is no difference between the spectra after reduction (shown in fig. 1) and after prolonged catalytic testing. These spectra which exhibit very different intensity scales can be interpreted following well established literature work [7,8]. Titania reflects most of the light intensity with energies below the band gap giving rise to its apparent white colour and to the edge jump in the spectra. High energy light is absorbed by a variety of interband processes. At energies below the band gap transitions

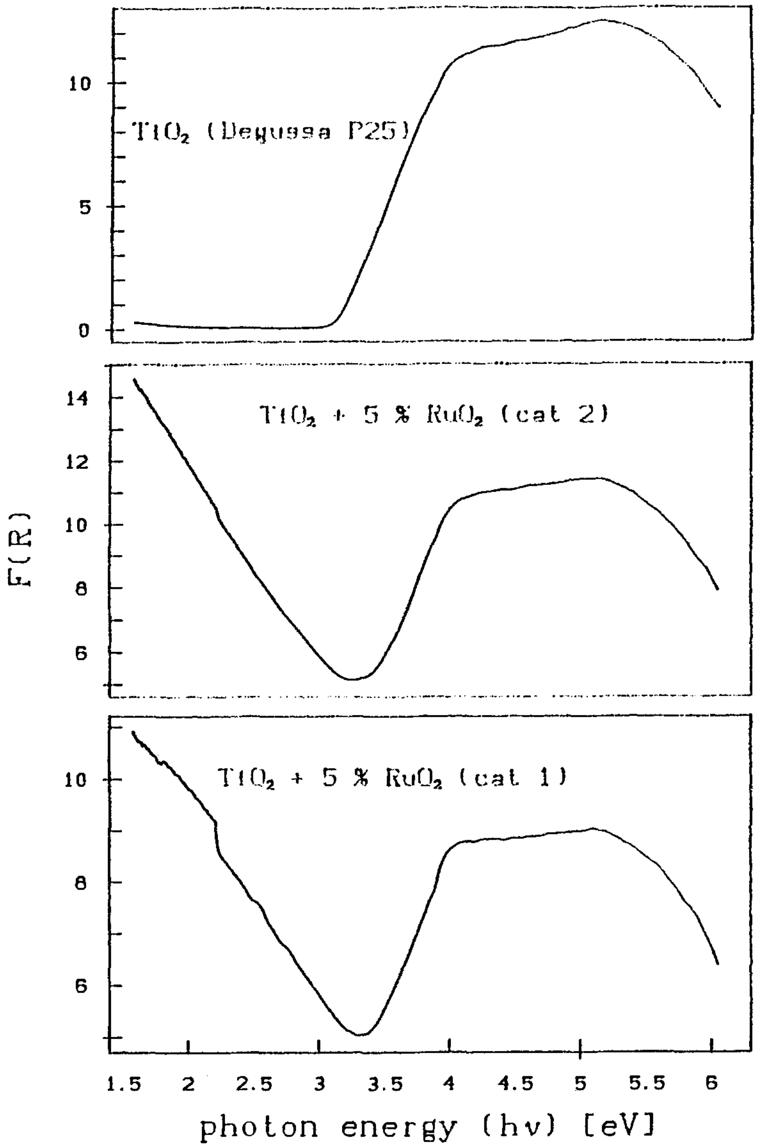

Fig. 1. Diffuse reflectance spectra of the catalyst support (top) and two catalysts after activation in situ. The spectra are corrected with the Kubelka-Munck-function, the logarithmic ordinates are different for each spectrum (see text).

between the valence band and isolated states in the band gap can occur. Such states can arise from nonstoichiometry, defects and impurities.

The band gap energy for the loaded catalysts can only be determined after a correct scaling of the spectra which are very weak due to the dark grey to black colour of the samples. The band edge jump does not disappear and its position changes systematically with the catalyst loading from 3.20 eV for the pure

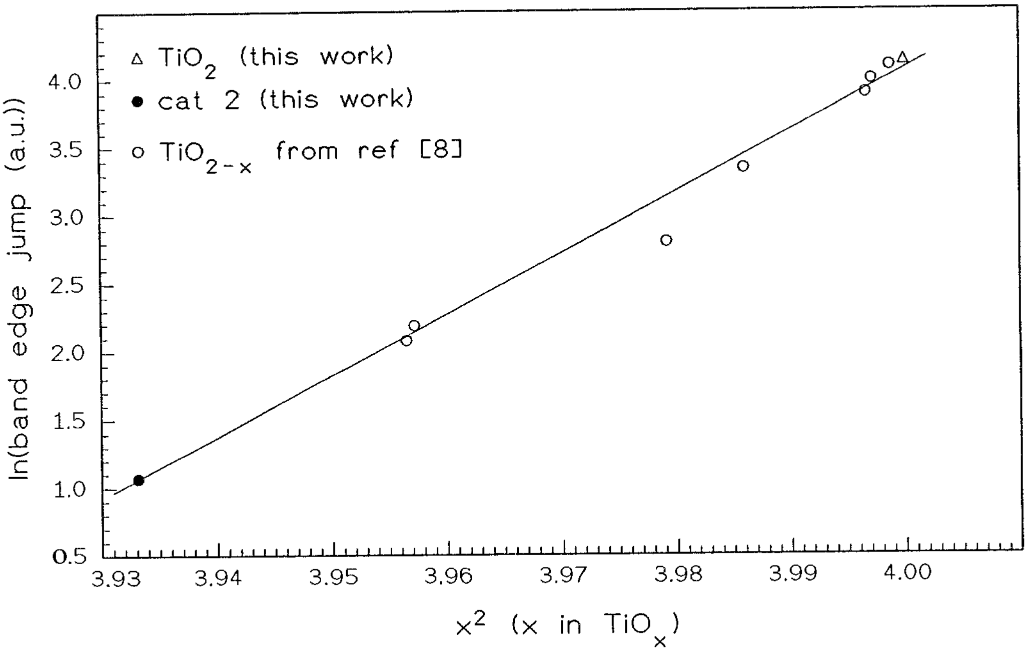

Fig. 2. Correlation of the reflectance edge height in the TiO_x spectrum (see fig. 1) with the oxygen deficiency (expressed as squared value of x). The data were taken from ref. [8] and completed by the value of the pure support.

support to 3.35 eV for 1% Ru, 3.38 eV for 3% Ru and to 3.58 eV for 5% Ru loading. The error estimated from several preparations for each loading is ca. 0.05 eV. The apparent increase in the band edge energy is an artifact caused by the extrapolation of a decreasing fraction of the band edge feature to zero F(R) indicating that with increasing catalyst loading the number of intra gap states increases. The still detectable edge jump, on the other hand, shows that a significant fraction of the analysed volume of the catalyst remains titania and is not e.g. reduced to a suboxide, which is in agreement with the XRD results.

The extra states may be intrinsic, i.e. caused by nonstoichiometry of the titania or extrinsic, i.e. caused by light absorption of the chemisorbed Ru. A series of catalysts of Ru on magnesia including the loadings of the titania catalysts gave structureless reflectance spectra totally dissimilar to the data of fig. 1. The loss in height of the band edge jump after suitable corrections may be used to estimate the oxygen deficiency. In fig. 2 data from ref. [8] are used to estimate the stoichiometry of the titania for the 5% loading to be ca. 1.983.

The titania support is thus transformed with increasing Ru loading into a material with an increasing number of intrinsic defects. This analysis is supported by the steep increase of absorption below band edge energies. A large variety of photoabsorption processes indicated by the featureless spectra in fig. 1 become thus possible with visible or even near infrared light energies which are

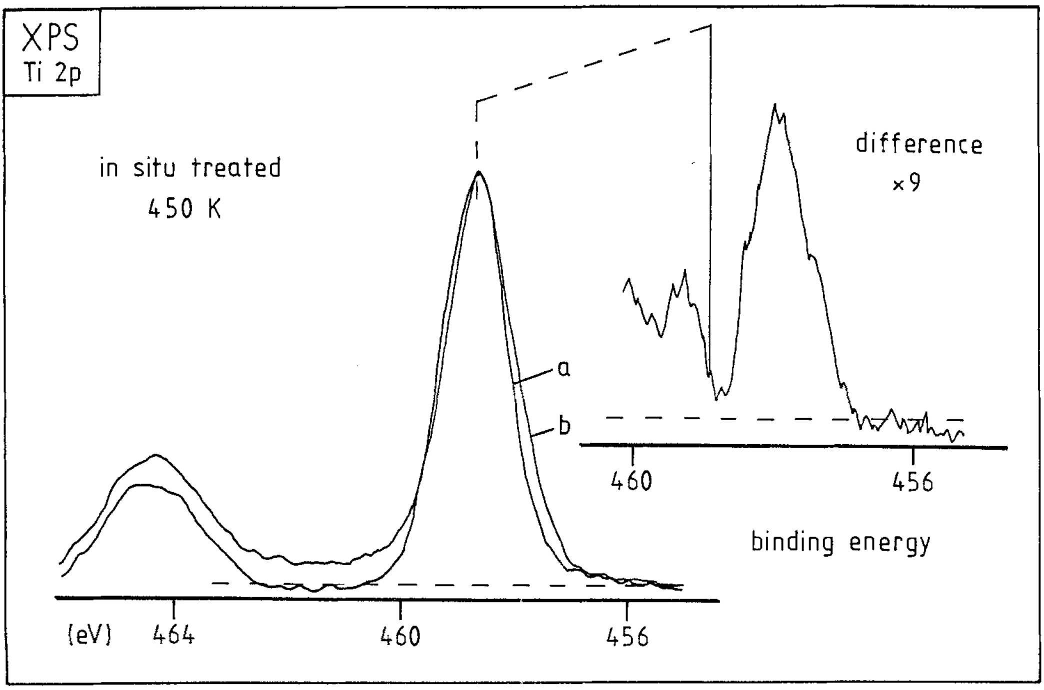

Fig. 3. Titanium 2p XPS data for the pure support (a) and the activated catalyst (b). The inset shows the difference spectrum in the region of the Ti 2p3/2 main transition.

not possible with the pure support.

A variety of samples was analysed by XPS in order to characterise the Ru species present. It turned out that a comparison of different catalysts by XPS is only possible after in situ activation since transfer and storage in air modify the spectra of titanium and ruthenium. The nominal loading of the catalysts studied was 5% Ru.

Quantitative surface analysis revealed a ratio O:Ti of 2.35:1 for the reference sample and 2.10:1 for the catalysts. Survey spectra showed that no other elements were present than Ti, Ru, C, O. A typical catalyst composition was 50 at% O, 24 at% Ti, 26 at% C and below 0.1 at% Ru. This lack of dispersion of Ru was characteristic of all samples irrespective of treatment and nominal loading. No meaningful difference in the Ru surface concentration was found for a total of 8 catalyst samples with the nominal loading of 5% from different sources. The low dispersion is in agreement with electron microscopy showing large metal crystals [6].

The titanium 2p spectra exhibit the expected doublet feature with a maximum of the Ti 2p 3/2 line at 458.8 eV in good agreement with the literature for TiO_2 [9]. The pronounced satellite spectrum was more intense and less resolved for the catalyst samples than for the reference sample. In fig. 3 the main doublet spectrum for pure P 25 (a) and for cat 2 (b) is shown. The increased satellite spectrum raises the background between the 1/2 and 3/2 component. The FWHM are different with 1.15 eV for P 25 and 1.52 eV for the catalyst. These findings point to the presence of a second titanium species in the catalyst. The difference spectrum shown in the inset for the 3/2 component reveals indeed a second Ti 2p3/2 line at 1.1 eV lower binding energy than the main line. It arises from Ti^{3+} [10] with its open d shell valence configuration accounting for the modified satellite spectrum. These results are in full agreement with the UV VIS data and illustrate that the small abundance of Ru on the surface (0.1%) can reduce a significant fraction of the support (ca. 10%) sampled by the XPS technique. This indicates that a Ru particle leads to partial reduction of the titania in a much wider environment than the immediate contact zone.

The main line of Ru (3d) almost coincides with the carbon 1s spectrum. This can be seen in fig. 4 illustrating characteristic spectra of the reference sample (a) showing only carbon and of catalysts 1 and 2 (b, c). Ru is present in both catalysts in the same abundance and as a single species with a binding energy of 279.8 eV identical to the value obtained from a Ru metal reference sample. After exposure of the catalyst to air the spectrum exhibits an additional structure at 280.7 eV indicative of partial oxidation of the metallic species present on the active catalyst. No indication of a special valence state of Ru caused by small particle effects or incorporation of carbon or oxygen as adressed by Graetzel [4–6] were found. Spectroscopic parameters and chemical reactivity of the Ru particles seen in the present study are well in agreement with those of Ru particles present on the outer surface of a zeolite [11].

Carbon is present in a graphitic state (binding energy 284.4 eV) already on the pure support and the preparation procedures do not lead to carbon accumulation. The widened C 1s profiles seen in the catalyst spectra of fig. 4 are due to an overlap with the Ru 3d 3/2 line which lies 4.1 eV above the Ru main line [11]. In addition, there is a new carbon component present after exposure of the catalyst to reaction conditions. This component can be localised in the difference spectrum at a binding energy of ca. 286.5 eV. It requires flushing to 850 K to remove this species which can–from its abundance only–be present on the whole of the support surface. It is not carbonate which exhibits a binding energy of ca. 288 to 289 eV (possibly present on the precursor, see feature in spectrum a). Its binding energy points to a structure like CH_2O–, in any case to a partial reduction product of CO_2 coordinated to surface vacancies of the oxide support. No positive evidence was found from quenching experiments that this species is involved in the mechanism of the methanation, it was present in all circumstances where methane was formed by the catalyst.

Conversion experiments with quantitative product analysis were performed in the quartz glass reactor attached to the UV spectrometer. Flow-through experiments were conducted in the differential limit with a transparent wafer and in the integral limit with a catalyst bed height of ca. 20 mm. Steady state conditions were reached after ca. 1 hour and maintained up to 100 hours after which the

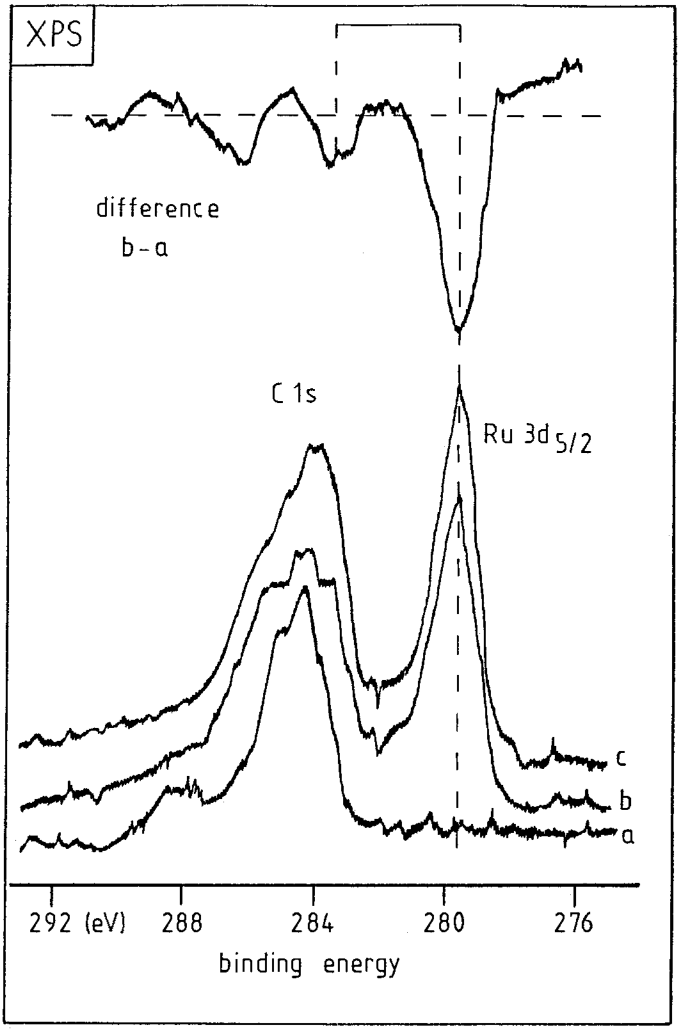

Fig. 4. Carbon 1s and superimposed Ru 3d photoelectron spectra for the pure support (a), and for the activated catalysts 1 (b) and 2 (c). The overlap of the Ru 3d 3/2 line with the C 1s line is indicated by the dashed line.

experiments were terminated. Reaction rates of 0.091 μMol g^{-1} s^{-1} at 373 K were reproducibly obtained.

Typical conversion versus temperature data for the dark reaction are for cat <2 given in fig. 5. These curves showing a small conversion at 300 K and a strong increase in activity with temperature are characteristic for a successful preparation. Variation of the most sensitive catalyst preparation parameter being the pH of precipitation led to much less and even totally ineffective catalysts. The same behaviour and very similar conversions were found with a set of catalyst samples provided by Graetzel.

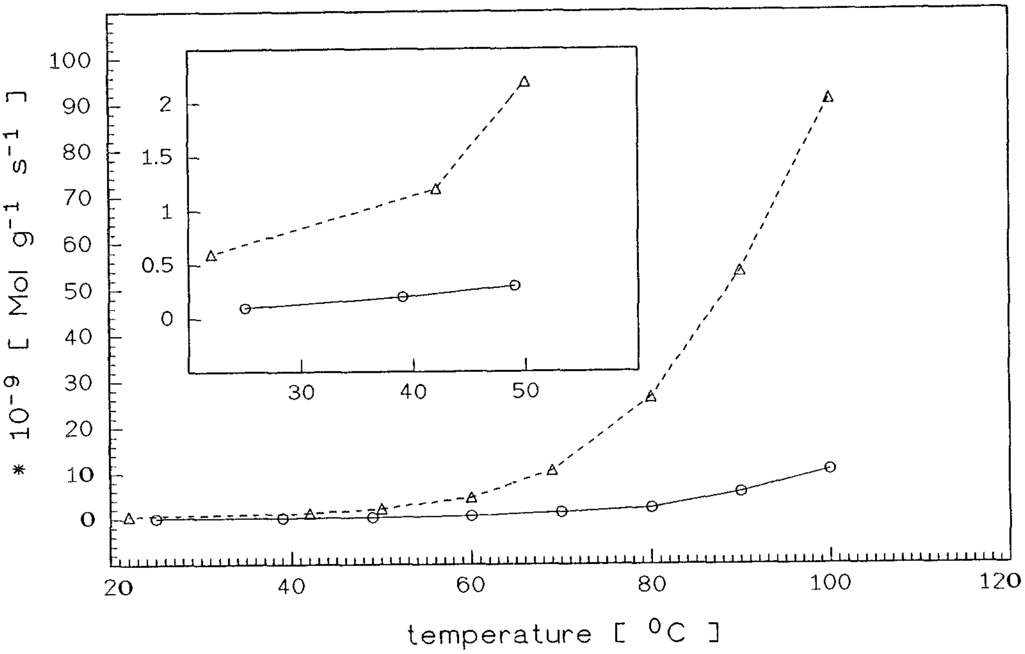

Fig. 5. Conversion vs. temperature plots for the dark reaction of catalyst 2 in the flow through reactor. The full line corresponds to the differential reactor mode, the dashed line to the integral reactor mode (see text).

The effect of UV light irradiation (Xe lamp, 150 W, distance 30 to 50 cm, all quartz apparatus) on conversion is shown for two characteristic runs in fig. 6. A thermocouple in intimate contact with the catalyst wafer allowed to monitor the actual temperature of the catalyst given in fig. 6. The conversion is significantly enhanced when the catalysts are irradiated with the enhancement factor depending on the catalyst preparation. The factor of about 2 at 298 K compares well with the factor of 4 at 319 K stated in the literature. The photoenhancement effect can be completely suppressed by passing the light through a filter consisting of a 25 mm pathlength of water. thermostated to 273 K in a quartz cell. This filter removes all low energy radiation without reducing the emission in the UV range as checked with a power meter behind the filter. The conclusion that it is not band gap light exciting the TiO_2 which causes the photoeffect is corroborated by the fact that a filter of pyrex glass which cuts out band gap light has no significant effect on the photoenhancement. The photoeffect is zero with the water filter independent of the irradiation power varied from ca. 2 mW cm^{-2} to 350 mW cm^{-2}.

The photoeffect is caused by heating the catalyst to significantly higher temperatures which is most effectively done by the low energy components of the light source. The same conversion can thus be reached by raising the temperature of the catalyst thermally to the same value as observed with light irradiation which is illustrated in the top experiment displayed in fig. 6. The

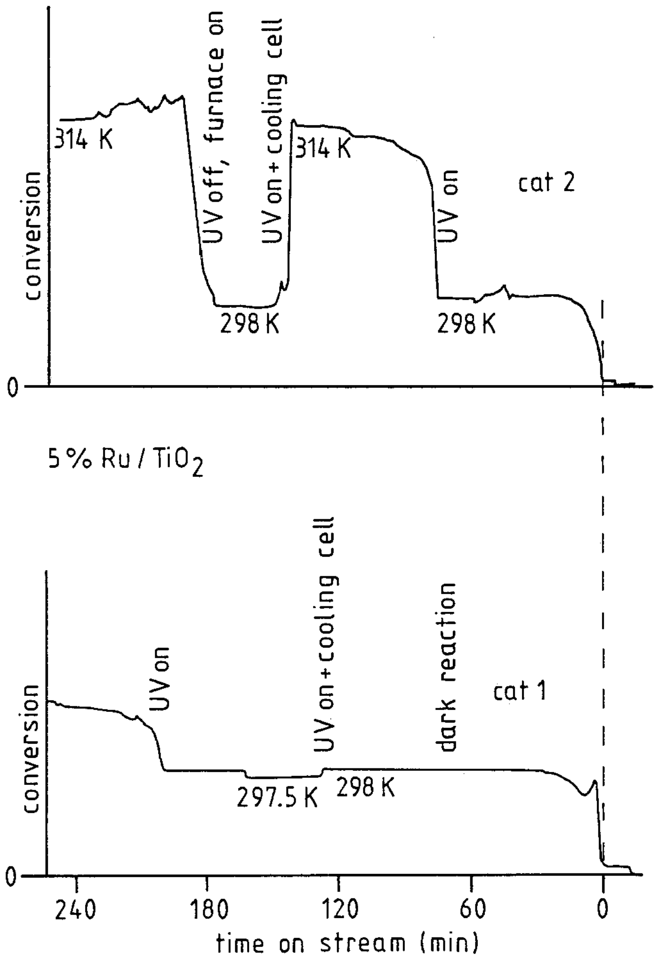

Fig. 6. Conversion vs. time plots from light irradiation experiments. The temperatures were measured on the catalyst wafers. For details of the experiments see text. The level of conversion for the dark reaction was 0.1 n Mol g^{-1} s^{-1}.

photoeffect in this system is a thermal effect supported by the partial reduction of the TiO_2 transforming it into an efficient receptor for low energy photons (see spectra in fig. 1). The photoconducting effect of the pure support is not responsible for the enhancement of the conversion. The present effect is different from the photoexcitation mechanism observed in homogeneous photomethanation [3] which is shown to proceed through a light induced redox reaction of the Ru complex.

4. Discussion

Special precipitation conditions followed by suitable calcination lead to a catalyst consisting of Ru metal particles supported on TiO_2. Assuming lateral homogeniety a mean value for the nonstoichiometry (x) of the titania was found from UV spectroscopy. The titania absorption band edge is unchanged in energy pointing to isolated Ti^{3+} states in the band gap of titania. In any case the support is sensitised by partial reduction for the absorption of low energy light (visible and infrared). With XPS it is shown that under metanation conditions only Ru metal particles without cluster size effects on the chemical shift are present. Due to the possible action of strong metal support interaction effects the true particle size was not determined from quantitative XPS. Exposure to air oxidizes some of the Ru. The presence of Ti^{3+} was substantiated in Ti 2p core level spectra. Carbon is present as inert graphitic material and as partially hydrogenated C-O species. No evidence for postulated Ru-C species as carbides [4,6] was found.

The selective conversion to methane at mild conditions was found to be strongly dependent on temperature. In flow-through experiments a photoenhancement effect on conversion was found. The magnitude of the effect depends on sample preparation and is strictly proportional to the temperature rise of the catalyst caused by light irradiation. No photoeffect of light with energies sufficient to interband transitions in excited titania was found. It is concluded that the photoenhancement of the conversion is a thermal effect under the present testing conditions (differential reactor, optical transparent catalyst wafer). The present performance of the catalyst at near ambient temperatures does clearly not merit any application [4] in pollution control.

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