Catalysis Letters 11 (1991) 95–104

Mechanism for the catalytic exchange of methane with deuterium on Pt(111) surfaces

Francisco Zaera

Department of Chemistry, University of California, Riverside, California 92521, U.S.A.

Received 23 July 1991; accepted 21 August 1991

The reaction of methane with deuterium on Pt(111) single crystals was studied using thermal programmed desorption (TPD) under ultra-high vacuum conditions. Methyl groups, believed to result from the dissociative adsorption of methane under catalytic conditions, were deposited directly by thermal decomposition of methyl iodide. TPD experiments after coadsorption with deuterium show that methane formation occurs in very high yields. Furthermore, the desorbing molecules display a bimodal distribution very similar to that obtained under atmospheric pressures, with maxima for CH_3D and CD_4. This distribution can be explained by a competition between two surface reactions, namely, direct incorporation of hydrogen in methyl groups and methylene formation followed by rapid interconversion to methylidyne before final hydrogenation to methane. We found that the rates for both reactions depend linearly on the coverage of methyl groups, but while the hydrogenation rate is also proportional to the coverage of deuterium, in the case of multiple H-D exchange an almost zero order dependence at low temperatures slowly becomes first order as the reaction temperature is increased. The activation energies for CH_3D and CD_4 formation were estimated to be 17.0 and 6.5 kcal/mol respectively even though the reaction rates displayed comparable values because of a compensation effect in the preexponential factors. Finally, the relative yields for CH_2D_2, CHD_3 and CD_4 are close to the equilibrium values, a result that is consistent with the proposed methylene-methylidyne interconversion step in our mechanism.

Keywords: Methyl; methyl iodide; methane, H-D exchange; platinum

1. Introduction

The interaction of alkanes with metal surfaces is at the heart of many catalytic processes such as oil reforming, Fischer-Tropsch, and other syn gas reactions. The understanding of alkane activation on transition metals was greatly advanced when deuterium became readily available and when mass spectrometers became widely accessible in research laboratories. Many studies were done in the 1950's in order to understand the catalytic conversion of alkanes [1–3], and though a wealth of information resulted from that work, the mechanism for those reactions were not entirely clarified. It is believed that the rate limiting step in these heterogeneous processes is the dissociative chemisorption of alkanes on the metal surface [1–5], and recent molecular beam studies under controlled environments have provided good estimates for the activation energy of that initial step [6–11]. However, much less is known about the subsequent surface reactions. Studies on H-D exchange reactions have shown that the deuteriated products often display a bimodal distribution, suggesting that at least two different mechanisms are operative on transition metal surfaces [1–4,12–14], and since most of that work was done on supported catalysts, it was originally proposed that such competing pathways take place on different sites on the surface. However, more recent studies obtained using single crystals have provided evidence for the existence of a common intermediate which forms on one single site with a particular local surface geometry [15,16]; we believe that such is also the case for the reaction of methane with deuterium on platinum catalysts.

The activation of both methane and ethane have been the most studied among the alkane reactions. Several research groups have undertaken the direct study of methane activation using modern surface sensitive analytical techniques [6–11,17,18] while others have focussed their attention on the isolation of potential surface intermediates such as methyl, methylene, ethyl and ethylidyne moieties [19–26]. We have recently been able to isolate and characterize both methyl and methylene groups on Pt(111) be starting from methyl iodide [27], and have also shown that, when coadsorbed with deuterium, those moieties produce methane with high yields and with a product distribution resembling that seen in catalytic processes [28,29]. In this report we present additional studies on the kinetics for the hydrogenation of methyl groups and analyze the resulting product distributions in order to elucidate the mechanism responsible for these processes.

2. Experimental

The experiments reported here were done in an ultra-high vacuum (UHV) stainless steel bell-jar pumped with a turbomolecular pump to a base pressure of about 1×10^{-10} Torr [30]. This chamber is equipped with a mass quadrupole used for thermal programmed desorption (TPD), a 50-mm radius concentric hemisphere electron energy analyzer used for Auger (AES) and X-ray photoelectron (XPS) spectroscopies, an electron gun, a X-ray source with aluminum anode, a sputtering gun for cleaning, gas dosing facilities, and a manipulator capable of cooling down the sample below 90 K and resistively heating it to above 1200 K.

The thermal desorption of up to ten different molecular fragments was followed simultaneously in a single experiment by using a computer interfaced to the mass spectrometer. Methane TPD spectra were corrected for contributions due to cracking of all possible combinations of isotopically substituted methane molecules using a method described in detail elsewhere [31]. The mass spectrometer sensitivities to methyl iodide, methane, and hydrogen were calibrated by a mass balance analysis also described elsewhere [27]. The resulting values for both the absolute reaction rates and the absolute surface coverages (from integration of the TPD traces) are only accurate within a factor of two, but the relative ionizer sensitivities for the different desorbing products are good within 5% even when comparing data from different experiments. Blank experiments were done in order to estimate the amount of preadsorbed hydrogen from background gases; it amounted to about 3% of a monolayer of atomic hydrogen on the surface [32]. Unless otherwise specified, the coadsorption experiments were done by dosing the deuterium first.

The platinum (111) single crystal was cut and polished using standard procedures and cleaned under vacuum by a combination of oxygen treatments and sputtering-annealing cycles until no impurities were detected by either AES or XPS. Deuterium gas was purchased from Matheson (9.5% D atomic purity) and used as supplied. Methyl iodide was obtained from Alfa (99% purity) and, because of its sensitivity to light, was kept in dark glass bulbs and freeze-pumped daily. The purity was periodically checked by mass spectrometry.

3. Results

TPD spectra from coadsorbed deuterium and normal methyl iodide on Pt(111) have shown that methane formation takes place with almost 100% efficiency at high deuterium surface coverages; fig. 1 displays results obtained from a platinum surface dosed sequentially with 0.5 L D_2 and 1.5 L CH_3I, which correspond to surface coverages of $\theta(D) = 0.165$ and $\theta(CH_3I) = 0.070$ respectively. We have plotted only the onset of the thermal desorption since in that region the surface concentrations do not change appreciably and therefore the data can be directly related to pseudo zero order reaction rates. Over 75% of the methane yield was comprised of CH_4 and CH_3D resulting from direct

Table 1
Dependence of the rates for methane formation on surface coverages ($T = 265$ K)

$\theta(CH_3)$	$\theta(D)$	$R(CH_3D)$ *	R(exchange) *
0.070	0.165	0.180	0.087
0.067	0.296	0.233	0.089
0.040	0.249	0.113	0.067
0.061	0.230	0.228	0.077

* Rates in monolayers/s.

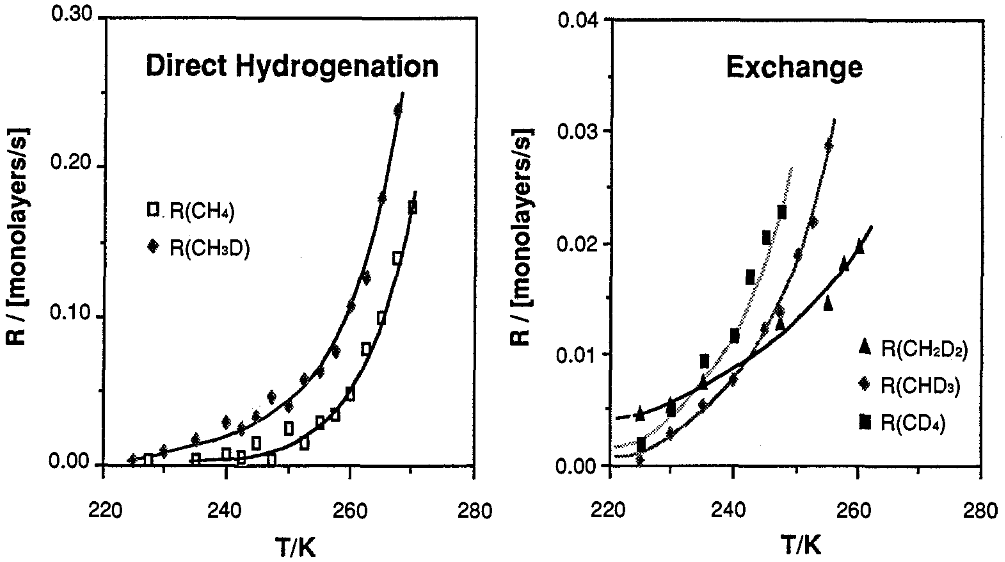

Fig. 1. Methane thermal desorption spectra after sequential adsorption of 0.5 L D_2 and 1.5 L CH_3I on Pt(111) at 100 K (1 L = 10^{-6} Torr.s). Desorption of all possible deuterium substituted methane molecules are shown; only the leading edge of the spectra is displayed here.

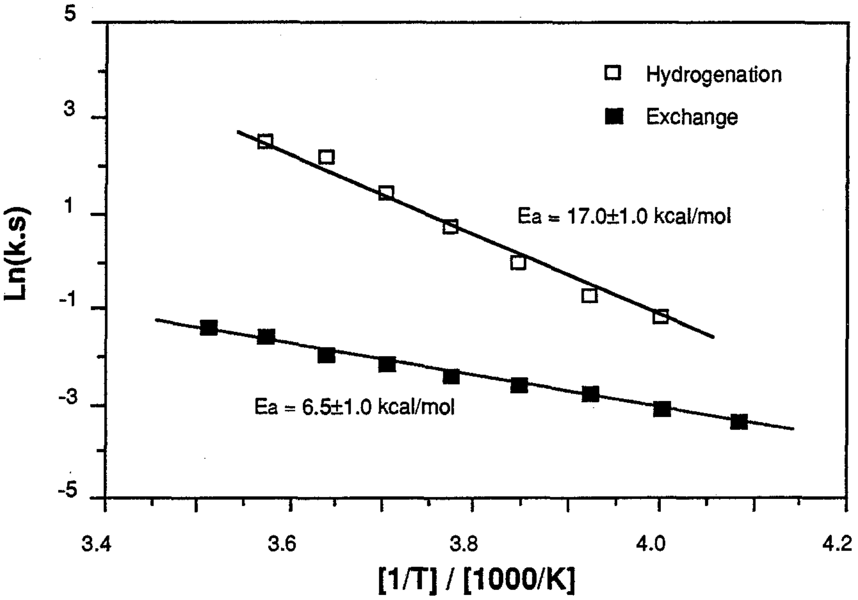

Fig. 2. Arrhenius plots of rate constants for direct methyl hydrogenation and for multiple H-D exchange reactions. These constants were calculated dividing the raw TPD data by the corresponding reactant surface coverages.

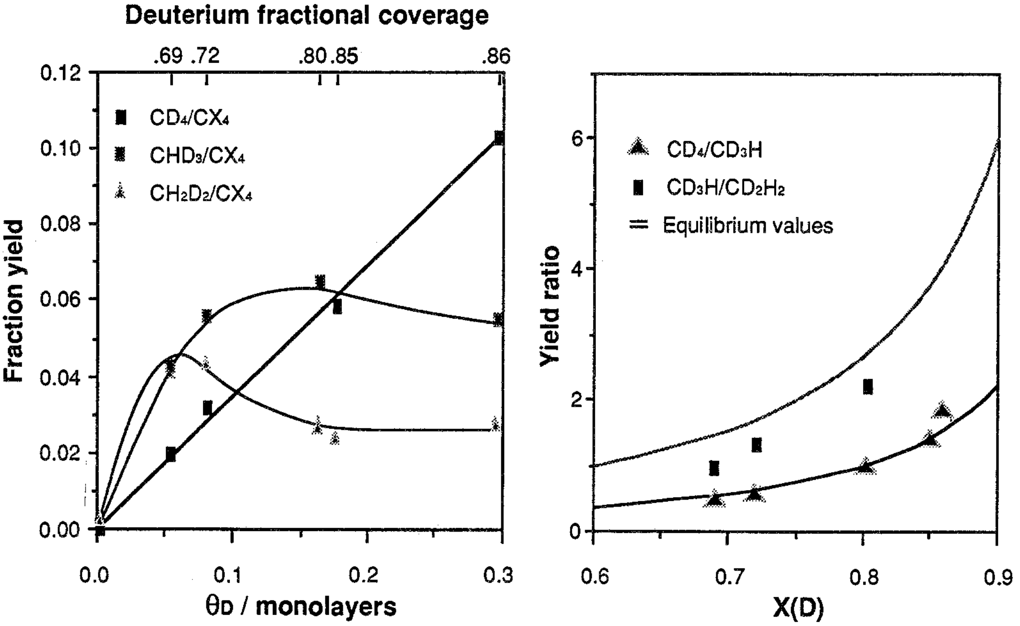

Fig. 3. Methane product distributions obtained from TPD experiments for methyl iodide and deuterium coadsorbed on Pt(111). The left frame displays fractional yields for CD_4, CHD_3 and CH_2D_2 as a function of both absolute and fractional (respect to total H+D) deuterium initial coverages. The right panel displays CD_4/CHD_3 and CHD_3/CH_2D_2 yield ratios as a function of the fractional deuterium coverages, both experimental (points), and calculated from equilibrium constants (solid lines).

hydrogenation of methyl groups with either surface hydrogen (from background adsorption) or deuterium, but extensive H-D exchange was observed as well.

Table 1 provides some of the values obtained from TPD like those in fig. 1 for reaction rates at 265 K as a function of initial surface coverages. It can be seen that direct methyl hydrogenation to methane displays a different coverage dependence than the reactions responsible for exchanged products: while the rate of production of CH_3D is roughly proportional to the coverages of both methyl iodide and deuterium, the rates for CH_2D_2, CHD_3 and CD_4 only seem to depend on the CH_3I surface concentration. The dependence of the rate constants on temperature is shown in an Arrhenius form in fig. 2; rate constants were calculated by dividing the raw data (fig. 1) by the corresponding surface coverages of the reactants and averaged for each given temperature using data from different TPD experiments [29]. The activation energies obtained for direct hydrogenation and for multiple exchange have significantly different values (17.0 and 6.5 kcal/mole, respectively), indicating that they follow two different mechanisms on the surface.

Finally, the methane product distributions obtained in these TPD experiments are shown in fig. 3 as a function of surface coverages. The extent of the multiple exchange is highlighted by the fact that the yield for CD_4 was in general larger than that for CH_2D_2; this effect was accentuated as the deuterium surface coverage was increased (fig. 3, left panel). Because small amounts of normal hydrogen from background adsorption are always present on the surface, the final exchange product distribution is expected to depend on the H/D coverage ratios. The right frame of fig. 3 shows yield ratios calculated from the data displayed on the left as a function of the deuterium fractional coverages. Also shown are the values estimated from equilibrium calculations based on a statistical distribution of the initial surface deuterium within the desorbing methane molecules (solid lines) [2].

4. Discussion

The thermal programmed desorption data presented here provide some insight into the mechanism for methane H-D exchange on platinum single crystal surfaces. Past studies on the reaction of methane with deuterium have shown that the resulting product distributions display maxima at the mono- and perdeuterio-methane, which suggests that at least two separate mechanisms operate for this reaction [1–5,12–14]. Moreover, since bimodal distributions have been observed for other alkanes as well [2,4,15,33–37], similar mechanisms may be used to explain all catalyzed H-D exchange reactions for saturated hydrocarbons. Unfortunately, the experiments reported to date present two main limitations:

1) They have been performed using either evaporated films or supported catalysts with exposed surfaces that contain many different reaction sites. This has lead to the suggestion that the two mechanisms seen for H-D exchange reactions take place on two different sites on the surface.

2) Since the initial dissociative adsorption of methane is believed to be the limiting step for its activation [1–5], little kinetic information can be extracted for the subsequent surface reactions from the catalytic data obtained experimentally.

By using single crystal surfaces under very controlled vacuum conditions we have been able to overcome both difficulties mentioned above. Pt(111) is a close packed surface with few possible adsorption sites, so it is quite likely that only one intermediate is formed during the catalytic H-D exchange of alkanes on this substrate, and in fact, we have shown that such is the case for the reaction of deuterium with ethane by using low energy electron diffraction [16]. The initial dissociative methane adsorption step was also bypassed by depositing methyl groups on the surface directly using methyl iodide. The formation of methyl groups starting from methyl iodide has been clearly shown by us [27] and by others [19], and similar results have been reported for other alkyl halides [20,25,27]. We have also proved that the iodine atoms codeposited by this procedure do not change the surface chemistry of the hydrocarbon moieties significantly [38].

Our TPD data shows that methyl groups can be selectively hydrogenated to methane and that multiple exchange does occur even under high vacuum. The methane product distributions obtained from deuterium and methyl coadsorption experiments resemble those seen in the published catalytic work; they both display the same bimodal distributions that argue for the existence of at least two distinct branches in the reaction mechanism. We envision this mechanism to be similar to that proposed earlier by Kemball [2] where CH_4 and CH_3D are formed by direct recombination of CH_3 groups with either H or D atoms from the surface while the rest of the products originate from the dehydrogenation of methyl to methylene (CH_2) moieties followed by a series of subsequent hydrogenation and dehydrogenation steps. However, given that our experiments were done on single crystals and that we have only detected one type of methyl groups on those surfaces [27], we rule out the possibility of having two sites, one for each of the two pathways mentioned above. It is clear from our experiments that the same methyl intermediates can undergo both direct hydrogenation and multiple exchange reactions.

The activation energies for direct hydrogenation and for methyl to methylene conversion were determined to be 17.0 ± 1.0 and 6.5 ± 1.0 kcal/mol respectively. These values differ considerably from those reported earlier (22.8 and 26.4 kcal/mol), but this discrepancy can be explained by the fact that the results from the catalytic work only provide effective values resulting from the combined effect of all the elementary steps involved, including the initial dissociative adsorption. It is interesting to note that even though the activation energy for surface dehydrogenation is quite lower than that for methane formation in our experiments, the reaction rates are comparable because there is also a marked difference in preexponential values. Also, the rates for both methyl hydrogenation and methylene formation depend linearly on the surface coverage of methyl groups, as expected from the proposed elementary steps. The rate for direct hydrogenation displayed a first order dependence on deuterium coverage, but the corresponding behavior of H-D exchange is a little bit more complex, below 265 K the rate is quite insensitive to changes in deuterium coverages, but as the reaction temperature is increased there is a slight increase in reaction rates with increasing surface deuterium (not shown here). The interpretation of this latter trend requires a more complete analysis of all the individual TPD traces for the multiply exchanged products in order to separate the contributions from the different steps that occur between the dehydrogenation of methyl to methylene and the final desorption of multideuteriated methane [29]. It is also worthwhile mentioning that the catalytic studies of methane reactions with D_2 have always yielded negative deuterium pressure dependences, more negative for multiple exchange processes than for CH_3D formation [1–5]. This behavior has traditionally been ascribed to the fact that since methane chemisorption is the limiting step for the overall exchange processes, competition for adsorption sites yields positive and negative orders on methane and deuterium pressures respectively. Methane adsorption does not play any role in the kinetics of our experiments, so the positive rate dependence on deuterium coverages is a direct reflection of the stoichiometry of the surface reactions.

Two additional observations from our data are relevant to the determination of the mechanism for multiple H-D exchange. First, we do see a slight positive dependence of the exchange rates on deuterium coverages at higher temperatures, a dependence that is more noticeable in the more substituted methane molecules ($CD_4 > CD_3H > CD_2H_2$), and second, the yield for CD_4 is generally larger than that for CD_2H_2. These two facts can only be reconciled if we assume that a rapid equilibration takes place between methylene groups and deuterium atoms on the surface, probably through a rapid interconversion with another unstable surface intermediate which we assume to be methylidyne (CH) moiety. The right frame of fig. 3 shows that indeed the experimental values for the CD_4/CD_3H yield ratios match those expected from a statistical equilibrium [2]; similar behavior was seen in the earlier catalytic work [12–13]. The CD_3H/CD_3H_2 ratios do deviate from equilibrium, perhaps because a third pathway responsible for the formation of CD_2H_2 molecules competes with direct hydrogenation of methyl groups and with methylene-methylidyne interconversion.

The picture that emerges from this discussion is that initially methane chemisorbs dissociatively on the metal surface and forms methyl groups. Those methyl moieties then react by following two possible and competing steps, namely, rehydrogenation to methane and dehydrogenation to methylene. Methylene in turn can exchange hydrogen and/or deuterium atoms via a rapid interconversion with a third intermediate (methylidyne) until reaching an equilibrium, and then undergo two sequential hydrogenation steps to yield methyl and methane. Our energy diagram for this mechanism is depicted schematically

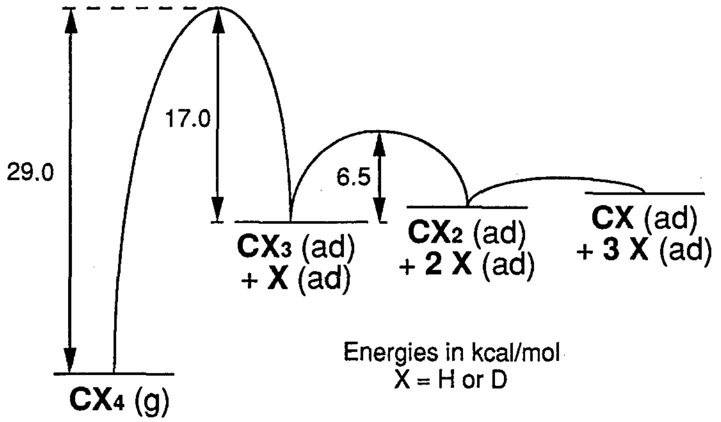

Fig. 4. Schematic representation of the energy diagram for methane H-D exchange reactions.

in fig. 4; this scheme includes a value for the initial activation of methane obtained from published molecular beam studies [10]. The formation of methyl and methylene groups on Pt(111) is supported by our previous spectroscopic data [27], but the isolation of methylidyne has not yet been accomplished. Finally, and alternative mechanism was proposed by Kemball in which methylene groups form directly from methane without going through a methyl moiety [2], but we can rule out that possibility since our experiments yielded similar product distributions even though we started directly from methyl groups.

5. Conclusions

Thermal programmed desorption experiments from deuterium and methyl iodide coadsorbed in Pt(111) have given us new insight into the mechanism for H-D exchange reactions. Methyl groups react on the surface through two reactions of comparable rates, namely, one in which a surface deuterium (or hydrogen) atom is incorporated to form methane, and another where a carbon-hydrogen bond breaking step results in the formation of surface methylene moieties. Methylene in turn can undergo rapid and reversible conversion to methylidyne before hydrogenating back to methyl and ultimately to methane. While the first pathway accounts for the formation of CH_4 and CH_3D (about 75% of the total methane yield), the second is responsible for the desorption of the multiple exchanged products, namely, CH_2D_2, CHD_3 and CD_4. We also obtained kinetic parameters for the different surface elementary steps.

Acknowledgement

Financial support for this research was provided by a grant from the National Science Foundation (CHE-9012560).

References

[1] T.I. Taylor, in: *Catalysis*, Vol. V, ed. P.H. Emmett (Reinhold, New York, 1957) pp. 257–403.

[2] C. Kemball, in: *Advances in Catalysis*, Vol 11, eds. D.D. Eley, P.W. Selwood and P.B. Weisz (Academic Press, New York, 1959) pp. 223–262.

[3] J.R. Anderson, Rev. Pure Appl. Chem. 7 (1957) 165.

[4] C. Kemball, Catal. Rev. 5 (1971) 33.

[5] L. Guczi and P. Tétényi, Acta Chim. Acad. Scient. Hung. 71 (1972) 341.

[6] C.N. Stewart and G. Ehrlich, J. Chem. Phys. 62 (1975) 4672.

[7] C.T. Rettner, H.E. Pfnür and D.J. Auerbach, Phys. Rev. Letters 54 (1985) 2716.

[8] A.V. Hamza and R.J. Madix, Surf. Sci. 179 (1987) 25.

[9] S.T. Ceyer, Ann. Rev. Phys. Chem. 39 (1988) 479.

[10] G.R. Schoofs, C.R. Arumainayagam, M.C. McMaster and R.J. Madix, Surf. Sci. 215 (1989) 1.
[11] A.C. Luntz and D.S. Bethune, J. Chem. Phys. 90 (1989) 1274.
[12] C. Kemball, Proc. Royal Soc. A207 (1951) 539.
[13] C. Kemball, Proc. Royal Soc. A217 (1953) 376.
[14] H.F. Leach, C. Mirodatos and D.A. Whan, J. Catal. 63 (1980) 138.
[15] S.M. Davis and G.A. Somorjai, J. Phys. Chem. 87 (1983) 1545.
[16] F. Zaera and G.A. Somorjai, J. Phys. Chem. 89 (1985) 3211.
[17] F.C. Schouten, E.W. Kaleveld and G.A. Bootsma, Surf. Sci. 63 (1977) 460.
[18] T.P. Beebe, Jr., D.W. Goodman, B.D. Kay and J.T. Yates, Jr., J. Chem. Phys. 87 (1987) 2305.
[19] M.A. Henderson, G.E. Mitchell and J.M. White, Surf. Sci. 184 (1987) L325.
[20] K.G. Lloyd, A. Champion and J.M. White, Catal. Lett. 2 (1989) 105.
[21] P.M. George, N.R. Avery, W.H. Weinberg and F.N. Tebbe, J. Am. Chem. Soc. 105 (1983) 1393.
[22] P.H. McBreen, W. Erley and H. Ibach, Surf. Sci. 148 (1984) 292.
[23] P. Berlowitz, B.L. Yang, J.B. Butt and H.H. Kung, Surf. Sci. 171 (1986) 69.
[24] M.A. Henderson, P.L. Radloff, J.M. White and C.A. Mims, J. Phys. Chem. 92 (1988) 4111.
[25] F. Zaera, Surf. Sci. 219 (1989) 453.
[26] H. Hoffmann, P.R. Griffiths and F. Zaera, Surf. Sci., in press.
[27] F. Zaera and H. Hoffmann, J. Phys. Chem., in press.
[28] F. Zaera, Langmuir, in press.
[29] F. Zaera, Surf. Sci., submitted.
[30] F. Zaera, J. Vac. Sci. Technol. A7 (1989) 640.
[31] F. Zaera, J. Phys. Chem. 94 (1990) 8350.
[32] F. Zaera, J. Phys. Chem. 94 (1990) 5090.
[33] J.R. Anderson and C. Kemball, Proc. Royal Soc. A223 (1954) 361.
[34] J.R. Anderson and C. Kemball, Proc. Royal Soc. A223 (1954) 377.
[35] C. Kemball, Trans. Faraday Soc. 50 (1954) 1344.
[36] M.A. Long, R.B. Moyes, P.B. Wells and J.L. Garnett, J. Catal. 52 (1978) 206.
[37] R.S. Dowie, D.A. Whan and C. Kemball, J. Chem. Soc., Faraday Trans. 1, 68 (1973) 2150.
[38] F. Zaera, Acc. Chem. Res., submitted.