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Activated dissociative chemisorption of methane on Ni(100): a direct mechanism under thermal conditions?

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The dissociative chemisorption of methane on a Ni(100) single crystal has been studied under thermal conditions as a function of pressure and temperature. The initial sticking coefficient was measured in the pressure range of 0.010–7.0 mbar at temperatures ranging from 375 to 500 K. A strong pressure dependence was observed, consistent with a direct dissociation mechanism under these thermal conditions. This was further confirmed by experiments where the gas at a low pressure was heated by a thermal finger facing the crystal surface. With the thermal finger at the same temperature as the surface, it was possible to ensure that the methane was fully equilibrated to the crystal and an activation energy of 59 ± 1.5 kJ/mol was determined under isothermal conditions.

Keywords: thermal sticking; direct dissociation mechanism; thermal finger; equilibration

1. Introduction

Steam reforming of hydrocarbons for production of synthesis gas (CO and H_2) is one of the most important large scale industrial chemical processes. There is general agreement that the initial dissociation of CH_4 is the rate limiting step of the steam reforming process. The interaction between methane and transition metals has therefore been the subject of intensive studies in recent years, both via molecular beam experiments and via thermal (bulb) experiments. From the latter, important parameters for modelling real catalysts may be obtained, e.g. Arrhenius parameters describing the exponential activation of the dissociative chemisorption by temperature [1,2]. From molecular beam studies, the dissociation mechanisms can be revealed by the dynamical aspects. It was concluded from all molecular beam experiments that the dissociation is a direct activated process since it is activated by translational energy of the incident molecules [3–6], the vibrational state of the molecule [5–7], and the surface temperature [6,8,9].

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Since the conditions are quite different in the molecular beam and in the thermal experiments, a central issue is whether the underlying mechanisms are the same in the two types of experiments. In the case of the Ni(111) surface, there seems to be a consensus that the process is direct in both. This was first suggested by Lee et al. [5] by use of molecular beams and later confirmed by Hanley et al. [10] who studied the dissociation of methane on Ni(111) in a thermal experiment and found a strong pressure dependence of the reaction rate at constant crystal temperature. This could only be consistent with a direct impact mechanism since a precursor mechanism is not expected to show such a behaviour.

In a very recent molecular beam study of methane on Ni(100) [6], the dependency of sticking of methane was studied in great detail as a function of normal energy, vibrational energy, the surface temperature, and isotopes. All results were in very good agreement with a dynamical model for direct dissociation [11]. By using the molecular beam data obtained in ref. [6], a very good prediction of previous thermal data on Ni(100) [2] was obtained, suggesting the same underlying mechanism in these two experiments. These findings are, however, in strong contradiction with the conclusions of Campbell et al. [12] who observed no pressure dependence of the dissociative sticking of methane on Ni(100) and concluded that the dissociation of methane is precursor mediated under thermal conditions.

The motivation of the present paper is therefore to have a close look at the mechanism under thermal conditions by studying the dissociation as a function of pressure and the separate dependencies of the gas and crystal temperatures. This latter was achieved by mounting a separately thermostated thermal finger close to the surface of the crystal. The temperature of the molecules incident to the crystal are then dominated by the temperature of the thermal finger which enables variation of the gas temperature while the surface temperature is kept constant. In addition, by setting the thermal finger at the same temperature as the surface, a very good thermal equilibration between the gas and surface can be achieved, so that a fully isothermal rate for sticking can be obtained. It is mandatory that the crystal and the gas be fully isothermal when the sticking is measured if the data is to be useful for estimations of rates relevant for high pressure commercial catalysts.

Because of the strong activation of the dissociation of methane on Ni(100) by energy in vibrational coordinates [6,11] as well as translational energy, true isothermal conditions are difficult to obtain since gas phase vibrational equilibration is generally much slower than equilibration of pure translational energy [13]. Experimentally observed rates of energy exchange are often expressed as collision numbers, i.e. the number of gas phase collisions with thermal bath molecules needed to reduce excess energy in that mode by a factor of e^{-1}. For translation, the collision number is ~ 2, while for vibration these are typically 10^4. It is thus rather easy to equilibrate the translational (and rotational) coordinates, whereas it is quite difficult to equilibrate the vibrational coordinates. As a result, very high pressures are required to equilibrate the gas and surface purely by gas phase collisions. By trapping the methane on the thermal finger, much more efficient thermalization of the methane vibrations occurs when the thermal finger is placed in front of the crystal face.

In the present work, several thermal sticking experiments on the Ni(100)/methane system were carried out. With Auger electron spectroscopy (AES) the build-up of carbon on the surface was measured after exposures under different conditions. First, the pressure dependence of the initial sticking coefficient was investigated over a wide pressure range, with and without the use of a thermal finger. Based on experiments with the thermal finger, the activation energy was determined under isothermal conditions. Finally, activation by gas and surface temperatures separately was studied.

2. Experimental

The experiments were carried out in the ultra high vacuum system (base pressure 7×10^{-11} mbar) previously described by Holmblad et al. in ref. [6]. The chamber was connected to a volume of ~ 0.2 ℓ from which the methane was expanded into the chamber. A large 450 ℓ/s turbo molecular pump, which could be isolated by a gate valve, enabled fast evacuation of gases. The pressure of the methane was measured by two baratron heads ranging to 1 mbar and 1000 mbar respectively.

The experiments were carried out on the Ni(100) single crystal described by Holmblad et al. [6] and used for the molecular beam studies of sticking. It is also described there how the crystal was cleaned. After this cleaning procedure the signals from carbon and oxygen were indistinguishable from the noise level, i.e. < 0.005 ML, in the AES measurements.

The dissociation of methane is an activated process and very sensitive to temperatures. To ensure that there was no temperature gradient across the crystal, the carbon coverage was measured along a diameter of the crystal after a dose of methane. No differences in the coverage (~ 0.25 ML) were observed. From this it was concluded that there was no significant temperature gradient across the crystal surface in the experiments.

For some of the experiments a thermal finger was used to heat the methane. In fig. 1 a schematic view of the finger, the crystal and the manipulator is given. The diameter of the finger was 35 mm, while the crystal diameter was 10 mm. The finger was made of oxygen free copper (OFHC) for optimal heat conduction. The surface facing the crystal was polished mechanically and just before installation etched by a solution of HNO_3. The temperature of the finger was controlled with a resistive heater and the temperature measured with a chromel–alumel thermocouple. In all experiments with the finger, the distance between the finger and the crystal was less than 1 mm.

The methane gas used in this work (AGA $\geqslant 99.9995\%$) was further purified in a nickel based catalyst as described in ref. [6].

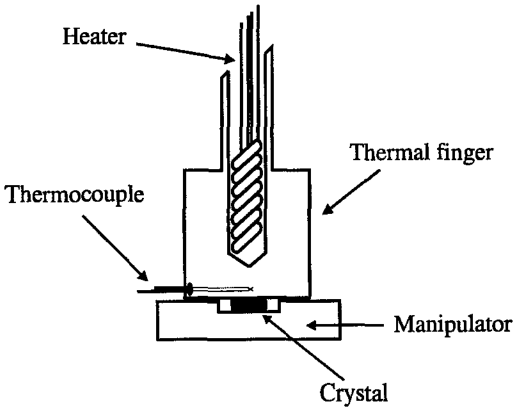

Fig. 1. A schematic view of the crystal, the thermal finger, and the manipulator.

The methane exposures were performed in the following way:

– The clean crystal with the desired surface temperature, T_s, was isolated in the chamber by closing the gate valves to the turbo pump and the analysis chamber. All filaments, including the ion gauges, were switched off.

– Subsequent to the isolation of the crystal the dose was started by expanding methane into the chamber.

– The dose was terminated when the gate valve to the 450 ℓ/s turbo pump was opened.

– After a few minutes of pumping the gate valve to the analysis chamber was opened, and the crystal was manipulated into the analysis chamber to record the Auger spectra. The coverage was determined as the average of coverages measured in two different positions on the surface.

After this procedure the crystal was either cleaned or exposed to at most one other dose of methane. No change in the carbon coverage was observed during an Auger analysis. Nevertheless, it seemed as if the structure of the carbon on the surface was affected by the electron beam of the AES if the carbon coverage was larger than 0.15 ML. When the dose was continued after an Auger measurement at coverages $\theta > 0.15$, the carbon uptake was larger than that obtained by giving the same dose in a single exposure. Therefore exposures were only repeated without cleaning in between when the carbon coverage was well below this critical value [#1].

The crystal temperature during doses was never lower than 375 K in order to allow hydrogen formed by dissociation of methane to recombine and desorb. By temperature programmed desorption, a hydrogen desorption peak was observed at

[#1] After electron beam exposures, the carbon probably orders in islands of local p4g reconstruction with high coverage ($\theta = 0.5$) leaving the rest of the surface open for sticking. A similar process has been observed to occur spontaneously by STM [14] when the carbon coverage (from ethylene) increases above 0.25 ML.

~ 340 K. This is consistent with a TPD study of Alstrup et al. [15]. Furthermore, molecular adsorption of CO was prevented by this choice of temperature [16].

The coverage of carbon was determined traditionally, i.e. by the ratio of the C(272 eV) and the Ni(848 eV) Auger electron peaks. For calibration, the crystal was exposed to methane ($T_s = 550$ K) of ethylene ($T_s = 475$ K) until saturation occurred, $\theta = 0.5$. With low electron energy diffraction (LEED) a p4g pattern was observed. This pattern was also observed after cracking of ethylene on Ni(100) and corresponds to a coverage of one carbon atom for every two nickel atoms in the surface lattice plane [17].

The initial sticking coefficient, S_0, was determined from the relationship between the carbon buildup and the dose of methane, which was calculated using the well known flux equation from kinetic gas theory. In experiments without the thermal finger, the surface temperature was used as the gas temperature for the dose calculations. In the experiments with the thermal finger, the temperature of the finger was used as the gas temperature for calculating the flux. At $T_s = T_f$, this ensures correct fluxes under isothermal conditions at high pressures, where quantitative conclusions are made. At low pressures the flux is somewhat ill defined anyway due to thermal transpiration. No quantitative conclusions are therefore made at these conditions.

The initial sticking coefficient was determined by fitting a sticking model previously described by Chorkendorff et al. [2] to the measured points with S_0 as the only fitting parameter.

The noise level in the AES measurements of the carbon coverage was typically 10%. Depending on the number of measured points on one uptake curve the uncertainty on the sticking coefficients is estimated to be 5–15%.

At pressures higher than 1 mbar, the time to pump out the methane was measurable and a correction for this was included in the dose times. Only at very short dose times of 10–20 s is the uncertainty on the time measurement significant. With an estimated error of 1 s, the relative uncertainty is 5–10% at short dose times.

To ensure that the carbon observed on the surface did not result from other sources than decomposition of methane, a number of control experiments were carried out:

- A cold crystal, i.e. $T_s \approx 300$ K, was exposed to methane at a pressure of 1 mbar for 40 min.
- In separate experiments the crystal was isolated in the preparation chamber without any kind of pumping at temperatures of 400 K and 500 K for 2 and 1 h respectively.
- The thermal finger and the crystal faced each other at a temperature of 400 K for 30 min while the chamber was not pumped.

No carbon nor oxygen was observed after these experiments, and it was concluded that the gases did not contain impurities with high sticking coefficients, that no carbon segregated out from the bulk of the crystal in the investigated temperature range, and that the chamber was sufficiently clean. However, at very long doses (>2 h) some small carbon uptake was observed and small corrections were necessary. The crystal at $T_s = 400$ K was left in the preparation chamber without any pumping for 16 h. After this a carbon coverage of 0.04 ML was observed. Assuming that the pressure rises linearly during the 16 h, a background deposition of 0.003 ML/h was estimated. This background contribution was subtracted from the measured coverage at doses longer than 2 h. This was, however, only necessary for a single point ($T_s = 400$ K, $p = 0.020$ mbar without finger)

3. Results

3.1. PRESSURE DEPENDENCE

The initial sticking coefficient was determined for pressures ranging from 0.010 to 7.0 mbar under different conditions as shown in fig. 2. The open symbols represent measurements where the crystal faced the ~ 300 K chamber wall at a distance of ~ 100 mm. The solid symbols represent measurements where the crystal faced the thermal finger kept at the same temperature as the crystal. The error bars reflect the number of measured points on the uptake curves. The $T_s = 500$ K points were

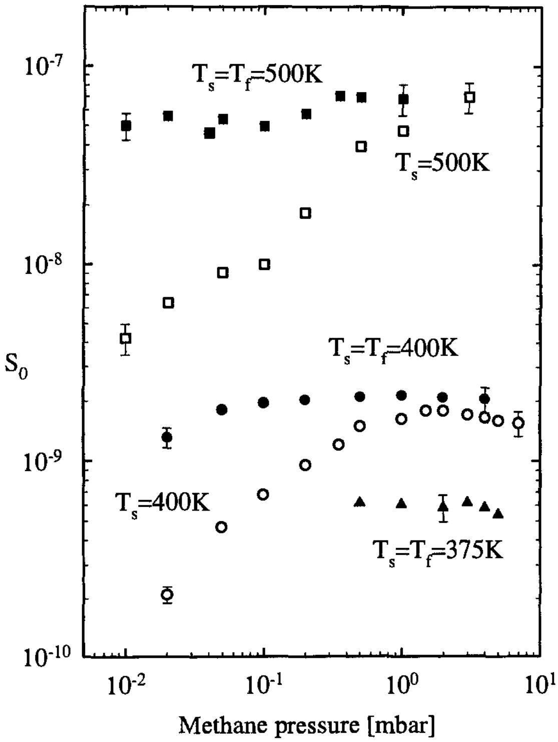

Fig. 2. Pressure dependence of the initial sticking coefficient, S_0, with (solid symbols) and without (open symbols) the presence of the thermal finger.

based on 1–2 measurements while the $T_s = 375$ K and $T_s = 400$ K points were determined from at least four points on each uptake curve.

3.2. ISOTHERMAL ACTIVATION

The sticking coefficient of fully equilibrated methane was measured by exposing the crystal to 0.50 mbar methane heated by the thermal finger ($T_f = T_s$). In addition, the crystal was also exposed to as high methane pressure as possible (3.0 mbar) that gave accurate sticking measurements over a broad temperature range using the procedures described before but without the thermal finger. In fig. 3 the initial sticking coefficient is shown as a function of the inverse temperature in an Arrhenius plot. The solid squares are the sticking coefficients measured at a methane pressure of 0.50 mbar with the thermal finger, while the solid diamonds represent the reaction for 3.0 mbar methane without the finger. The filled circles are measured at a pressure of 0.050 mbar without the thermal finger. Under these latter conditions, the methane was not thermally equilibrated with the sur-

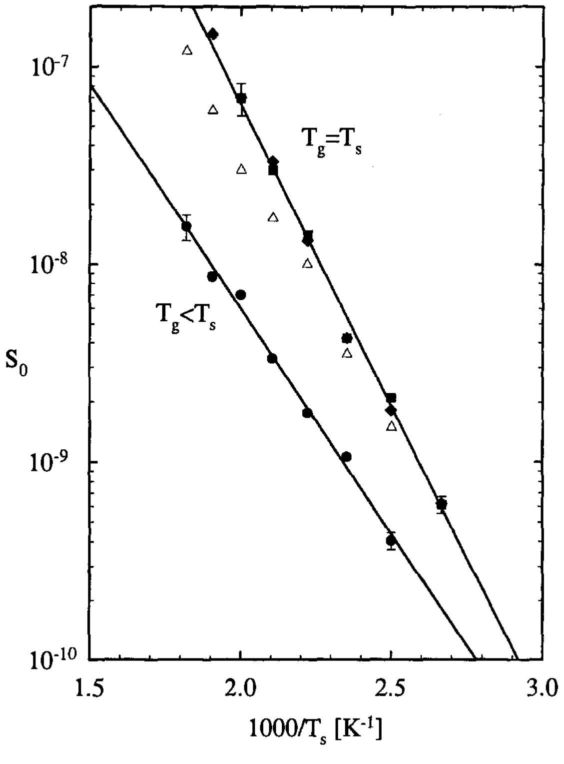

Fig. 3. Isothermal activation of the dissociation of methane. Methane was equilibrated to the surface at 3.0 mbar (solid diamonds) and 0.50 mbar heated by the finger (solid squares). The reaction rate of a gas which is not equilibrated is shown as solid circles. For comparison the results of Chorkendorff et al. [2] are shown as open triangles.

face. The solid lines are the best least squares fit to the measured data. For comparison, the previous results of Chorkendorff et al. [2] are shown as hollow triangles.

3.3. NON-EQUILIBRIUM ACTIVATION

The molecular beam experiments show independent activation through gas temperature and surface temperature, although activation by gas temperature dominates. In an attempt to investigate this effect in the thermal experiments, non-equilibrium activation was studied by having different temperatures on the crystal and the thermal finger. All experiments were carried out at a pressure of 0.020 mbar, where the mean free path (~ 5 mm) is larger than the distance between the finger and the surface (<1 mm). In this pressure limit, the methane suffers almost no gas phase collisions; molecules only collide with the finger and the surface. The results are shown in figs. 4 and 5 together with the isothermal curve (open diamonds) from fig. 3. The points marked with $T_c = 300$ K are made with the crystal facing the chamber wall at low pressures. At $T_s = 500$ K the pressure was 0.010 mbar and 0.020 mbar at $T_s = 400$ K.

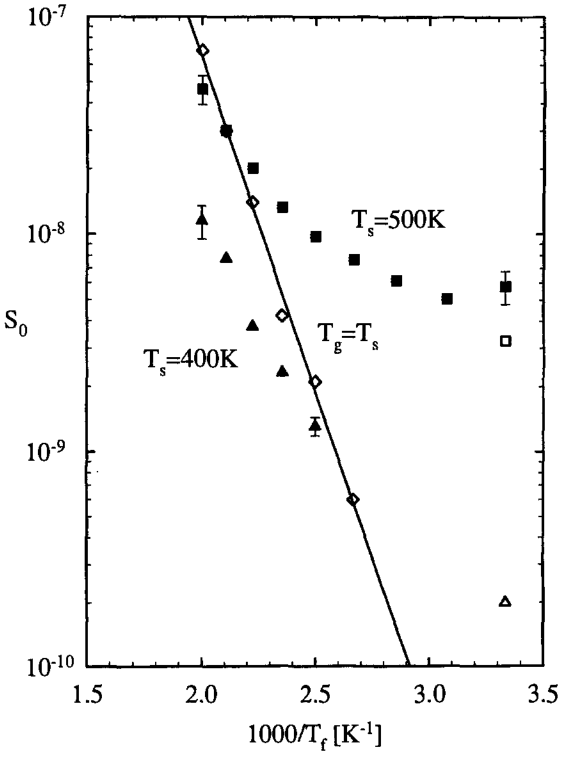

Fig. 4. The initial sticking coefficient activated by the thermal finger while the surface temperature is kept constant at 400 and 500 K. The open points at $T_f = 300$ K are measured without the thermal finger. The open diamonds are measured under isothermal conditions.

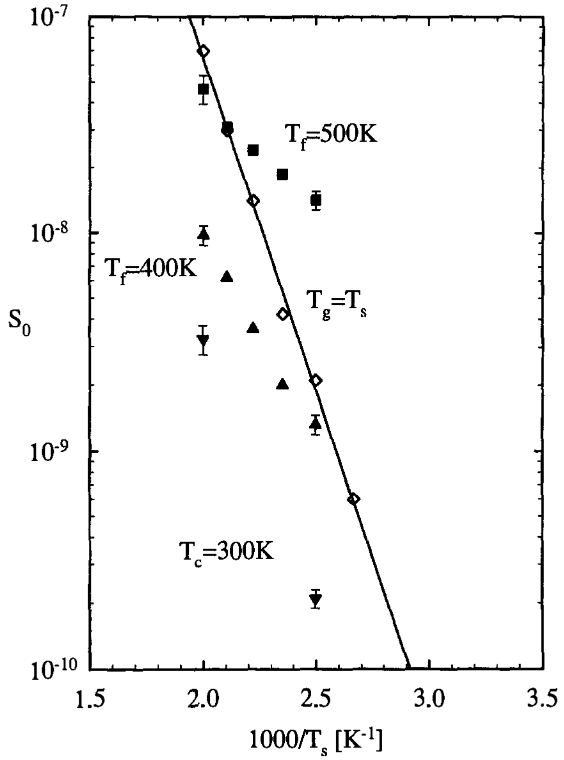

Fig. 5. The initial sticking coefficient shown as a function of inversed surface temperature for $T_f = 400$ and 500 K. The points marked $T_c = 300$ K are measured without the thermal finger at a pressure of 0.010 mbar ($T_s = 500$ K) and 0.020 mbar ($T_s = 400$ K). The open diamonds represent the isothermal activation experiments.

4. Discussion

4.1. EVIDENCE FOR A DIRECT MECHANISM

In recent experiments, the sticking of methane on Ni(100) was investigated by molecular beams in great detail [6]. It was found that the sticking increased rapidly by increasing translational energy and even more dramatically by increased beam temperature i.e. increased vibrational energy. Also the influence of the crystal temperature and the effect of isotopic labelling was investigated. From this rather complete set of molecular beam data, the sticking coefficients were estimated under thermal conditions, and very good agreement was found with the earlier thermal experiments of Chorkendorff et al. [2]. It was also found that all the experimental results could be described qualitatively by a dynamical model where the sticking proceeds via a direct process [11]. Thus, there was a strong indication that not only was the dissociation dominated by direct processes under molecular beam conditions, but also under thermal conditions as well.

While it is easy to conclude that the dissociation is dominated via direct rather than precursor-mediated processes under molecular beam conditions because of the strong dependence on incident translational energy and vibration, it is not as easy to decide in thermal bulb experiments. One method that has been used with some success on Ni(111) [10] and on Pt(110) [18] to show that direct activated processes dominate under thermal conditions is to observe an increase in the sticking coefficient with methane gas pressure due to the formation of a hot buffer gas adjacent to the surface at higher pressures.

The conclusions that methane dissociation on Ni(100) is dominated by direct processes under thermal conditions is further supported by the previous work by Beebe et al. [1] where the sticking of methane on Ni(100) was found to increase nearly linearly (by a factor of three) with pressure in a rather limited pressure range (0.5–1.5 Torr). This conclusion is also consistent with previous coverage dependent studies of sticking, e.g. in work by Jiang et al. [19] on the effect of sulphur on the sticking of methane on Ni(100). Here, as in ref. [2], it was concluded that the uptake was consistent with a direct process.

Contrary to this substantial evidence, Campbell et al. [12] recently concluded that the sticking of methane on Ni(100) under thermal conditions is dominated by a precursor-mediated mechanism. This conclusion was based on the fact that they did not observe a pressure dependence in the dissociation over the region 0.06–1.0 Torr, in disagreement with Beebe et al. [1].

As can be seen from fig. 2, the present work strongly contradicts the experimental results and conclusions of Campbell et al. The initial sticking coefficient measured without the thermal finger shows a significant pressure dependence at crystal temperatures of 400 and 500 K. At $T_s = 400$ K, S_0 increases almost an order of magnitude when the pressure was increased from 0.020 to 2 mbar. At $T_s = 500$ K, S_0 increased even more, approximately a factor of ~ 20. The increase in the initial sticking coefficient is closely related to the decrease in the mean free path. In the pressure range under consideration the mean free path of the methane molecules is decreased from ~ 5 to ~ 0.05 mm. When the mean free path is very short compared to the distance to the chamber wall and the diameter of the crystal, a layer of hot methane molecules is formed at the crystal surface. As the mean free path increases for lower pressures the probability of escape from the heated region is increased and the average gas temperature of the incident molecules decreases. The dependence on the gas temperature is only consistent with a direct activated dissociative chemisorption mechanism.

In the experiments with a crystal temperature of 400 K, there is a small decrease in S_0 at pressures higher than 2 mbar. This is an artifact caused by transient cooling of the crystal when a high pressure of cold methane gas is initially expanded into the chamber.

The results of the experiments without the thermal finger are consistent with the experiments made by Hanley et al. [10] and Luntz et al. [18] on the Ni(111) and Pt(110) surfaces, respectively. The rate of dissociation showed a major dependence on the methane pressure in those cases and both concluded that the dissociation of methane proceeds by an activated direct process. This means that the mechanism of the dissociative chemisorption is of the same nature on the (100) and (111) surface facets of Ni, a very reasonable but not necessarily universal finding.

In fig. 2 the solid points represent experiments where the thermal finger ($T_f = T_s$) faced the crystal surface. The sticking coefficient is significantly larger in the low pressure regime that in the experiment without the thermal finger since the methane molecules are now heated both by the thermal finger and the surface. At $T_s = T_f = 400$ K and $T_s = T_f = 500$ K, the sticking coefficient is nearly constant in the investigated pressure range. In the low pressure range the reaction rate decreases slightly. In this pressure range the mean free path gets longer than the distance between the finger and the crystal. The decrease in the sticking coefficient is therefore due to diffusion of cold molecules into the centre of the heated region. In fact the reaction rate is even lower than shown in the figure due to thermal transpiration [20] which increases the effective pressure over the crystal with a factor $\sqrt{T_s/300\,\mathrm{K}}$ in the low pressure limit. However, since the effect is not known in the intermediate pressure range this effect was not included. Nevertheless, the finger proves a much more efficient manner to equilibrate the gas than just increasing the gas pressure, and as such it expands the range in which this sort of experiment can be performed.

4.2. ISOTHERMAL ACTIVATION

As discussed earlier, it is mandatory to obtain isothermal conditions for determining overall activation energies relevant for modelling real catalytic processes. It is especially difficult to obtain such conditions in this case, where the sticking is enhanced by vibrational excitations [6], since a rather large number of collisions in the gas phase are necessary for equilibration. From fig. 3 it can be seen that such conditions can be obtained by either using a gas pressure higher than 3 mbar methane or using 0.5 mbar heated with the thermal finger. The results are identical within the errors of the experiments. The measured points form a straight line in an Arrhenius plot, see fig. 3. Hence, the chemisorption is activated exponentially and an activation energy of 59 ± 1.5 kJ/mol was determined for isothermal conditions.

The importance of being in full equilibrium to determine meaningful activation energies was demonstrated by comparing to conditions where the gas and surface were not fully equilibrated. At a pressure of 0.050 mbar and without the thermal finger, the sticking represented by solid circles was found. The initial sticking coefficient is significantly lower under these non-equilibrated conditions. Again there is exponential activation, but the activation energy is only 45 ± 1.5 kJ/mol in this case.

Experiments by Beebe et al. [1] on the activation of methane on (100), (110) and (111) facets of nickel crystals all showed exponential activation by temperature. For the (110) and (111) facets, the activation energies were 56 and 53 kJ/mol respectively. For the (100) facet, a very low activation energy of only 27 kJ/mol was reported. Methane activation on the (100) facet was re-measured by Chorkendorff et al. [2]. They also found exponential activation, but an activation energy of 52 ± 1 kJ/mol, in reasonable accord with values on the other facets of Ni. The results of these latter measurements are shown as open triangles in fig. 3.

The experiments by Beebe et al. [1] and Chorkendorff et al. [2] were all carried out at a methane pressure of 1 Torr = 1.3 mbar. The study of the pressure dependence reported here shows that the methane gas was nearly, but not fully, equilibrated at T_s at this pressure (without a thermal finger). This explains why the activation energy determined previously [2] is slightly lower than the one found in the present work.

4.3. NON-EQUILIBRIUM ACTIVATION

In figs. 4 and 5, the initial sticking coefficient was determined at a low pressure and different temperatures of the crystal and the thermal finger in an attempt to separate the dependencies on T_g and T_s. A direct dynamical model developed earlier [11] predicts the behaviour shown in figs. 6a and 7a, where the dependency of the sticking coefficient is shown as a function of T_g for constant surface temperature and T_s for constant gas temperature respectively. Comparison with figs. 4 and 5 shows that, although there is some agreement, there is also some qualitative discrepancy. However, figs. 6a and 7a were generated assuming that methane molecules striking the Ni(100) surface were at the finger temperature T_f. This assumes that all methane fully accommodates on the finger before striking the surface (i.e. that the trapping coefficient $\alpha = 1$ and that desorption occurs only after full accommodation of all degrees of freedom with the surface). This ideal situation cannot be fulfilled under the experimental conditions used in figs. 4 and 5 since the trapping coefficient is unlikely to be unity on the finger. We assume that methane is trapped both on the finger and on the surface in a weak physisorption state like the one observed by Ceyer et al. [21] for methane on Ni(111). In this case the binding energy was estimated from temperature programmed desorption to be 26 kJ/mol leading to an average residence time on the surface of the order of 100 vibrations so that the assumption of full accommodation of trapped molecules is likely to be valid. Trapping into such a weak physisorption state is estimated as $\alpha \approx 0.75$ based on a molecular beam study on trapping of methane on Pt(111) [22].

A more reasonable approximation to figs. 4 and 5 is to assume that molecules incident on both the surface and finger are either trapped or reflected. In case of trapping, the molecule obtains the temperature of the surface on which it is trapped. Otherwise, we simply assume the molecule is reflected without exchanging energy (neglect inelastic processes) and assume the molecule retains its original temperature. Since we do not expect any major difference between the physisorbed state on the finger compared to the crystal, the trapping probability is assumed to be equal

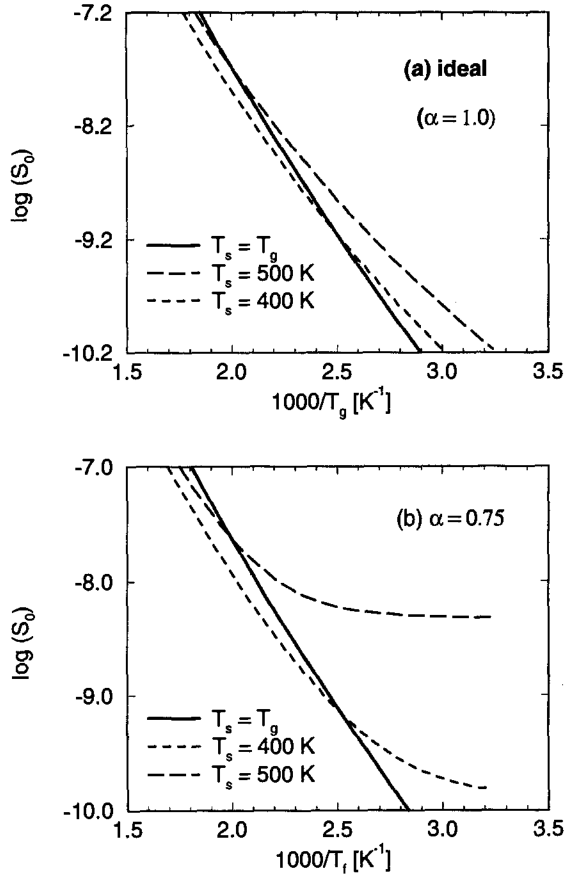

Fig. 6. Model calculation on (a) ideal activation by gas temperature, and (b) activation under experimental conditions.

on the two surfaces. If this probability of trapping is denoted α, the total reaction rate can then be written as

$$S(T_s, T_f) = \frac{1}{2-\alpha} S(T_s, T_g = T_f) + \frac{1-\alpha}{2-\alpha} S(T_s, T_g = T_s), \tag{1}$$

where $S(T_s, T_g)$ is obtained from the direct dynamical model.

Fig. 6a presents the calculation assuming pure activation by the gas temperature. This corresponds to the ideal experiment ($\alpha = 1$). As a reference, the calculated isothermal ($T_g = T_s$) activation curve is also shown. This comparison shows that the dissociation is activated mainly by the gas temperature, in complete agreement with the findings of the molecular beam experiments. In fig. 6b the experimental conditions is modelled assuming $\alpha = 0.75$. This is in excellent qualitative agreement with the experiments reported in fig. 4. At high T_f the activation curve behaves qualitatively like the one activated purely by gas temperature, while at

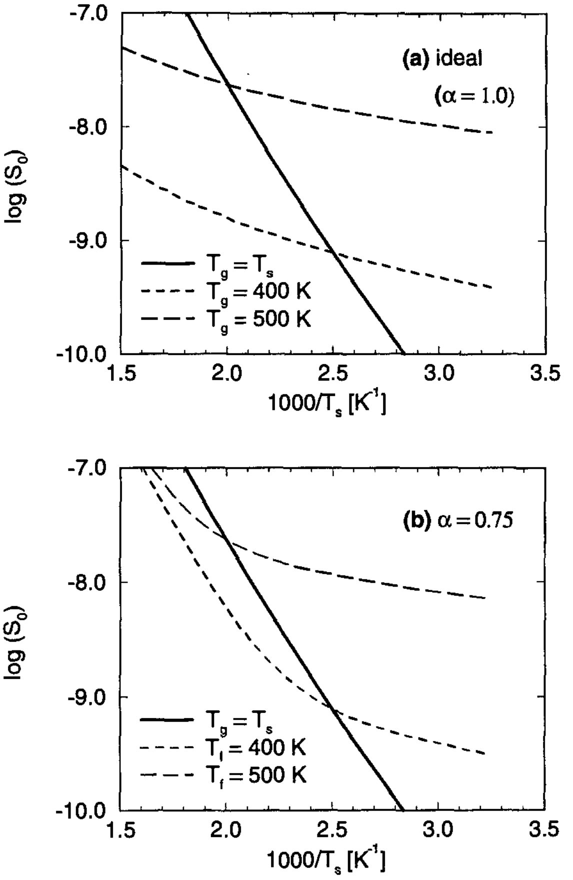

Fig. 7. Model calculation on (a) ideal activation by surface temperature, and (b) activation under experimental conditions.

$T_f < T_s$, the reaction rate is enhanced by the small fraction of methane at the surface temperature that has not trapped on the finger but rather scatters from it.

In fig. 7a the reaction rate activated purely by the surface temperature is shown. Compared to the activation by the gas temperature, the surface temperature has only a minor effect. The experimental simulation is shown in fig. 7b. Again, excellent qualitative agreement with the experiments of fig. 5 is obtained. The sticking is enhanced when $T_s > T_f$ since a small fraction of the gas is heated by the crystal surface.

It is seen that figs. 6b and 7b qualitatively explain the behaviour observed in figs. 4 and 5. The model calculation (that contained no fitting parameters) on the experimental conditions shows that the reaction in the experiments was mainly activated by the gas temperature and the model relying on a direct process is in complete agreement with these partially separate T_s, T_g experiments – a further confirmation of a direct mechanism.

5. Conclusion

The results and conclusions presented in this paper can be summarized as follows:

– The dissociative chemisorption of methane on Ni(100) was proved to be a direct impact mechanism under thermal conditions – both under isothermal as well as non-equilibrium conditions. This result is in good agreement with molecular beam results [6] and a direct dynamical model [11] that was developed to explain the molecular beam results.

– The temperature dependence of the dissociation was investigated under isothermal conditions either by using a relatively high pressure (3 mbar) or a new method – a thermal finger – which allows for isothermal conditions at lower pressure (0.5 mbar). It was found that the chemisorption is exponentially activated by the temperature with an activation energy of 59 ± 1.5 kJ/mol and a sticking coefficient of 1.7×10^{-9} at 400 K. This rate can be used to estimate rates on the real catalysts if the curvature indicated in more detailed investigations of the underlying mechanisms [6,11] is neglected.

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