128. Physicochemical Properties of Deuterated Compounds

7th Communication[1])

The H/D Exchange between Hydrogen and Methane over Ni Catalyst

by **Marc Poretti** and **Tino Gäumann***

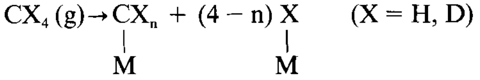
Institute of Physical Chemistry, Federal Institute of Technology, CH-1015 Lausanne

(25.III.85)

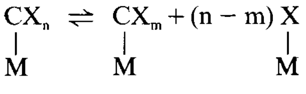
The isotopic exchange between hydrogen and methane over Ni catalyst has been studied as a function of temperature, isotopic substitution, and ratio of hydrogen to methane. The experimental results can be described by means of a model in which methane is adsorbed either as methyl or as methylene. The adsorbed species undergo one or several exchanges. The four required parameters are adjusted to the experimental results. The exchange of partially deuterated methane with H_2 or D_2 allowed us to study the isotopic effect on the adsorption and the exchange processes.

1. Introduction. – The exchange between D_2 and CH_4, either on Ni films [2–4] or other types of catalysts [5] [6], has been described in several publications. CH_4 is an especially interesting molecule for exchange studies because of its high symmetry and low reactivity [7]. On our catalyst, no exchange can be observed below 500 K, where the isotopic equilibrium for hydrogen is instantaneously attained. The speed of exchange is largely determined by the rate of adsorption of the hydrocarbon [8], *i.e.* the ease of formation of one or several C–Ni bonds.

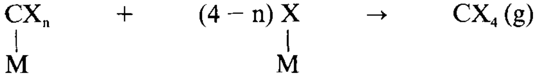
The major differences between the models proposed for the exchange between CH_4 and D_2 [2] [6] [9–14] are due to the nature of the adsorbed species and their interconversion on the metal surface. The aim was to achieve a good representation of the experimental results using a minimum of parameters, because very little is known about the elementary reactions on the surface. Usually, the following scheme is assumed (M–C and M–X describe simple or multiple bonding between the metal and C or H):



$$\mathrm{CX_4(g)} \rightarrow \underset{\substack{| \\ \mathrm{M}}}{\mathrm{CX_n}} + (4-n)\underset{\substack{| \\ \mathrm{M}}}{\mathrm{X}} \qquad (\mathrm{X} = \mathrm{H, D}) \tag{1}$$



$$\underset{\substack{| \\ \mathrm{M}}}{\mathrm{CX_n}} \rightleftharpoons \underset{\substack{| \\ \mathrm{M}}}{\mathrm{CX_m}} + (n-m)\underset{\substack{| \\ \mathrm{M}}}{\mathrm{X}} \tag{2}$$



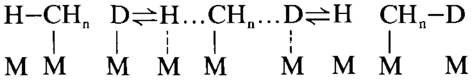
$$\underset{\substack{| \\ \mathrm{M}}}{\mathrm{CX_n}} + (4-n)\underset{\substack{| \\ \mathrm{M}}}{\mathrm{X}} \rightarrow \mathrm{CX_4(g)} \tag{3}$$

In the first step, CH_4 reacts reversibly with dissociative adsorption on the metal surface. The adsorbed species undergo additional reversible dissociations on the surface before

---

[1]) 6th Communication: [1].

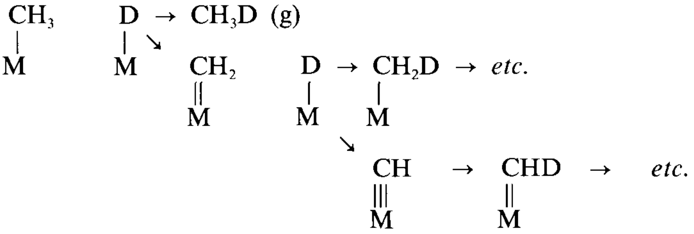
hydrogenation and desorption from the metal surface. It is often assumed that the adsorbed hydrocarbon undergoes an exchange with adsorbed hydrogen according to *Reaction 4:*



$$\begin{array}{cccccccccc} H{-}CH_n & D & \rightleftharpoons & H\ldots CH_n\ldots D & \rightleftharpoons & H & CH_n{-}D & \\ | & | & & |\ \ |\ \ | & & | & | & \\ M\ M & M & & M\ \ M\ \ M & & M & M & M \end{array} \qquad (4)$$

This reaction may lead to a multiple or even a complete exchange. Differences emerging among various authors are often based on different experimental agreements.

Kemball's theory [6] [10] [15–17] is based on the assumption that all deuterated species (CH_3D, CH_2D, CHD_3, CD_4) can be formed following a single adsorption step. Two main reaction paths are postulated: a stepwise exchange by an adsorbed methyl and a multiple exchange by more dehydrogenated species *(Reaction 2)*. Thus, the following reaction sequence is proposed:



(5)

In more recent studies, *Kemball* [18], and *Cece* and *Gonzalez* [10] proposed models in which interconversion between all dehydrogenated species is involved [16].

Leach et al. [19] and *Frennet* [7] based their models on the existence of only two possible exchanged species in the initial step: CH_3D, CD_4. Methane is either adsorbed as methyl or as carbon. It appears to us that most of the models proposed suffer from the disadvantage that the time evolution of D_2 exchange process has been insufficiently or not at all evaluated. A mean reason for this is that a precise determination of the isotopic distribution of methane is not a simple task, especially at the very low conversions needed for the study of the initial reaction. Since several independant methods for the determination of the isotopic distribution and samples of partially deuterated methanes were available to us, we measured the methane/hydrogen system again to complement our earlier exchange studies on higher hydrocarbons [1].

2. Experimental. – The study of the substitution kinetics for $CH_{4-i}D_i$ was performed in the open dynamic flux system depicted in *Fig. 1*. Five tubular stainless steel reactors (A; ⅛" diam.) are filled with various measured

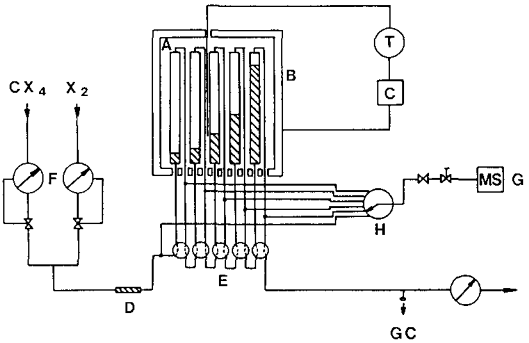


Fig. 1. *Diagram of the apparatus*

amounts (20, 30, 60, 100, and 200 mg) of the catalyst with a diameter of 0.15 mm. The reactors are assembled in series in a temperature-controlled oven (B) to ±0.05° by means of a controller (C). The homogeneity of the temperature is assured by embedding the reactors in a Cu block. A prereactor (D) containing 1 g of the same catalyst at r.t. reacts with traces of catalyst poisons. A system of valves (E) permits any combination of the reactors, thus allowing many values for one independent variable: the weight of the catalyst. The preparation (85% Ni on alumina) and the activation of the catalyst (24 h at 623 K under a flux of H_2) has been described in [20].

The flow of the hydrocarbon is stabilized (0.85 ml/min) by a flow regulator (F). The reaction between CH_4 and D_2 has been studied at five different molar fractions (MF) of methane varying between 0.53 and 0.04. The molar ratios for the exchange measurements with deuterated methanes (synthetized in our laboratory [21]) were kept constant at 0.085. Deuterium was produced by electrolysis.

The reaction mixture is continuously analyzed (H) by a small mass spectrometer (*Micromass 2* of *Vacuum Generators*, operating pressure $5 \cdot 10^{-5}$ Torr) and samples are introduced directly into a GC. The MS of all isotopic species were measured separately in order to correct for the strong isotope effect in the fragmentation of methane ion [22].

A pyrolytic method developed in this laboratory [23] allowed the determination of the degree of deuteration of the methane: the mixture is separated in a GC, decomposed over Cr at 1600 K into graphite and hydrogen; the hydrogen isotopes are continuously measured with a quadrupole mass spectrometer. High-resolution MS provided an additional control on selected samples.

3. Results and Discussion. – In *Fig. 2*, some results of the evolution of the exchange as a function of the amount of catalyst (which corresponds to the reaction time) are shown for CH_4, CH_3D, and CHD_3 with D_2, and CH_3D, CD_3H and CD_4 with H_2. The decrease in methane concentration with the initial isotope content made it possible to determine the reaction constant *k* for the consumption of methane.

The proposed model shown in the *Scheme* follows an analogous scheme put forward earlier [1]. Two different adsorbed species with the relative probabilities p and 1 – p are assumed to undergo exchange: methylene and methyl. According to the terminology of *Rowlinson*, they would be described as ($\alpha\alpha$) and (α) [25]. The ratio p/(1 – p) describes the

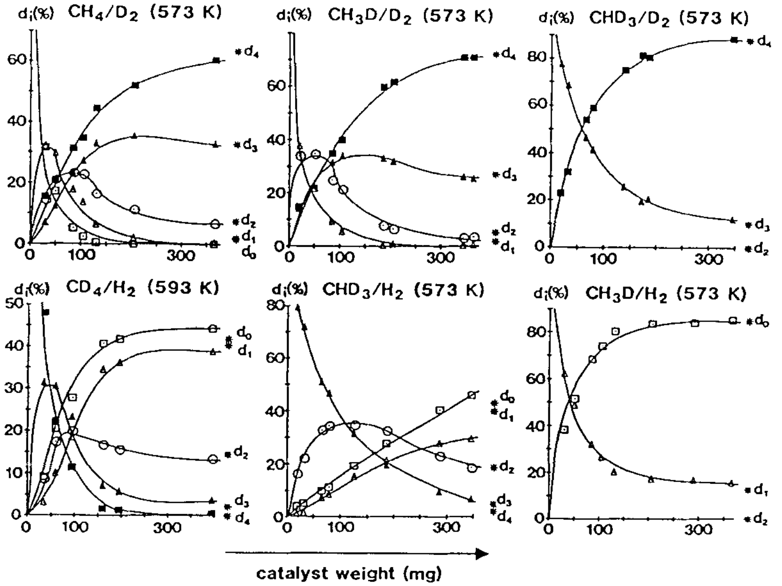
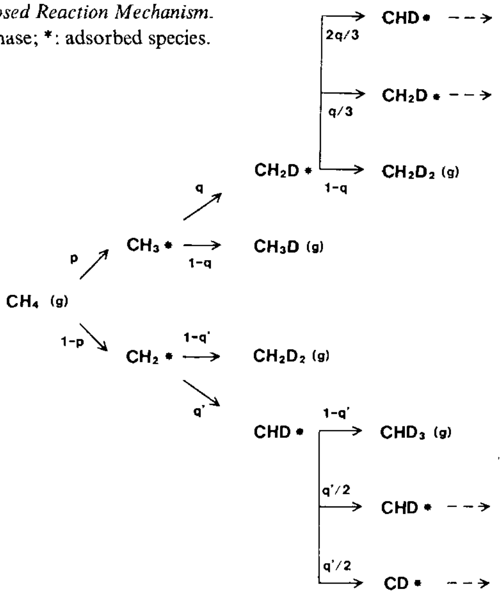


Fig. 2. *Isotopic distribution of methane* vs. *weight of catalyst.* MF = 0.085. CH_4: □; CH_3D: △; CH_2D_2: ○; CHD_3: ▲; CD_4: ■. The thermodynamic equilibrium values are indicated by *.

Scheme. *Proposed Reaction Mechanism.*
(g): gaseous phase; *: adsorbed species.



selectivity of the catalyst as proposed by *Germain* [26]. In the case of CH_3D and CHD_3, we infer an H- or a D-atom the same probability to be lost in the adsorption process. Before a further exchange, the species (α) and (αα) are desorbed with a probability (1 − q) and (1 − q), respectively. Since hydrogen is in excess and the H/D equilibrium on the surface is rapidly attained [24], the lost H- or D-atoms are replaced by the H- or D-atoms of the carrier gas. q and q′ represent the probability for a further exchange with the carrier gas on the surface. They are corrected by a statistical factor in the case where the adsorbed species contain H- and D-atoms simultaneously.

The rate constant *k* is determined by *Eqn. 6* where $d_{i,x}$ denotes the concentration (in %) of $CH_{4-i}D_i$ at the beginning (x = 0, 100%) after having passed x mg of catalyst and at equilibrium (x = ∞).

$$\ln\frac{(d_{i,x}-d_{i,o})}{(d_{i,o}-d_{i,o})} = -\frac{k\cdot x}{(d_{i,o}-d_{i,o})} \tag{6}$$

A statistical factor $\sigma = 4/3$ is required in the exchange of CH_3D with D_2. The adaptation of the coefficients is only performed at low conversions. In such a case, a methane molecule undergoes a maximum of one exchange, and the isotopic concentration of the carrier hydrogen can be assumed to be constant (*e.g.*: $[D_2]$, $[H_D]$, $[H_2]$) and an inverse exchange can be neglected. However, this increases the necessity of the precision of the isotopic analysis.

For the exchange of CH_4 with D_2, the concentration $d_{i,x}$ (in %) of the species $CH_{4-i}D_i$ after x mg of catalyst is given by *Eqn. 7*.

$$d_{i,x} = \left[\frac{3!}{(4-i)!\cdot 3^{i-1}}\cdot p\cdot q^{i-1}\cdot(1-q)\cdot\prod_{j-1}^{i}\frac{3}{3-(i-j)\cdot q} + \right. \tag{7}$$
$$\left. + \frac{2!}{(4-i)!\cdot 2^{i-2}}\cdot(1-p)\cdot(1-q')\cdot q'^{(i-2)}\cdot\prod_{h-2}^{i}\frac{2}{2-(i-h)\cdot q'}\right]\cdot(100-d_{ax})$$

The initial isotopic distributions are given in *Table 1* as a function of temperature and for the system CH_4/D_2 of the mole fraction. It is evident that all isotopic species have a non-zero probability of formation in the first exchange step. These conditions are maintained up to about 25% exchange.

Table 1. *The Initial Distribution of the Products as a Function of the Catalyst Temperature* T *and the Molar Fraction* (MF) *of Methane*

MF(CX_4/X_2)	T	k[mg^{-1}]	Initial rate of products [%]				
	[K]	CX_4	CH_4	CH_3D	CH_2D_2	CHD_3	CD_4
CH_4/D_2 0.529	554	0.049		53	21	15	11
	535	0.019		66	19	7	8
	526	0.011		74	11	6	9
	506	0.0045		77	16	3	4
CH_4/D_2 0.257	553	0.034		49	17	14	20
	534	0.013		72	10	5	13
	513	0.0048		77	9	5	9
	494	0.0017		80	11	3	6
CH_4/D_2 0.159	574	0.039		47	17	13	23
	564	0.026		55	14	10	21
	543	0.011		67	12	6	15
	533	0.0064		75	11	2	12
CH_4/D_2 0.085	569	0.027		53	17	7	23
	550	0.0094		61	14	5	20
	543	0.0077		72	10	3	15
	533	0.0046		70	16	4	10
	526	0.0034		85	9	0	6
	516	0.0020		84	10	1	5
CH_4/D_2 0.041	569	0.010		65	8	2	25
	549	0.0040		68	10	3	19
	540	0.0023		79	7	1	13
	530	0.0015		76	11	2	11
	520	0.0008		87	5	0	8
CH_3D/D_2 0.085	554	0.012			71	15	14
	545	0.0074			72	16	12
	535	0.0043			77	13	10
	526	0.0026			81	11	8
CH_3D/H_2 0.085	593	0.013	100				
	573	0.0053	100				
	554	0.0020	100				
	535	0.0007	10				
CHD_3/H_2 0.085	573	0.010	18	4	78		
	554	0.0035	16	5	79		
	545	0.0021	15	7	78		
	535	0.0012	14	6	80		
CHD_3/D_2 0.085	573	0.012					100
	554	0.0041					100
	545	0.0024					100
	535	0.0014					100
CD_4/H_2 0.085	573	0.0073	9	4	16	71	
	564	0.0046	7	2	16	75	
	554	0.0027	5	4	9	82	
	535	0.0009	3	3	5	89	

Since no analytical expression can be formulated between the relative concentrations of the different species d_i, where i is the number of D-atoms in the desorbed methane, a graphic approximation procedure was used in order to obtain values for the three parameters p, q, and q'. Two examples are shown in *Fig. 3*. The broken lines demonstrate a reliability of the method to a few percent up to a degree of conversion of 40–50%. It is important to know that a mutual compensation of the parameters is not observed, *i.e.* the observed deviations are due to experimental errors at low conversion and/or neglection of multiple exchange and isotopic depletion of the carrier gas at higher conversions.

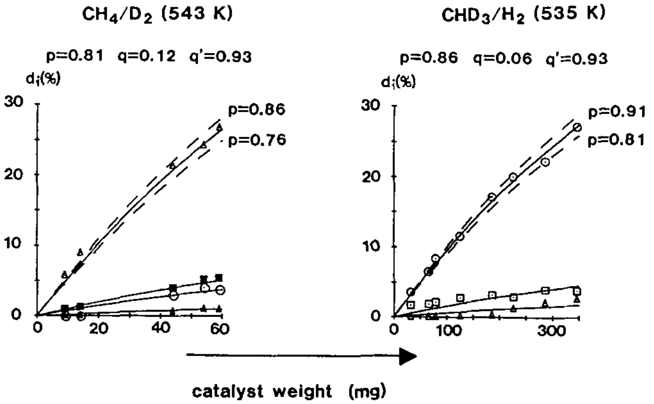


Fig. 3. *Simulation of the evolution of the isotopic distribution* (continuous line). The symbols are the same as in *Fig. 2*.

The temperature dependence of k, p/(1 − p), q'/(1 − q') can be expressed as a logarithmic dependence around a reciprocal temperature $1/T_g$, corresponding to average temperatures of our measurements of $T_g = 545$ K as is given for k in *Eqn. 8*. The subscript g indicates the values of the parameters at T_g given in *Table 2* and the temperature dependence is expressed as some sort of activation energy E_k.

$$\frac{k}{k_g} = \exp\left[-\frac{E_k}{R}\cdot\left(\frac{1}{T}-\frac{1}{T_g}\right)\right] \tag{8}$$

The mean standard error given at the bottom of *Table 2* provides some indication about the reproducibility of the results.

Table 2. *The Model Parameters for* T_g = *545 K and their Temperature Dependence*

Mf(CX_4/X_2)	k_g [mg^{-1}]	E_k [kJ/mol]	p_g	ΔE_p [kJ/mol]	q*	q'_g	ΔE_g [kJ/mol]
CH_4/D_2 0.529	0.0312	114	0.66	−110	0.12	0.69	−40
CH_4/D_2 0.257	0.0230	114	0.61	−58	0.09	0.78	−24
CH_4/D_2 0.159	0.0115	112	0.75	−97	0.13	0.88	−54
CH_4/D_2 0.085	0.0088	122	0.77	−95	0.13	0.91*	
CH_4/D_2 0.041	0.0031	127	0.79	−67	0.10	0.96*	
CH_3D/D_2 0.085	0.0077	143	0.84	−53	0.20	0.83*	
CH_3D/H_2 0.085	0.0012	136					
CHD_3/D_2 0.085	0.0024	142					
CHD_3/H_2 0.085	0.0021	140	0.84	−27	0.04	0.93*	
CD_4/H_2 0.085	0.0015	148	0.90*		0.11	0.79*	
Mean standard error		+/−3		+/−12	+/−0.04		+/−15

The parameters q and q′, *i.e.* the probability for a further exchange after adsorption, seem to be rather independent of the degree of deuteration of the adsorbed species. The significance of the temperature dependence of q′ is questionable, since at values of q′ near 1 the uncertainty of the ratio $(q'/1 - q')$ becomes large. The temperature dependence of p increases with the number of H-atoms in the adsorbed species. Only the adsorption process of methane, considered to be the rate-determining step, shows a marked isotope effect, especially for H_2/D_2.

The probability for a methane to be adsorbed as a methyl compared to an $(\alpha\alpha)$ species decreases with temperature and the molar fraction of methane, due to an inhibiting effect of D_2 for the adsorption of the latter species and the higher activation energy required for its adsorption compared to methylene. *Kemball* [2] and *Guzci et al.* [27] observed a similar effect explained by the strong adsorption of deuterium compared to methane on the metal surface. The small and constant value of q underlines the greater ease of methyl to be desorbed before further exchange. The contrary is true for methylene as adsorbed species. Since it takes more energy to be adsorbed, a further exchange is more likely; this could also be an indication of a greater lability of its remaining H-atoms.

Gas-phase thermochemical data have been obtained by mass spectrometry for $(N_iCH_3)^+$ and $(N_iCH_2)^+$ by the reaction of Ni^+ with CH_4 in collision chamber. *Beauchamp* and coworkers obtained the following values [28] for the dissociation energy:

$$D(Ni^+ - CH_3) = 200 \pm 20 \text{ kJ/mol} \qquad D(Ni^+ - CH_2) = 360 \pm 25 \text{ kJ/mol}$$

The species $(NiCH)^+$ postulated by other authors was not observed. Although the direct comparison of mass spectrometry with catalytic data seems to be premature, it substantiates the choice of our model. To simplify the discussion of $k \cdot \sigma$, the kinetics can be approximated by an exchange by an adsorption as methyl ($p \approx 1$, $q' \approx 0$). k_H and k_D designate the rate constant for an exchange of a H- or D-atom of methane with the carrier. The isotope effect k_H/k_D for the rate constant is given in *Table 3*. It depends only slightly on temperature and is nearly unity for D_2 as carrier gas, but somewhat substantial for H_2. In the latter case methane prefers a chemisorption rather by a loss of a H- than a D-atom.

Table 3. *The Isotope Effect of the Rate Constant* k (MF 0.085, 545 K)

CX_4/X_2	k_g [mg^{-1}]	σ	$k_g \cdot \sigma$ [mg^{-1}]		k_H/k_D
CH_4/D_2	0.0088	1	0.0088	$4k_H$	
CH_3D/D_2	0.0077	4/3	0.0103	$3k_H + k_D$	0.9
CHD_3/D_2	0.0024	4	0.0096	$k_H + 3k_D$	
CH_3D/H_2	0.0012	4	0.0048	$3k_H + k_D$	
CHD_3/H_2	0.0021	4/3	0.0028	$k_H + 3k_D$	3.7
CD_4/H_2	0.0015	1	0.0015	$4k_D$	

Table 4. *Comparison of the Rate Constants of this Work with the Adhesion Coefficient S Defined by* Winters [29]

	CX_4/CY_4	$k \cdot \sigma(CX_4/CY_4)$	$S(CX_4/CY_4)$
H_2	CH_4/CD_4	5.9	4.5
	CH_3D/CD_4	3.2	3.5
	CHD_3/CD_4	1.9	1.7
D_2	CH_3D/CH_4	0.9	0.8
	CHD_3/CH_4	1.1	0.4

Table 4 shows the comparison of $k \cdot \sigma$ for two species of different degrees of deuteration with the adhesion coefficient S as defined by *Winters* for tungsten [29]. The latter defines the probability that a colliding molecule will be dissociatively adsorbed (chemisorption). *Winters* explains the isotope effects of S by the existence of a tunnel effect. The postulated reaction paths go through an excited symmetric vibration mode of methane on a particular site of the surface, so that the tunneling permits a side-by-side adsorption of H and CH_3. We had to introduce a similar tunnel effect for the calculation of the isotope effect of the H/D abstraction of alkanes by hydrogen [30]. The similarity of the data of the present work with the data of *Winters* obtained using a different method is very gratifying and underlines the importance of the isotope effect of the chemisorption for the exchange with H, but not with D [3] [9]. Several attempts for a quantitative calculation failed so far to explain the experimental results in a satisfactory fashion [30–33].

We thank *A. Heusler* and *C. André* for the synthetic work, *A. Ruf* and *H. Oez* for control analysis and helpful discussions, and the *Swiss National Science Foundation* for the financial support.

REFERENCES

[1] G. Dessauges, T. Gäumann, *Helv. Chim. Acta* **1982,** *65,* 268.
[2] C. Kemball, *Proc. R. Soc. London, A* **1953,** *217,* 376.
[3] D. W. McKee, *J. Phys. Chem.* **1966,** *70,* 525.
[4] L. Guzci, P. Tétényi, *Z. Phys. Chem. (Leipzig)* **1968,** *237,* 356.
[5] D. W. McKee, F. J. Norton, *J. Catal.* **1965,** *510,* 4.
[6] J. R. Anderson, R. J. McDonald, *J. Catal.* **1969,** *13,* 345.
[7] A. Frennet, *Catal. Rev.* **1975,** *10,* 37.
[8] P. Tétényi, L. Guzci, Z. Paal, *Acta Chim. Acad. Sci. Hung.* **1974,** *83,* 37.
[9] J. G. Larson, W. K. Hall, *J. Phys. Chem.* **1965,** *69,* 3080.
[10] J. M. Cece, R. D. Gonzalez, *J. Catal.* **1973,** *28,* 260.
[11] C. Lifshitz, M. Sapiro, *J. Chem. Phys.* **1966,** *45,* 4242.
[12] A. Sarkany, K. Matusek, P. Tétényi, *J. Chem. Soc., Faraday Trans. 1* **1977,** *73,* 1699.
[13] M. Utiyama, H. Hattori, K. Tanable, *J. Catal.* **1978,** *53,* 237.
[14] L. Baining, C. Kemball, D. A. Wahn, *J. Chem. Res. (M)* **1982,** 3010.
[15] R. S. Dowie, C. Kemball, D. A. Wahn, *J. Phys. Chem.* **1976,** *80,* 2900.
[16] V. Ponec, 'The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis', Ed. D. A. King, Elsevier, Amsterdam, 1981,Vol. 4, p. 366.
[17] C. Kemball, *Adv. Catal.* **1959,** *11,* 223.
[18] C. Kemball, *Catal. Rev.* **1971,** *5,* 33.
[19] H. F. Leach, C. Mirodatos, D. A. Wahn, *J. Catal.* **1980,** *63,* 138.
[20] Al. Olariu, P. Margineau, *Rev. Rom. Phys.* **1968,** *13,* 823.
[21] A. Heusler, T. Gäumann, to be published.
[22] F. H. Field, J. L. Franklin, 'Electron Impact Phenomena and the Properties of Gaseous Ions', Academic Press, London, 1957.
[23] A. Ruf, T. Gäumann, to be published.
[24] G. C. Bond, P. B. Wells, *Adv. Catal.* **1964,** *15,* 91.
[25] H. C. Rowlinson, R. L. Burwell Jr, R. H. Tuxworth, *J. Phys. Chem.* **1955,** *59,* 225.
[26] J. F. Germain, 'Catalytic Conversion of Hydrocarbons', Academic Press, London, 1969.
[27] L. Guzci, A. Sarkany, P. Tétényi, *Z. Phys. Chem.* **1971,** *74,* 26.
[28] R. Houriet, L. F. Halle, J. L. Beauchamp, *Organometallics* **1983,** *2,* 1818.
[29] H. F. Winters, *J. Chem. Phys.* **1976,** *64,* 3495.
[30] N. Fujisaki, A. Ruf, T. Gäumann, *J. Am. Chem. Soc.* **1985,** 107, 1605.
[31] S. Palti, A. Sarkany, P. Tétényi, *J. Chem. Soc., Faraday Trans. 1* **1981,** *77,* 177.
[32] D. N. Stewart, G. Ehrlich, *J. Chem. Phys.* **1975,** *62,* 4672.
[33] A. Ozaki, 'Isotopic Studies of Heterogeneous Catalysis', Academic Press, London, 1978.