Improved properties of the catalytic model system Ni/Ru(0001)

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The dissociative chemisorption of CH_4 on Ni overlayers on Ru(0001) has been investigated. It is found that the initial sticking probability at $T = 530$ K is approximately a factor of 20–30 higher on a pseudomorphic overlayer of Ni than on Ni(111) and a factor of two higher than on Ru(0001) illustrating the unique properties of metal-on-metal systems. The effect of enhanced reactivity is primarily ascribed to electronic effects induced by a straining of the Ni overlayer. The enhanced reactivity towards CH_4 is accompanied by new features in the thermal desorption spectra of CO. The reactivity of the system depends strongly on the annealing temperature. Molecular beam experiments at high translational energy are qualitatively different from thermal data showing a monotonic decrease of the CH_4 sticking probability as Ni is added.

KEY WORDS: bimetallic catalysts; metal overlayers; Ni; Ru; methane dissociation

1. Introduction

Since Ni is widely used as a catalyst for the steam reforming of natural gas to synthesis gas ($CH_4 + H_2O \rightarrow CO + 3H_2$) it would be advantageous if the surface properties could be modified to yield higher reaction rates and better selectivity. In this process the rate-limiting step is believed to be the dissociative adsorption of CH_4.

Alloy catalysts are very promising candidates for the improvement of rate and selectivity in a variety of catalytic reactions [1–3]. In this context, it is important to understand and control the reactivity of metal-on-metal structures that serve as model systems. Here phenomena such as epitaxial growth and surface alloys offer the opportunity to construct structures that are not otherwise found in nature. Already, a quite detailed picture of the electronic factors determining surface reactivity has been established [4]. Hereby, the astonishing correlation between the core level shift and the CO chemisorption energy found for a number of both pristine metal surfaces and overlayer structures [5] can be rationalized. Using density functional theory (DFT) calculations it was shown that the position of the d-band center determined the CO chemisorption energy [6]. A similar relationship between d-band center and activation energies for dissociation of simple molecules exists for a wide range of surfaces [7]. Future research should exploit this detailed knowledge in the design of novel materials for heterogeneous catalysis.

For late transition and noble metals, a surface strain can shift the d-band upwards and thus enhance the surface reactivity. This was demonstrated by Gsell *et al*. by producing local protrusions in the surface of Ru(0001) with incorporated argon bubbles [8]. Another way to induce strain is by growing pseudomorphic overlayers of one metal atop of another. Since the shifts in d-band center for such structures has been tabulated by Ruban *et al*. [9] one can predict which systems that should display enhanced reactivity. An increase in sticking probability has been observed for CH_4 on Co/Cu(111) [10] and N_2 on Fe/W(110) [11]. In the present study we focus on the properties of strained Ni overlayers on Ru(0001) – in particular the ability of these surfaces to dissociate CH_4. The adsorption of CO is investigated to examine how adsorption and dissociation of different molecules are linked. If both adsorption of CO and activation of CH_4 is governed by the position of the d-band center there should be a correlation between these two chemically very different processes.

The applicability of the d-band model in this system has been established in the investigations by Kratzer *et al*. on CH_4 dissociation on the Au/Ni(111) surface alloy [12]. Here it was shown that neighboring Au atoms lowered the d-band center resulting in a higher CH_4 activation barrier [12] as confirmed by experiments [13,14]. The graphite formation is even further suppressed making the system a promising candidate for a more stable steam reforming catalyst [13]. In a previous study of CH_4 activation on the clean Ni(111) and Ru(0001) surfaces, apparent activation barriers of 74 and 51 kJ/mol, respectively, were found [15]. At 530 K the initial sticking probability of Ru(0001) is approximately a factor of 10 higher than that of Ni(111). Both metals are catalytically active in steam reforming, ruthenium being the most active and stable, but also considerably more expensive than Ni.

Pseudomorphic growth of Ni on Ru(0001) causes the Ni overlayer to be strained 8% as compared to the pristine Ni(111) surface. As a consequence the d-band will become

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narrower and move upwards and we expect a lower activation barrier for CH_4 on this surface. Calculations show that the d-band center for a pseudomorphic monolayer of Ni on Ru(0001) will shift up by 0.29 eV [9]. Thus, if a pseudomorphic overlayer can be formed this should possess higher reactivity than Ni(111). Other calculations reveal that a Ni atom at the Ru(0001) surface has a surface segregation energy of -0.71 eV [16] and a mixing energy of -0.20 eV [17]. This implies – neglecting kinetic hindrances – that at low temperatures the Ni will remain at the surface and tend to form an alloy with Ru. At higher temperatures, entropy will drive the Ni into the bulk of the Ru crystal. However, this may not be a major problem when considering small Ru particles. The entropy drive will in that case be strongly limited as it was also argued for the Au/Ni system [18].

Previous studies on the system have shown that the growth of the first Ni overlayers adopts the Ru(0001) surface structure [19–21]. Annealing the surface may create 3D islands [20,21]. The reactivity towards CO chemisorption has been investigated by Berlowitz *et al*. [20]. The TPD of chemisorbed CO is shifted 60 K to higher temperatures as compared to Ni(111) [20] thus providing evidence that Ni/Ru(0001) is more reactive than Ni(111). An increase in activity was also seen in a study of Ni–Ru alloy catalysts on a SiO_2 support for dry reforming ($CH_4 + CO_2 \rightarrow 2CO + 2H_2$) by Crisafulli *et al*. [22]. NiRu alloy catalysts produced from aqueous solutions of $Ni(NO_3)_2$ and $Ru(NO)(NO_3)_3$, had activities superior to both pure Ni and Ru catalysts and deactivation rates comparable to Ru.

2. Experimental

All experiments are conducted in an ultrahigh vacuum (UHV) chamber with base pressure below 10^{-10} mbar described previously in [18]. Available equipment is Auger electron spectroscopy (AES), temperature-programmed desorption (TPD) and low-energy electron diffraction (LEED) optics. The Ru(0001) crystal is oriented using Laue X-ray diffraction to within 0.5° of the crystallographic plane which implies a step density of 1% or less [23]. The temperature was monitored with a chromel/alumel thermocouple spotwelded to the crystal. The crystal is initially cleaned using Ar^+ sputtering and then routinely cleaned by heating to 1473 K in an atmosphere of 3×10^{-8} mbar O_2 followed by 3 min annealing at 1473 K. This procedure results in a contaminant-free surface as detected by AES. The coverage of carbon was determined by heating the crystal in an atmosphere of 3×10^{-7} mbar O_2 and monitoring the $m/e = 28$ amu quadrupole mass spectrometer (QMS) signal (temperature-programmed oxidation – TPO). The amount of carbon on the surface is then proportional to the area below this curve. Calibration is done by comparing with the area of a CO TPD following CO saturation at room temperature which corresponds to 0.56 ML [24] (1 ML $= 1.58 \times 10^{19}$ sites m^{-2} on Ru(0001)). This TPO method allows accurate determination (sensitivity ~0.5% ML) of the carbon coverage but does not give direct information on the nature of the carbon species (carbide, graphite and CH species).

Bulb CH_4 exposures are initiated by sealing of the UHV chamber and then rapidly filling it with CH_4 until the needed pressure was reached. The experiment was terminated by dumping the CH_4 gas into a turbo molecular pump. In this manner experiments with pressures up to 10 mbar could be conducted. The ultra-clean methane gas (>99.999%) was further purified by flowing it through a Ni catalyst at room temperature. During experiments, all hot filaments in the chamber were turned off and the pressure was measured with a capacitance pressure gauge (Baratron). To ensure equilibration between crystal and gas temperature even at low pressures a thermal finger of Cu [25] is brought very close to the crystal surface. Previous experiments [25] have shown that when this procedure is followed, the gas temperature will equal that of the surface even at pressures below 10^{-2} mbar. After CH_4 exposure the surface composition is examined by AES and the amount of carbon on the surface is measured by a TPO experiment.

Supersonic molecular beams were formed by expanding a 3% CH_4/He gas through a 80 μm diameter nozzle. The nozzle was resistively heated to 1200 K. During these experiments all hot filaments in the chamber were turned off (except for the QMS) and the surface temperature was kept at 500 K. Sticking probabilities were determined by the method of King and Wells [26].

High-purity Ni (99.99%) was deposited by evaporation. Prior to deposition, the evaporator was outgassed for extended periods. The deposition procedures described below left no detectable impurities on the surface.

3. Results and discussion

3.1. Growth

As in the study by Berlowitz *et al*. [20] two different Ni deposition procedures were used: (a) Ni was deposited at a crystal temperature of 500 K and subsequently the crystal was flashed to 700 K. (b) Ni was deposited at 500 K followed by a 2 min anneal at 1100 K. In the following we will see that the reactivity of these two different surfaces are very different. The growth pattern was examined by plotting the AES Ni(61 eV)/Ru(273 eV) ratio versus the amount of Ni deposited as measured by the area of the Ni $m/e = 58$ TPD peak at 1350 K. The Ni(61 eV) and Ni(848 eV) AES signals were observed to be proportional but the higher surface sensitivity of the 61 eV line caused us to prefer this. For Ni overlayers flashed to 700 K a monotonic increase in AES Ni/Ru ratio is observed. This indicates multilayer growth, as observed by Berlowitz *et al*. [20]. We did not observe clear breaks in the slope of the AES data (layer-by-layer growth), as reported previously [20,21]. When the Ni films are annealed to 1100 K the AES Ni/Ru intensity ratio for thick Ni films saturates at a constant level. Berlowitz *et al*. also find this behavior, and report that the saturation

level corresponds to an Ni coverage of ∼2.2 ML [20]. We therefore calibrate our Ni coverage by identifying the AES Ni/Ru saturation value for Ni films annealed to 1100 K with 2.2 ML. Some uncertainty is related to determining the saturation level, but we are confident that this coverage calibration is correct within ±20%.

The reduction in AES Ni/Ru ratio upon annealing was interpreted as the result of 3D island formation on top of a Ni monolayer (Stranski–Krastanov growth). Kołaczkiewicz and Bauer [21] also observe that annealing of low-temperature deposited multilayer Ni films results in agglomeration and a decrease of the Ni AES signal.

Our LEED observations show that both preparation procedures lead to pseudomorphic overlayers (*i.e.*, (1×1) LEED patterns) at Ni coverages below ∼0.7 ML. In the regime 0.7–1.6 ML a Moiré pattern (approximately (14 × 14)) appears for the samples flashed to 700 K, whilst the samples annealed to 1100 K still display the (1 × 1) structure. Thorough analysis of LEED pictures from a clean Ru(0001) surface and pictures from 1 ML Ni annealed to 1100 K showed no difference in the spot distances. This means that any deviation from pseudomorphic growth is undetectable using our LEED setup. At coverages above ∼1.7 ML only the Moiré pattern is seen for both deposition methods. This interference pattern implies that the Ni overlayer assumes the Ni(111) lattice parameter ($d = 2.49$ Å). Both deposition procedures thus initially lead to pseudomorphic growth. As more than ∼0.7 ML Ni is added extensive annealing to 1100 K is needed to produce pseudomorphic overlayers.

A STM study by Meyer *et al.* [19] shows that the first monolayer grows pseudomorphically when deposited at 550 K. Additional Ni leads to a reconstruction of that layer to form a denser phase, whilst bilayer and thicker films lead to Moiré structures.

The decrease of the AES Ni/Ru ratio when annealing multilayer samples may also be caused by diffusion of excess Ni into the bulk of the Ru crystal. Based on the present data, we will only conclude that Ni initially grows pseudomorphically and then relaxes to the Ni(111) structure. The annealing temperature influences the Ni coverage where this relaxation takes place.

3.2. Adsorption of CO

We have tested the reactivity of the Ni overlayers by desorption of adsorbed CO. In figures 1 and 2 the TPD spectra following exposure to 30 L CO at room temperature are shown. The Ni coverage is indicated at each spectrum. For the samples that have been flashed to 700 K we observe a gradual decrease of the characteristic Ru(0001) double peak [27]. As we reach ∼1.9 ML Ni the TPD is very similar to the data published for CO desorption from Ni(111) [28]. No new features appear in the TPD spectra.

The surfaces that have been annealed 2 min at 1100 K display quite different properties. A new peak at ∼500 K evolves when Ni is added to the surface and only disappears as the Ni coverage exceeds ∼1.5 ML. This has previ-

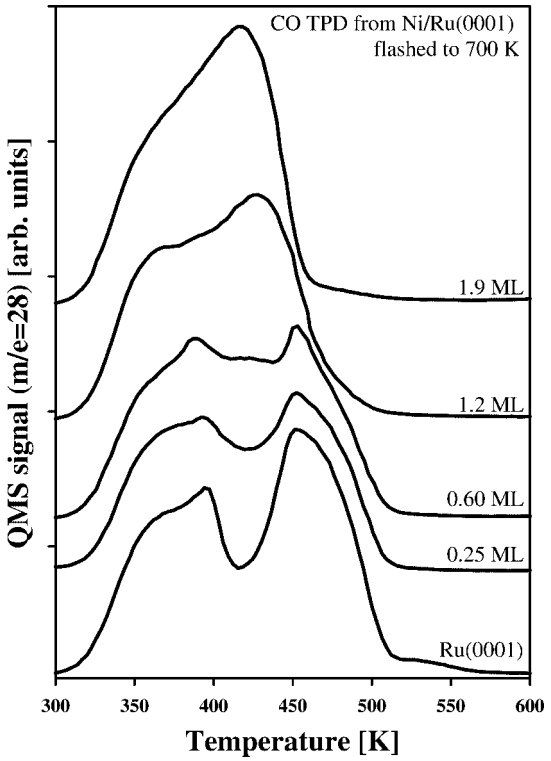

Figure 1. CO TPD following exposure to 30 L CO at room temperature. Ni was deposited at 500 K and subsequently flashed to 700 K. The heating rate was 2 K/s. The Ni coverage is given at each spectrum.

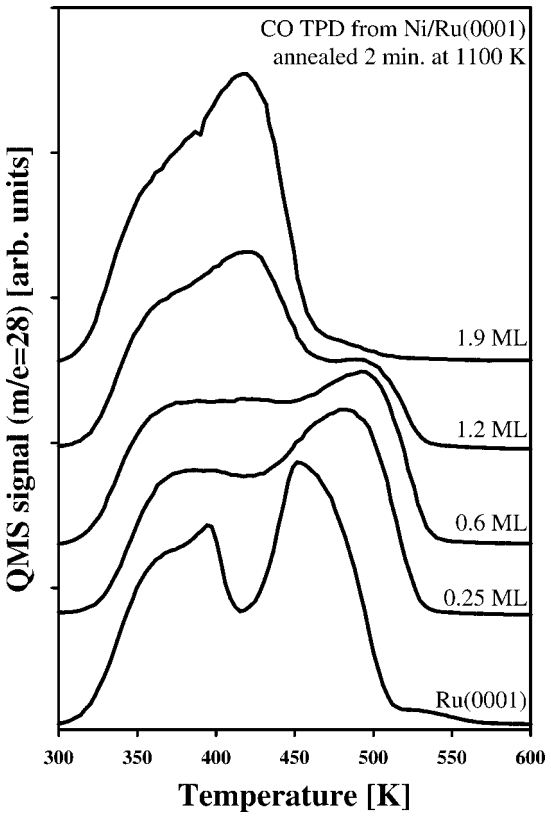

Figure 2. CO TPD following exposure to 30 L CO at room temperature. Ni was deposited at 500 K and subsequently annealed 2 min at 1100 K. The heating rate was 2 K/s. The Ni coverage is given at each spectrum.

ously been observed but from a differently prepared surface. Berlowitz *et al*. [20] only anneal the surface to 700 K and observe that the CO desorption peak is situated at 500 K for 1 ML Ni/Ru(0001). This is in agreement with our data from samples annealed 2 min at 1100 K. Possibly, the duration of the 700 K anneal could influence the results. Berlowitz *et al.* [20] do not give information on the annealing time used.

When ∼2 ML Ni has been deposited, the further addition of Ni does not change the shape and position of the spectra significantly. At this point the Ni layers seem fully relaxed, since the CO TPD spectra are almost identical to that obtained on Ni(111) [28] and from Ni/Ru(0001) surfaces annealed to 700 K. Judging from the areas beneath the TPD curves the amount of adsorption sites on the two differently prepared surfaces is almost equal.

For Ni coverages below 1.2 ML we observe a new feature at 500 K in the CO TPD spectra from surfaces annealed at 1100 K. This is a sign of stronger binding of CO on these surfaces and we ascribe this stronger binding to the higher position of the d-band on the pseudomorphic overlayers [9]. We do not observe the 500 K feature in the CO TPD spectra from surfaces that have only been flashed to 700 K, indicating a difference in surface structure depending on annealing treatment. Although both structures seem to be pseudomorphic for Ni coverages below ∼0.7 ML there is a strong difference in reactivity as seen by CO adsorption and also – as we shall see in the following – for CH_4 dissociation.

3.3. CH_4 dissociation

The dissociative sticking probability, s_0, of CH_4 was measured by exposing the crystal to CH_4 gas and subsequently determining the amount of carbon on the surface by TPO. The initial sticking coefficient is calculated as the ratio of adsorbed carbon atoms to the number of CH_4 molecules that have impinged on the surface during the gas exposure. This will lead to an underestimation of s_0 at high carbon coverages, but as we restrict ourselves to coverages below 0.1 ML the error will be less than 20%.

In figure 3 we show s_0 as a function of the Ni coverage at $T_{\text{surface}} = T_{\text{gas}} = 530$ K. This temperature is high enough that no CO will adsorb on the crystal. Furthermore, at this temperature the value of s_0 is low enough that reasonable pressures ($\sim 10^{-2}$ mbar) can be used. We observe two very different behaviors of s_0 depending on the preparation procedure. For Ni overlayers flashed to 700 K the sticking probability decreases monotonically from the value on Ru(0001) (2.4×10^{-7}) to $(1.5 \pm 1) \times 10^{-8}$, which within uncertainty is the value reported for Ni(111) at this temperature [15]. When the surface is annealed to 1100 K we observe that s_0 goes through a maximum at approximately 0.7–0.8 ML. For higher amounts of Ni deposited the sticking coefficient decreases and levels off at the same value as for the samples flashed to 700 K.

The results obtained in the CH_4 dissociation experiments are in qualitative agreement with the CO TPD spectra presented above. In both cases the properties of the surface become similar to those of Ni(111) as the Ni coverage exceeds ∼2 ML. Furthermore, in both cases the Ni surfaces that have been annealed 2 min at 1100 K exhibit the highest reactivity. In the CO TPD experiments this higher reactivity manifests as the appearance of a new desorption peak at higher temperatures. In the dissociative adsorption of CH_4 we observe a higher value of s_0. The Ni coverage at which the surface is most reactive seems to concur in the two types of experiments. Examining the spectra of figure 2 we note that the peak temperature of the feature at ∼500 K is maximal for a Ni coverage in the range 0.6–1.2 ML. This agrees with the position of the maximum in figure 3. If the increased reactivity is a result of the strain induced by the pseudomorphic growth we would expect that 1 ML Ni/Ru(0001) is the most reactive overlayer. When the maximum in figure 3 occurs slightly below this value it could in part be due to a small error in the coverage calibration. Possibly, the growth of the second Ni layer starts before the first monolayer is completed. In all cases, we have by deposition of Ni (that is less reactive than Ru) on Ru(0001) created a surface more reactive than both Ni(111) and Ru(0001). The initial sticking probability of CH_4 is a factor of 20–30 higher than on Ni(111) and a factor of 2 higher than on Ru(0001). This clearly demonstrates the unique properties of metal-on-metal systems.

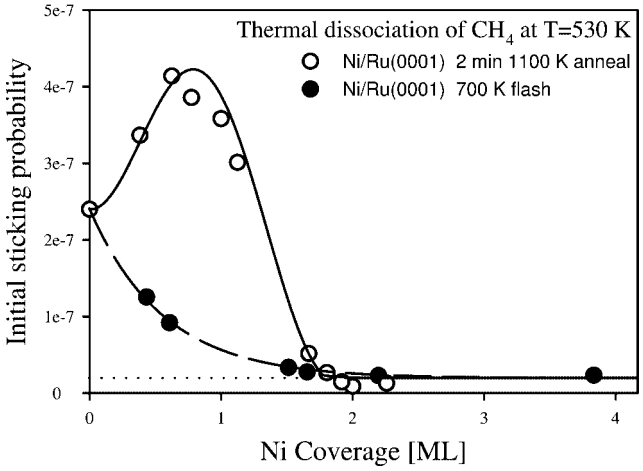

Figure 3. Initial sticking coefficient of CH_4 on Ni/Ru(0001) overlayers at $T_{\text{gas}} = T_{\text{surface}} = 530$ K. Filled symbols are surfaces annealed 2 min at 1100 K whilst open symbols have been flashed to only 700 K. The solid and dashed lines are guides to the eye. The dotted line indicates the value of s_0 on Ni(111) at this temperature [15]. The sticking probability of CH_4 is higher than both Ni(111) and Ru(0001) on the overlayers that have been annealed at 1100 K.

The observed reactivity increase can be discussed in terms of ensemble and geometrical effects, special reactivity of steps and defects or it may be the result of electronic factors. Let us first consider the influence of ensemble and geometric factors. Theoretical studies have shown that dissociation proceeds *via* a path right over one of the Ni atoms [12,29], so the geometry of the transition state should not be affected by a change in Ni–Ni distance. The fact that we observe a sticking coefficient higher than both Ru(0001) and Ni(111) can therefore not be rationalized in terms of

a geometric or ensemble effect. The influence of atomic steps and surface defects must also be addressed. In a recent paper [15] the influence of such special sites on the CH_4 dissociation on the pristine Ru(0001) and Ni(111) surfaces was investigated. It was concluded that the steps indeed are more reactive but are quickly blocked with adsorbed carbon. When the carbon coverage exceeds the step density, no sign of the steps can be seen. As we conducted our measurements at carbon coverages of 5–10% ML we do not expect any influence of such sites. To corroborate this, we measured carbon coverage *versus* exposure data (the uptake curve) for a few Ni overlayers. A first-order Langmuir expression gave a satisfactory fit, and no sharp kinks were seen in the curve. Therefore, the increased reactivity cannot be explained by the presence of steps or defects.

The enhanced reactivity must therefore be related to electronic effects: the d-band of the strained overlayer is shifted upwards by 0.29 eV [9] stabilizing the transition state complex as compared to Ni(111). The d-band center position is a general measure of surface reactivity, so both chemisorption energies and activation barriers are lowered as the d-band center shifts up [7]. The correlation between the higher CO adsorption energy and the increased sticking probability of CH_4 can thus be understood. Furthermore, the implications of our findings extend to the activity of real catalysts. Crisafullli *et al*. [22] ascribe in agreement with the present data the higher activity (measured at 873 K) of NiRu catalysts to metal–metal interactions. The alloy particle surfaces are mainly covered by Ni, and our system is thus a very realistic model of these catalysts. In this context, it should be noted that the endothermic steam reforming process usually is carried out at high temperature (900–1300 K). This means that the data from surfaces annealed to 1100 K are the most relevant for applications within industrial catalysis.

The surfaces that are only annealed to 700 K show no signs of enhanced reactivity. The available surface analysis equipment does not allow us to speculate on the origin of this phenomenon. For low coverages there is a big difference in reactivity between surfaces flashed to 700 and annealed to 1100 K, respectively, but LEED pictures and AES spectra only display significant differences at Ni coverages above 0.7 ML. In short, we do not understand the cause of the observed reactivity difference between surfaces annealed to 700 and 1100 K, respectively. With the available equipment we cannot detect any difference. To resolve this issue, a more detailed atomic scale study (*e.g.*, by STM) on the influence of annealing on the surface structure must be carried out.

Finally, we have investigated CH_4 dissociation at high translational energies using a 3% CH_4/He supersonic molecular beam with a nozzle temperature of 1200 K. This mixture results in a translational energy of the CH_4 molecules impinging on the surface of 78 kJ/mol, as measured by time of flight techniques [31]. At this energy, s_0 is sufficiently high that it can be measured by the procedure of King and Wells [26]. In figure 4 the results are presented for Ni surfaces annealed 2 min at 1100 K. The surface temperature during these experiments was 500 K. Also shown is the behavior of the thermal sticking probability at $T = 530$ K (dashed line) reproduced from figure 3. The behavior of s_0 at high translational energies produced by molecular beams is markedly different. s_0 decreases monotonically until it reaches a constant level for Ni coverages above ∼2 ML. Still, the sticking probability slightly below 1 ML Ni is higher than that of many layers of Ni, but a maximum is not observed.

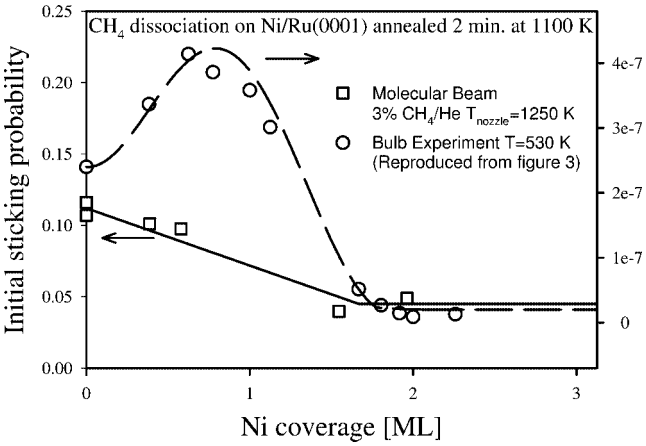

Figure 4. Initial sticking coefficient of CH_4 molecules produced by a supersonic molecular beam of 3% CH_4/He with $T_{nozzle} = 1200$ K. The Ni surfaces have been annealed 2 min at 1100 K. The dashed line and open circles show the thermal sticking at 530 K. The solid line is a guide to the eye. We see a monotonic decrease of s_0 as Ni is added. This behavior is in contrast to the thermal experiments.

We cannot offer any explanation of the different behavior of the sticking coefficient as function of Ni coverage in beam and bulb experiments. Certainly the gas–surface interaction depends strongly on incident translational energy and it may be that – as for N_2/Ru(0001) [23] – the dissociation route at beam energies is different from that at thermal energies. Further studies at different translational energies are needed to clarify this point. One may speculate that in bulb experiments the dissociation occurs over Ni atoms displaced normal to the surface as discussed in [15] and [30]. This route is not probed in a beam experiment where the flux of CH_4 molecules is much lower. This would mean the sticking coefficient is related to the elastic properties of the surface. Furthermore, dynamical effects may come into play at the high translational energies.

3.4. Temperature-programmed oxidation

After CH_4 exposures a TPO was conducted. Such an experiment is the reverse process of CO dissociation and may yield information on this reaction. Representative spectra from Ru(0001), 1.1 ML, and 2.6 ML Ni films annealed 2 min at 1100 K are shown in figure 5. The coverage of carbon is indicated at each spectrum. The spectra for Ru(0001) are similar to what has been published previously [31]. It is clear that on all surfaces, the peak moves towards higher temperatures with increasing coverage. This could be due to a blocking of the sites available for oxygen dissociation

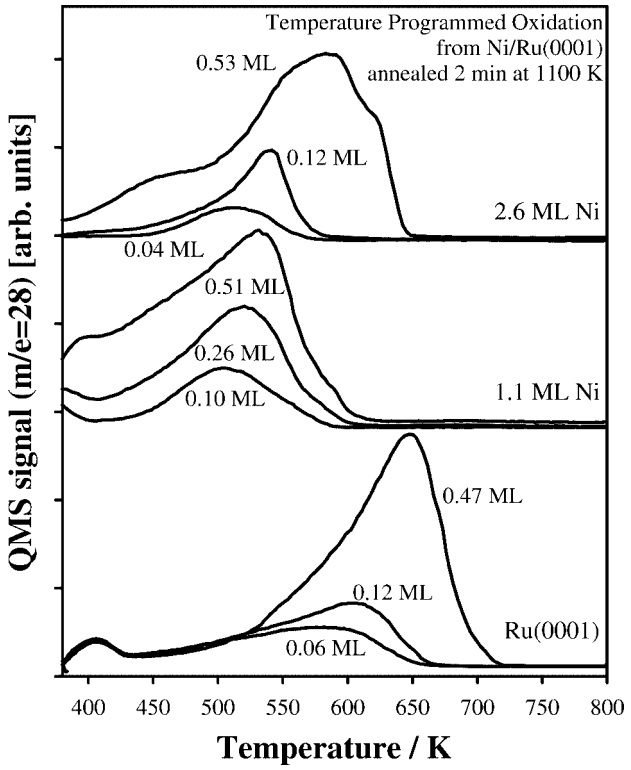

Figure 5. Temperature-programmed oxidation reaction on Ru(0001) and Ni/Ru(0001) surfaces annealed to 1100 K. The heating rate was 2 K/s. The carbon coverages are indicated. The desorption peak is situated at lower temperatures on the 1.1 ML Ni sample compared to the thicker Ni film. This implies a lower CO dissociation barrier and that the adsorbed carbon is more reactive.

or carbon island formation. On Ni(111) recombination of carbide and oxygen on the surface ($\theta_C = 0.20$; $\theta_O = 0.25$) gives rise to a peak around 670 K [32]. We observe that the TPO peak for thick Ni films ($\sim$2.6 ML) is situated at somewhat lower temperatures. We ascribe this to the fact that in our experiments a much higher amount of oxygen is present to react with the carbon and desorb as CO.

When we compare the spectra from 1.1 to 2.6 ML Ni we observe that the desorption peak lies at lower temperatures for the 1.1 ML surface for similar carbon coverages. This means that the barrier for oxidation of the adsorbed carbon is lower on thin Ni layers on Ru(0001) than on thick films, which resemble Ni(111). In agreement with this Crisafulli *et al.* find that hydrogenation of the surface carbon starts at a lower temperature on NiRu catalysts compared to pure Ni catalysts [22]. This causes a lower deactivation rate of NiRu catalysts since the amount of inactive carbonaceous species is decreased. Furthermore, our results also imply that the barrier for CO dissociation is lower on Ni/Ru(0001) than on Ni(111) making the NiRu system an interesting candidate for a better methanation catalyst.

On Ru(0001) it was observed that for small ($<$0.03 ML) carbon coverages, addition of Au to the surface causes the TPO peak to move towards higher temperatures [15]. Since Au preferentially decorates the steps and defects of the surface [33] it was concluded that the barrier for the reaction between C and O was lower at a step site. Possible influence of step-related effects should also be considered for these experiments on the Ni/Ru(0001) surface. However, one would expect the thicker Ni layers to have the highest defect density and it thus seems that steps/defects have minor influence on this reaction.

4. Conclusions

The reactivity of Ni/Ru(0001) towards CO adsorption and CH_4 dissociation was investigated. We find that

- Pseudomorphic Ni overlayers can be produced that both bind CO stronger and dissociate CH_4 a factor of 20–30 better than Ni(111).
- The reactivity depends critically on the preparation annealing procedure. Flashing the samples to only 700 K resulted in overlayers significantly less reactive.
- Molecular beam experiments showed a monotonic decrease of the sticking probability of CH_4 as Ni was added.
- Temperature-programmed oxidation reaction indicated the adsorbed carbon to be more reactive on Ni/Ru(0001) than on Ni(111). The barrier for CO dissociation is lowered.

We observe a correlation between enhanced binding of CO and increased sticking probability of CH_4 and we ascribe the higher reactivity of Ni/Ru(0001) to an electronic effect: the d-band of the strained Ni overlayer is moved upwards compared to Ni(111) making the surface more reactive.

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