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Catalysis Today 32 (1996) 163-169

CATALYSIS TODAY

Partial oxidation of methane to synthesis gas over Pt/MgO Kinetics of surface processes

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Abstract

Particular reaction steps of the partial oxidation of methane to synthesis gas over Pt/MgO, i.e. methane dissociation, CO_2 adsorption, CO adsorption and oxidation, were studied under reduced pressure in the temporal-analysis-of-product-(TAP) reactor. Kinetic rate equations and parameters were derived which led to adequate description of experimental data. Methane dissociation occurs on partly reduced metal sites and is related to a cooperative effect of surface oxygen. CO_2 adsorption proceeds via a weakly bonded precursor which is consequently transformed into carbonate and bicarbonate species. CO oxidation probably takes place on oxygen islands of the platinum surface. Two different adsorption states of CO seem to be relevant under reaction conditions. The applicability of kinetic parameters obtained from the transient studies to steady-state conditions is discussed.

Keywords: Partial oxidation of methane; Synthesis gas; Kinetics; Transient studies; CO oxidation; CO_2 adsorption; Platinum; Magnesium oxide

1. Introduction

The partial oxidation of methane to syngas catalyzed by supported noble metals usually reveals very high reaction rate resulting in strong mass and heat transfer limitation of methane conversion [1]. This, in turn, confines the derivation of intrinsic kinetic data which are required for optimizing catalyst and reactor performance. Pulse experiments under vacuum conditions, however, do allow mechanistic and kinetic investigations of particular surface reaction steps without significant heat generation under defined transport conditions (Knudsen-diffusion).

The complex network of surface reaction steps in the partial oxidation of methane was identified during earlier mechanistic studies [2] (see below). The reaction steps considered in the present work are methane dissociation [Eq. (1)], CO_2 adsorption [Eq. (7a)], CO adsorption [Eq. (7b)] and oxidation [Eq. (6a)]. Rate constants, activation energies and adsorption enthalpies of these surface reaction steps were obtained by modelling transient responses of reactants in the 'temporal-analysis-of-products'-(TAP)-reactor. Dependencies between reaction rates and surface coverages by oxygen were analyzed. Initial results on the applicability of the kinetic parameters for atmospheric pressure conditions are presented by comparing simulated data obtained on the basis of these parame-

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PII S0920-5861(96)00076-4

ters with experimental ones obtained in a fixed bed reactor.

(1) Methane activation:
$CH_4 + [\ ]_{(Pt)} \rightarrow [CH_x]_{(Pt)} + (4-x)[H]$
$(x = 1, 2, 3)$ $[CH_x]_{(Pt)} \rightarrow [C]_{(Pt)} + x[H]$
(2) Total oxidation:
(a) $[CH_x]_{(Pt)} + [O_{x/2+2}] \rightarrow [CO_2] + x/2[H_2O]$
(b) $2[H] + [O] \rightarrow [H_2O]$
$2[H] + 2[O] \rightarrow 2[OH]$
(3) Reversed Boudouard-reaction:
$[CH_x]_{(Pt)} + [CO_2] \rightleftarrows 2[CO] + x[H]$
(4) Reforming:
(a) $[CH_x]_{(Pt)} + [H_2O] \rightleftarrows [CO] + (x+2)[H]$
(b) $[CH_x]_{(Pt)} + [OH] \rightleftarrows [CO] + (x+1)[H]$
(5) Surface reoxidation:
$O_2 + 2[\ ] \rightarrow 2[O]$
(6) Consecutive oxidation:
(a) $[CO] + [O] \rightarrow [CO_2]$
(b) $2[H] + [O] \rightarrow [H_2O]$
(7) Adsorption equilibria:
(a) $CO_2 + [\ ] \rightleftarrows [CO_2]$
(b) $CO + [\ ] \rightleftarrows [CO]$
(c) $H_2 + [\ ] \rightleftarrows 2[H]$
(d) $H_2O + [\ ] \rightleftarrows [H_2O]$

2. Experimental

2.1. Catalyst preparation

The Pt(1 wt%)/MgO catalyst was prepared by incipient wetness impregnation of MgO (Johnson Matthey) with an aqueous solution of $PtCl_4$. Before impregnation MgO was calcined at 1273 K for 14 h. The impregnated precursor was dried at 393 K and calcined at 1073 K in a flow of N_2/H_2 mixture (1:1) for 6 h. The particle size amounted to 0.25–0.35 mm. A Pt dispersion of 3% was obtained by CO chemisorption.

2.2. Transient experiments

The pulse experiments were carried out in the TAP reactor described elsewhere in detail [3]. Before pulsing reactants (CH_4, CO, CO_2) the catalyst was reduced in-situ in H_2 or CO at 1050 K. The reactant gases were premixed with neon as internal standard in a ratio of 1:1. Methane dissociation was investigated using a pulse size of 0.8×10^{15} CH_4 molecules. When studying the interaction of CO and CO_2 with the catalyst surface pulse sizes of 0.7×10^{15}–1.5×10^{15} molecules were applied. For mass spectrometric analysis the following atomic mass units were used: 44 (CO_2), 32 (O_2), 28 (CO_2, CO), 20 (Ne), 15 (CH_4), 2 (H_2).

2.3. Steady-state kinetic experiments

The experiments were carried out using a U-shaped quartz reactor ($d_{inner} = 3$ mm) immersed in a heated fluidized sandbed. The Pt/MgO-catalyst was packed between two layers of quartz grains (0.250–0.355 mm). Before reaction the catalyst was heated up to the reaction temperature in a nitrogen flow of 50 cm^3(STP) min^{-1} and consequently reduced in a hydrogen flow of 50 cm^3(STP) min^{-1}. Finally, the reactor was flushed with nitrogen and fed with the reactants. After 20 min of steady-state operation the products were analyzed by gas chromatography.

3. Evaluation of kinetic data

Evaluation of kinetic data obtained in the TAP-reactor was based on a reactor model by Rothaemel [4]. The solution of the partial differential equations

$$\frac{\partial c_i}{\partial(t,x)} = f(c_i)$$

(where c_i is the concentration of component i, t is time, and x the axial reactor coordinate) was performed by a software routine PDEONE (Sincovec et al. [5]) which was based on the method of lines. The estimation of kinetic parameters was carried out applying the Nelder–Mead algorithm.

4. Results and discussion

4.1. Methane dissociation

In earlier mechanistic studies the initial step of methane conversion was identified as its dissociation on partly reduced metal sites [Eq. (1)]. Both completely reduced as well as oxidized catalyst inhibited the methane conversion [2] and a cooperative effect of small amounts of surface oxygen in the methane dissociation and formation of surface carbon species was evident. At higher coverages by oxygen a fast oxidation of carbon species to CO_2 was observed. In the present study the initial step to carbon deposits was considered [Eq. (1)] excluding consecutive formation of CO_2 or CO. For this purpose methane was pulsed over the partly reduced catalyst surface. A simple reaction model was assumed to describe the methane conversion:

$$CH_4 + Pt/O_y \rightarrow [CH_x - Pt/O_y] + (4 - x)[H]$$

Since hydrogen could not be observed as product due to its strong adsorption or formation of OH-groups only the methane signal was used for estimating the rate constant. The comparison between experimental and calculated methane response is illustrated in Fig. 1. The adequate description of experimental pulse shape was obtained within the whole investigated temperature range. The dependency between the logarithm of rate constants and reciprocal temperature reveals a linear relationship resulting in an activation energy of 46 kJ mol^{-1}. The number of active sites was obtained by parameter estimation on the basis of the transient data. The value corresponding to 0.3% of total surface Pt atoms was significant but appears rather low. In this context the cooperative effect of surface oxygen for methane dissociation which was found in former experiments [2] have to be mentioned. Since the catalyst was widely reduced the concentration of active platinum–oxygen ensembles should be low.

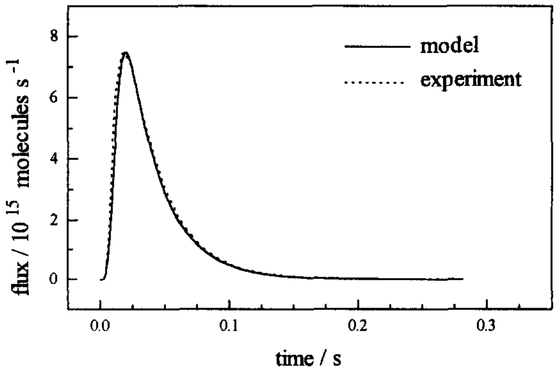

Fig. 1. Comparison between simulated and experimental methane response at the reactor outlet obtained after pulsing methane over Pt/MgO pre-reduced at 847 K.

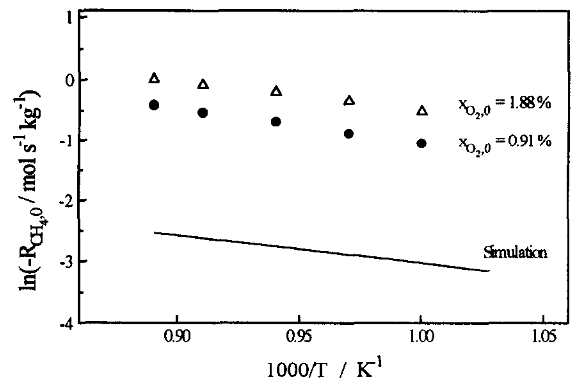

Fig. 2. Comparison between experimental initial rates of methane conversion in a steady-state fixed bed reactor with simulations on the basis of kinetic parameters resulting from TAP data (steady-state conditions: total pressure $p = 1.8$ bar, molar fraction: $x_{CH_4} = 6\%$) (△,●, experiment; —, simulation).

Applying the rate constants derived from the transient experiments under vacuum conditions to steady-state conditions at atmospheric pressure it becomes evident (Fig. 2) that significant deviations between experimental data of initial rate of methane conversion and those calculated on the basis of the estimated rate constants exist. These deviations by a factor of 5–10 are more distinct at higher oxygen partial pressure. This fact can also be assigned to the cooperative effect of surface oxygen in the methane dissociation, i.e. the number of active platinum–oxygen ensembles would increase caused by the presence of gas-phase oxygen. The agreement between the simulated and experimental slope of the logarithmic reaction rate in Fig. 2 which corresponds to a good agreement on the activation energy is an additional indication that the deviations are caused by a different number of active sites existing under transient and steady-state conditions.

4.2. CO_2 adsorption

Since the reaction between CO_2 and surface carbon [Eq. (3)] is one of the main pathways of CO formation in the partial oxidation of methane the active state of CO_2 as well as its surface coverage is of interest.

CO_2 was reversibly adsorbed within the investigated temperature range 847–1050 K. At low temperature (847 K) the transient response of CO_2 at the reactor outlet is described by a sharp narrow signal with a long tailing and a maximum at very short time (cf. Fig. 3a). This feature becomes less distinct with increasing temperature (cf. Fig. 3b). For the description of the experimental transient response following models were proposed:

Model L: Langmuir adsorption model $CO_2 + [\,] \rightleftarrows [CO_2]$

Model P: adsorption model including two different adsorption states of CO_2 on the catalyst surface – a weakly adsorbed precursor and a stronger adsorbed CO_2 or carbonate species.

$CO_2 + [\,] \rightleftarrows [CO_2]_{precursor}$

$[CO_2]_{precursor} \rightleftarrows [CO_2]$

The comparison between experimental and calculated CO_2 signal (Fig. 3a) clearly shows that at low temperature only model P was able to describe the experimental data adequately. At high temperature, however, no discrimination between the two models was possible. Taking into account the estimated activation energies and adsorption enthalpy (Table 1) it becomes evident that for model P the desorption of the precursor is more accelerated at high temperature than its transformation into the strongly

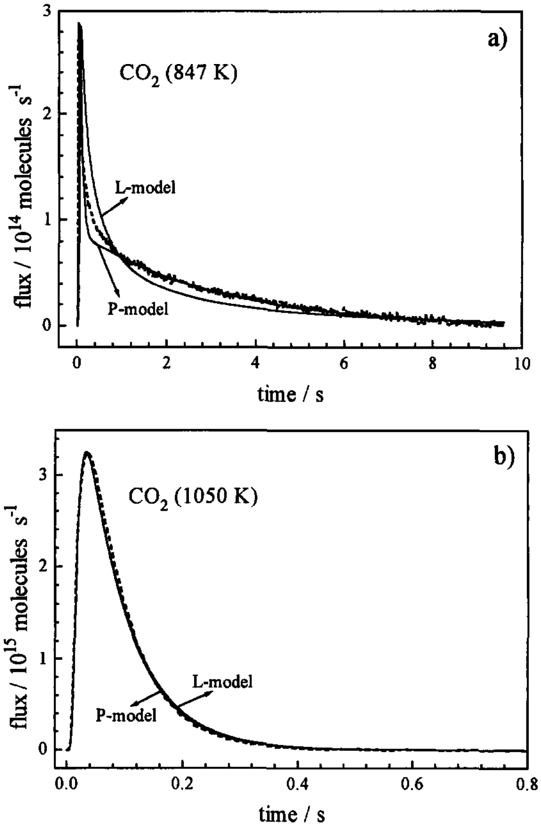

Fig. 3. Comparison between simulated and experimental CO_2 response obtained at the reactor outlet after pulsing CO_2; simulation performed on the basis of Langmuir adsorption and adsorption via a precursor (· · ·, experiment; —, simulation).

Table 1
Kinetic parameters estimated on the basis of transient data over Pt/MgO

Reaction step	k_0 (s^{-1})	k_0^{rev} (s^{-1})	E_A (kJ mol^{-1})	E_A^{rev} (kJ mol^{-1})	$\Delta_R H_{ads}$ (kJ mol^{-1})
$CH_4 + [Pt/O_y] \rightarrow [CH_x\text{-}Pt/O_y] + (4-x)[H]$	8.7×10^4		46		
$CO_2 + [\,] \rightleftarrows [CO_2]_{precursor}$					−241
$[CO_2]_{precursor} \rightleftarrows [CO_2]$	4.9×10^3	9×10^3	49	71.4	
$CO + [\,] \rightleftarrows [CO]$					−163
$[CO] + [O]_{island\ A} \rightarrow [CO_2] + [O]_{island\ B}$	7.4×10^{15}		265		
$CO_{gas} + [O]_{island\ A} \rightarrow [CO_2] + [O]_{island\ B}$	1.6×10^6		82		

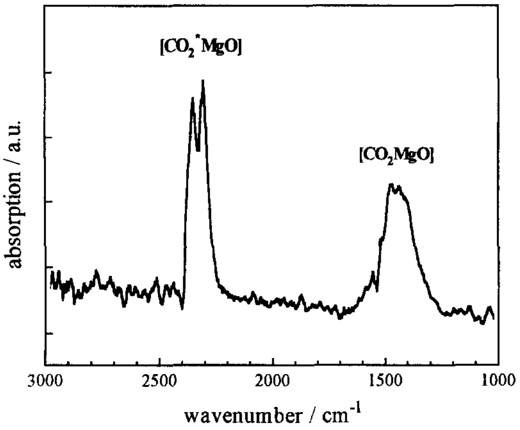

Fig. 4. DRIFT spectrum of CO_2 adsorbates on Pt/MgO during admission of CO_2 at 973 K.

adsorbed CO_2 species. Hence, the surface coverage of these strongly bonded species approaches zero at higher temperature and the adsorption kinetics becomes analogous to the Langmuir type.

The assumption of a weakly adsorbed CO_2 precursor is supported by the DRIFT spectrum obtained after CO_2 adsorption on Pt/MgO at 973 K (cf. Fig. 4). Here, adsorption bands were observed at 2353 cm^{-1} and 2342 cm^{-1}. Since the antisymmetric stretching vibrations of gas-phase CO_2 lead to a band at 2326 cm^{-1}, with shoulders at 2364 cm^{-1} and 2392 cm^{-1} the observed bands should result from weakly adsorbed CO_2 species on MgO as it was already proposed in literature [6]. The band shift compared to gas-phase CO_2 was explained by lateral interactions of the linearly adsorbed CO_2 with surface OH groups. The bands in the range 1400–1600 cm^{-1} correspond to carbonate and bicarbonate species.

4.3. CO oxidation

CO oxidation was considered for the transient study since it was expected to occur rapidly under steady state conditions in the fixed bed reactor.

CO oxidation was studied depending on the coverages of the catalyst surface by oxygen. These different coverages were obtained by pulsing different amount of CO molecules which was accompanied by consumption of surface oxygen. The transient responses of the reactant CO and the product CO_2 are presented in Fig. 5a–d.

In order to fit the experimental responses of CO and CO_2 the following models of CO oxidation were tested.

Langmuir–Hinshelwood model:
$[CO] + [O] \rightarrow [CO_2] \rightarrow CO_{2(gas)}$
Eley–Rideal model:
$CO_{(gas)} + [O] \rightarrow [CO_2] \rightarrow CO_{2(gas)}$
Combined Langmuir–Hinshelwood/Eley–Rideal model, i.e. both reaction steps (a) and (b) occur simultaneously, as already proposed in the literature for CO oxidation on Pt surfaces [7].

The comparison between the fits obtained on the basis of the three different reaction models showed that the Langmuir–Hinshelwood model was not able to describe especially the CO_2 response at low temperature (847 K) (Fig. 5c). Thus, the maximum of the calculated transient signal appeared too late compared to the experimental findings. At higher temperature for both CO and CO_2 satisfying fitness was obtained (Fig. 5b, d). The Eley–Rideal model on the other hand, revealed also discrepancies between experimental and calculated signals at low temperature. These differences were most pronounced in the range of the tailing of the CO_2 response, indicating that the CO adsorption cannot be neglected completely. Satisfying description of both CO and CO_2 responses in the whole investigated temperature range was only obtained assuming the parallel formation of CO_2 via Langmuir–Hinshelwood and Eley–Rideal mechanism. Experimentally, however, there is no proof for a reaction between CO from the gas-phase with surface oxygen according to the Eley–Rideal mechanism. In the literature it was proposed that two different states of adsorbed CO species exist on Pt surfaces – chemisorbed CO molecules and weakly bonded species being highly mobile on the surface [7]. In this context

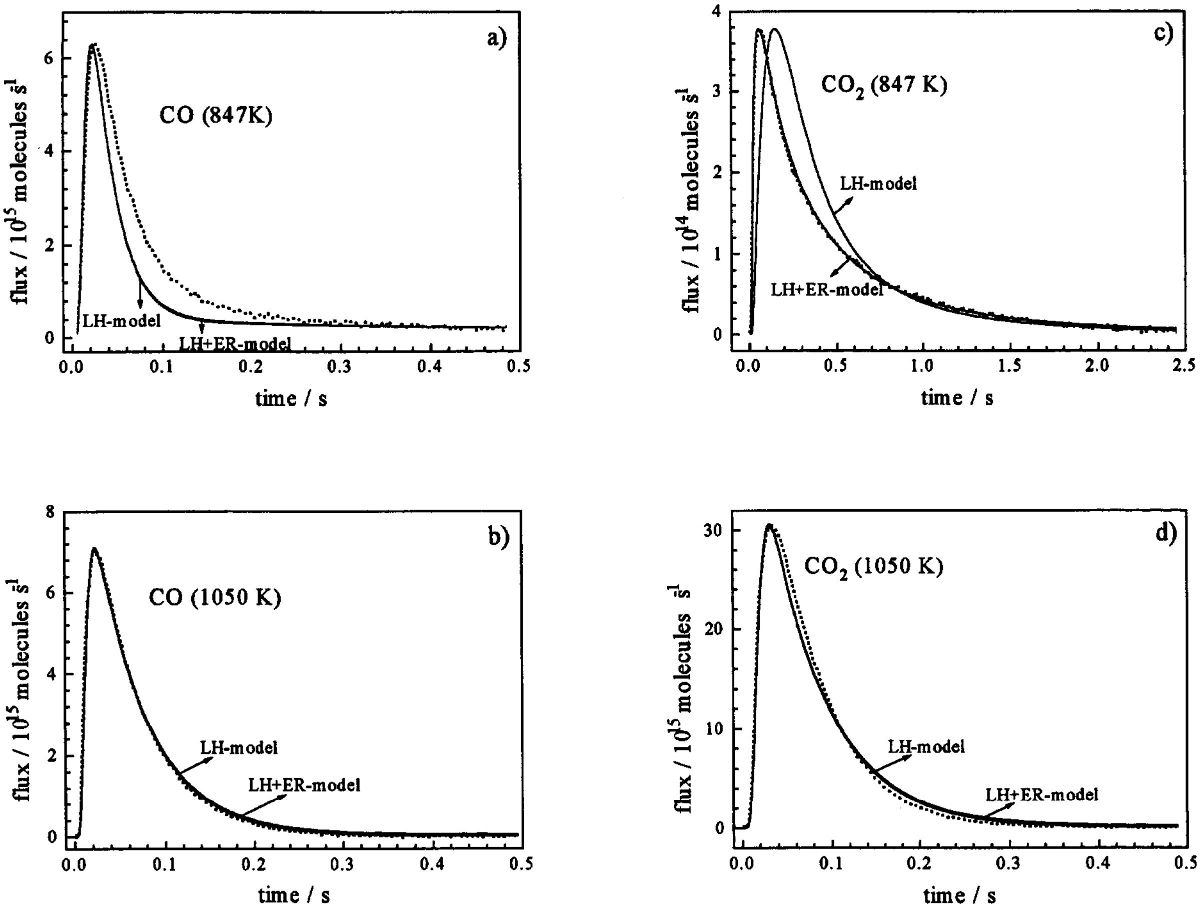

Fig. 5. Comparison between simulated and experimental CO and CO_2 responses at the reactor outlet obtained after pulsing CO; simulation performed on the basis of a Langmuir–Hinshelwood and a combined Langmuir–Hinshelwood/Eley–Rideal mechanism (· · ·, experiment; —, simulation).

the combination of both types of reaction mechanism can be interpreted as indications for these two states of surface CO where the mobile CO species have very low adsorption enthalpy and can be described as a two-dimensional gas.

In the beginning of modelling procedure a rate equation including first order with respect to CO concentration as well as concentration of surface oxygen (Θ_O) was assumed. To verify the validity of this assumption the term $k \times \Theta_O$ (k = rate constant, Θ_O = coverage by oxygen) resulting from parameter estimation on the basis of the combined Langmuir–Hinshelwood/Eley–Rideal model was analyzed. No influence of the initial surface coverage by oxygen on the calculated value of $k \times \Theta_O$ could be found indicating that the reaction order with respect to surface oxygen cannot be 1 but must be zero. This can be explained by the existence of oxygen agglomerates on the surface. Their number which determines the reaction rate would be constant even for a high number of converted CO molecules and consumed oxygen atoms, respectively. This hypothesis is supported by literature reports on the observations of oxygen islands on Pt surfaces [8]. With increasing temperature these islands are transferred into subsurface oxygen. As the surface oxygen the subsurface oxygen appears in high local concentrations. At reaction temperatures applied in the present kinetic study the surface oxygen should be completely transformed into subsurface oxygen. Nevertheless, it is known from other studies on CO oxidation that CO promotes the re-transformation of subsurface oxygen into surface oxygen [9]. Taking into account these findings, the relevance of oxygen islands as active sites also under the present reaction conditions is assumed.

The pre-exponential factors, activation energies and adsorption enthalpies obtained for the various reaction steps are summarized in Table 1.

5. Conclusion

On the basis of transient experiments intrinsic kinetic parameters were obtained for particular surface reaction steps of the partial oxidation of methane to synthesis gas. On the basis of these parameters experimental data of methane dissociation, CO_2 adsorption, CO adsorption and oxidation were adequately described.

The comparison between simulated rates of initial methane conversion and experimental ones in a steady-state fixed bed reactor pointed out the underestimation of the reaction rate. This result indicated that the cooperative effect of surface oxygen on the methane dissociation must be taken into account under steady-state condition.

The study of CO_2 adsorption and CO oxidation on Pt/MgO illustrated that mechanistic models of complex surface processes reflecting the physico-chemical findings can be derived from transient data. This includes the derivation of different states of adsorbates, the state and number active sites. It was found that CO_2 adsorption proceeds via a weakly bonded precursor which is consequently transformed into carbonate and bicarbonate species. CO oxidation probably takes place at oxygen islands of the platinum surface. Two different adsorption states seem to be relevant under reaction conditions – weakly bonded mobile species and chemisorbed CO species.

Kinetic parameters obtained in the present study will be applied to further modelling of the more complex steps in the partial oxidation of methane, i.e. the oxidation of surface carbon species [Eq. (2)] and the reversed Boudouard-reaction [Eq. (3)].

Acknowledgements

This work has been funded by the European Union (contract no. JOU2-CT92-0073).

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