Promotion through gas phase induced surface segregation: methanol synthesis from CO, CO_2 and H_2 over Ni/Cu(100)

Jesper Nerlov and Ib Chorkendorff

Center for Atomic-scale Materials Physics (CAMP), Physics Department, Building 307, Technical University of Denmark, DK-2800 Lyngby, Denmark

Received 14 April 1998; accepted 5 August 1998

We have studied the rate of methanol formation over Cu(100) and Ni/Cu(100) from various mixtures of CO, CO_2 and H_2. It is found that the presence of submonolayer quantities of Ni leads to a strong increase in the rate of methanol formation from mixtures containing all three components whereas Ni does not influence the rate from mixtures of CO_2/H_2 and CO/H_2, respectively. The influence of the partial pressures of CO and CO_2 on the rate indicates that the role of CO is strictly promoting. From temperature-programmed desorption spectra it follows that the surface concentration of Ni depends strongly on the partial pressure of CO. In this way the increase in reactivity is interpreted as a CO-induced structural promotion introduced by the stronger bonding of CO to Ni as compared to Cu. It is suggested that this type of promotional behavior will be of general importance in existent catalysts and perhaps even more relevant in the development of new or improved bimetallic catalysts.

Keywords: promotion, methanol synthesis, segregation, Ni, Cu(100), CO, CO_2, H_2

1. Introduction

It is well recognized that bimetallic alloy systems are very promising subjects in the development of new or improved catalysts [1–4]. This holds both with respect to achievement of an increase in activity, selectivity as well as stability of the catalyst. Single crystalline surface science based experiments are obviously a good starting point in the development and characterization of alloy model systems since a more detailed characterization of both structure and reactivity of the surface can be obtained.

This point of view is very well illustrated by recent studies of the Au/Ni(111) system where it was shown that the two immiscible metals Au and Ni do form surface alloys [5] and that the reactivity of the alloy surface with respect to CH_4 dissociation can be controlled by the gold coverage [6,7]. Therefore, also subsurface carbon migration and segregation, which may lead to catastrophic carbon filament formation on conventional Ni-catalysts, are inhibited. This knowledge then formed the basis of the development of a recently patented steam reforming catalyst [9] based on a Au/Ni surface alloy [8].

The interest in surface alloy systems also emphasizes the need for a theoretical description of surface alloy phase diagrams. A database has lately been obtained for all combinations of transition metals where it is shown that most bimetallic systems can be grouped in one of four generic classes depending on the signs of the heat of segregation and the surface mixing energy [10]. Although this database is very useful in terms of a guideline towards choosing a system with the desired phase diagram, there are additional considerations which should be taken into account. In case of catalytic reactions one must also consider the chemical potential of the gas phase, since strong bonding of adsorbates will result in a gain in energy of the system. For a bimetallic system this means that an enrichment at the surface of the component that binds a given adsorbate stronger may occur. This phenomenon is very well understood from a theoretical point of view just as the likely influence on catalytical activity is recognized [11,12]. There are, however, to our knowledge no studies involving well-defined single crystalline surfaces which deal with this phenomenon from the point of view of reactivity.

In the present work we demonstrate by detailed reactivity studies of a modified single crystalline surface that variation of the chemical potential of the gas phase may lead to dynamical changes of the surface structure and that it is possible in this way to promote a given chemical reaction. As a model system we have chosen methanol formation over Ni/Cu(100). According to the database of Christensen et al. [10] both the segregation energy for Ni in Cu and the surface mixing energy are positive. This means that one would expect Ni and Cu to alloy but that Cu will segregate to the surface. This behavior has indeed been found both in theoretical and experimental studies of the segregational behavior of NiCu alloys [13–15]. This means that a modification of a Cu surface by deposition of small amounts of Ni appears to be quite uninteresting from a chemical point of view, since one would expect the Ni to go subsurface and not contribute to the chemical properties of the surface. This is also found in the case of reaction of CO_2 and H_2 over Ni/Cu(100) where the presence of Ni does not influence the rate of MeOH formation. However, by adding CO to the gas mixture one does obtain a strong increase in the turnover frequency (TOF) of MeOH formation over Ni/Cu(100), which is not obtained over the clean Cu(100) surface. It is demonstrated that the enhanced reactivity is

due to a CO-induced change in the surface concentration and structure introduced by the considerably stronger bonding of CO to Ni as compared to Cu. The role of CO appears to be strictly promoting, emphasizing the dynamic nature of the promotion. It is suggested that the observed promotional mechanism will be of general importance in existent catalysts, just as it emphasizes the potential, but also complexity, of using bimetallic systems for development of new and improved catalysts.

2. Experimental

All experiments were performed in a conventional stainless steel UHV chamber equipped with a high-pressure cell (HPC). The UHV system has been described in detail elsewhere [16]. The high-pressure cell has, however, been subject to some changes. Firstly, it has been rebuilt in Ni-free steel. This was done in order to avoid formation of nickel carbonyls (mainly $Ni(CO)_4$) in the cell at elevated CO pressures, since it was found that these carbonyls decompose on the sample leading to severe Ni contamination of the surface. Even so, a small Ni contamination level could not be completely avoided. Whether this originated from the bulk of the Cu crystal, from carbonyls present in the synthesis gas or, most probably, from the Ni-containing feedthroughs within the HPC is not clear. A contamination level of 0.1% Ni/h at $P_{CO} = 100$ mbar and $T_{sample} = 543$ K was, however, regarded as insignificant for the interpretation of the obtained data. In addition, the post-reaction gas composition was studied by means of a gas chromatograph (GC) instead of a quadrupole mass spectrometer (QMS). Both a thermal conduction and a flame ionization detector were employed which allowed quantitative detection of both reaction products as well as the components of the synthesis gas. The gases used were H_2 (ALFAX N57), CO_2 (ALFAX N48) and CO (ALFAX N47). H_2 and CO_2 were subject to additional purification as described in [16]. CO was led through a Cu coil which was freezed at 77 K before introduction to the HPC. This was done mainly in order to remove $Ni(CO)_4$ which, as described above, is a critical contaminant for the present experiments.

The Cu(100) crystal was cut, polished on both sides and prepared as in [17]. It was mounted on 0.5 mm gold wires which were also used for resistively heating. Ni was evaporated by resistively heating of a tungsten filament which had thin Ni wire wrapped around it. The Ni coverage was determined by means of X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption (TPD) and will be discussed in detail elsewhere [18]. For the coverages given below, $\theta_{Ni} = 1$ ML corresponds to the Ni coverage at which the saturation level of adsorbed CO is obtained. The CO TPD spectra used for coverage determination were obtained after a reaction at $T = 543$ K over Ni/Cu(100) involving a synthesis gas mixture of 100 mbar CO, 30 mbar CO_2 and 1370 mbar H_2. In the experiments reported here equal amounts of Ni were deposited on both faces of the crystal and the coverages given below are the mean values. A deviation of 10% from the mean value was allowed. It was found from separate poisoning experiments that the faces of the crystal are responsible for approximately $2/3$ of the activity of a clean Cu crystal [18]. Consequently, a value corresponding to $1/3$ of the intensity obtained from the clean surface, which originates from the edges and the spark cut holes of the crystal, is subtracted from all data, whereby an intensity corresponding to the amount of methanol formed on the faces of the crystal is obtained.

The components of the synthesis gas were introduced one at a time into the HPC following the sequence, CO_2, CO and H_2. The gas mixture was then allowed to mix for 15 min before the reaction started. The reaction was run in batch mode for $\Delta t = 45$ min at $T = 543$ K and $P_{total} = 1.5$ bar. The walls of the HPC and the tubes in the setup for admittance and removal of the gases were kept at $T = 350$ K in order to avoid adsorption of MeOH, which would lead to memory effects. Never were two experiments performed the same day and the amount of MeOH present in a blind experiment (involving pure H_2) carried out the day after a synthesis experiment was below the detection limit of our system.

The rate of MeOH formation over Cu(100) from CO_2/H_2 mixtures has previously been investigated in our system [16]. In that case methanol was detected by means of a QMS. Calibration of the present GC signal with respect to the amount of methanol synthesized was then obtained by conducting experiments at the same conditions as in [16]. This allowed us directly to relate a given GC signal to a turnover frequency/sites (TOF). For convenience we have in the present work defined one site as one Cu surface atom and anticipated that 1 ML of Ni atoms is equal to that of Cu (in [16] one site corresponded to two Cu surface atoms but since we will deal with reactivity/Ni surface atom in this work, we have changed the unit).

3. Results and discussion

Initially, the reactivity of the clean Cu(100) surface towards various mixtures of CO, CO_2 and H_2 was measured (figure 1, $\theta_{Ni} = 0$). It is found that the amount of methanol formed from a mixture of 100 mbar CO and 1400 mbar H_2 admixture is below the detection level of our system (TOF/sites $< 1 \times 10^{-6}$). For a mixture of 30 mbar CO_2 and 1470 mbar H_2 and a mixture of 30 mbar CO_2, 100 mbar CO and 1370 mbar H_2 it is found that the rates are essentially identical. This indicates that CO does not influence the rate of MeOH formation over Cu(100). In fact, we observe a small decrease in activity as CO is admitted to the synthesis gas. This is considered to be within the error bar of the measurements, but apart from that, one should, given that the rate is zeroth order in CO, expect a small decrease in the MeOH rate, since CO is added to the synthesis gas on the expense of H_2 (the reaction order in H_2 is

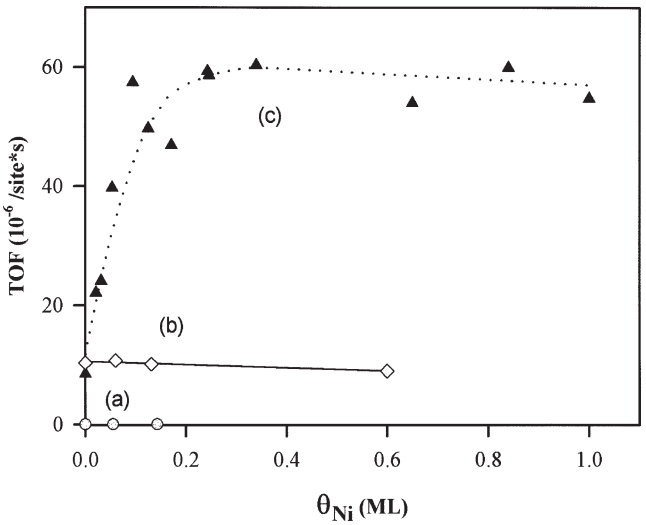

Figure 1. MeOH turnover frequencies obtained over Ni/Cu(100) at $T = 543$ K as a function of Ni coverage for three different gas mixtures. (a) 100 mbar CO and 1400 mbar H_2, (b) 30 mbar CO_2 and 1470 mbar H_2, and (c) 100 mbar CO, 30 mbar CO_2 and 1370 mbar H_2.

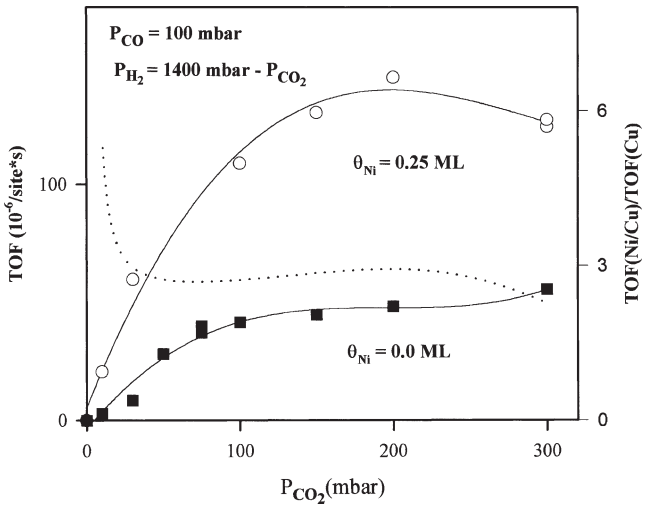

Figure 2. Turnover frequencies of MeOH over clean Cu(100) and Ni/Cu(100) ($\theta_{Ni} = 0.25$ ML) obtained for varying partial pressures of CO_2, at $P_{CO} = 100$ mbar ($P_{H_2} = 1400$ mbar $- P_{CO_2}$) at $T = 543$ K. The solid lines through the data points are third-order polynomial fits to the data points, while the dotted curve is the ratio between the two fitted curves.

positive [16]). This result will be further discussed in [18] just as the apparent discrepancy between the present observation and the result of Yoshihara and Campbell [19], who observed an increase in reactivity upon admission of CO, will be dealt with. The rate of MeOH formation from the three types of mixtures described above was also measured after submonolayer quantities of Ni were deposited onto the Cu(100) crystal (figure 1). For the CO/H_2 mixture the level of MeOH formation remains below the detection level when Ni is deposited, just as the amount of MeOH formed from the CO_2/H_2 mixture does not change significantly. The first observation emphasizes that direct hydrogenation of CO at the present conditions is not feasible over Ni/Cu(100) either, whereas the second observation indicates that Ni does not affect the hydrogenation of CO_2 over Cu(100). On the other hand, we do observe a drastic increase in the rate of MeOH formation from the $CO/CO_2/H_2$ mixture as submonolayer quantities of Ni are deposited. The initial increase is linear at $\theta_{Ni} < 0.15$ ML after which a fairly constant level is reached.

In this way one can attribute the increase in MeOH formation to the presence of Ni at the surface, which allows us to relate the increase in MeOH formation to a TOF/Ni site. From the initial slope of the fitted curve given in figure 1 we obtain that the initial TOF/Ni site corresponds to approximately 60 $\times$ TOF/Cu site making it a rather substantial promotional effect. Thus, we are obviously dealing with a synergy effect where neither of the combinations (CO, CO_2, H_2), $(CO, H_2/Ni)$ and $(CO_2, H_2/Ni)$ appears to affect the rate of MeOH formation over Cu(100), whereas the presence of all four components $(CO, CO_2, H_2/Ni)$ leads to a dramatic increase in reactivity. If we consider the possible reaction mechanisms (hydrogenation of CO_2 or CO) there are essentially two possibilities which can account for the observed behavior. Either CO (and Ni) promotes the hydrogenation of CO_2 or, alternatively, CO_2 (and Ni) promotes the hydrogenation of CO. One may take the fact that no measurable direct hydrogenation takes place from a CO/H_2 mixture over Ni/Cu(100) as a strong indication that it is the CO promotion which is effective in the present case, although the other possibility cannot be completely excluded.

In order to investigate the nature of the promotional effect in more detail we then studied the influence of the CO and CO_2 partial pressures on the MeOH rate over Cu(100) and Ni/Cu(100). Figure 2 shows the variation of the MeOH rate as the CO_2 partial pressure is varied in the 0–300 mbar range, while the CO partial pressure is kept constant (at 100 mbar) for the clean Cu(100) surface as well as for $\theta_{Ni} = 0.25$ ML ($P_{H_2} = 1400$ mbar $- P_{CO_2}$, $T = 543$ K). Though differences exist between the two curves, the ratio between the MeOH conversion of the two systems (figure 2, dotted line) is fairly constant over a large pressure regime. This is taken as an indication of a similar reaction mechanism in the two cases. Since MeOH is formed strictly from CO_2 and H_2 over clean Cu(100) (according to figure 1), this most likely also holds for the reaction over Ni/Cu(100). Thus, CO appears to be promoting MeOH synthesis over Ni/Cu(100).

In the same manner information on the effect of adding CO to the synthesis gas can be obtained from figure 3 which shows the variation of the MeOH rate with CO partial pressure at $P_{CO_2} = 30$ mbar and $\theta_{Ni} = 0.20$ ML ($P_{H_2} = 1470$ mbar $- P_{CO}$, $T = 543$ K). In the case of Cu(100) the rate obviously is zeroth order in CO pressure as discussed above. For the $\theta_{Ni} = 0.20$ ML system we observe a linear increase in the rate with increasing CO pressure up to $P_{CO} = 35$ mbar after which the influence of additional CO appears to be negligible (essentially a zero-order dependence as it is observed for Cu(100)). This indicates that a certain partial pressure of CO is necessary in

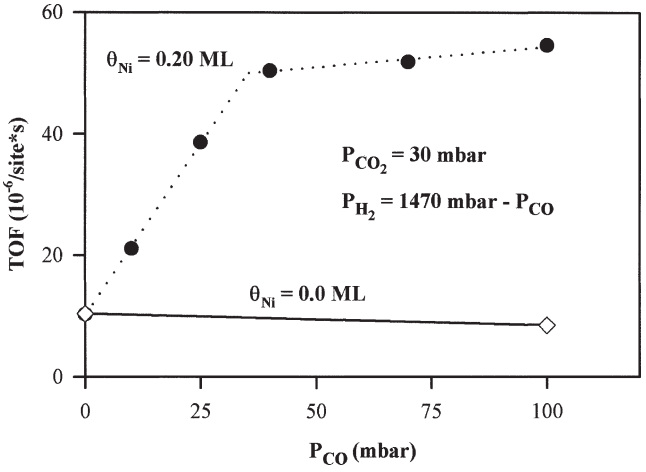

Figure 3. Turnover frequencies of MeOH over clean Cu(100) and Ni/Cu(100) ($\theta_{\mathrm{Ni}} = 0.20$ ML) obtained for varying partial pressures of CO, at $P_{\mathrm{CO_2}} = 30$ mbar ($P_{\mathrm{H_2}} = 1470$ mbar $- P_{\mathrm{CO}}$) and $T = 543$ K.

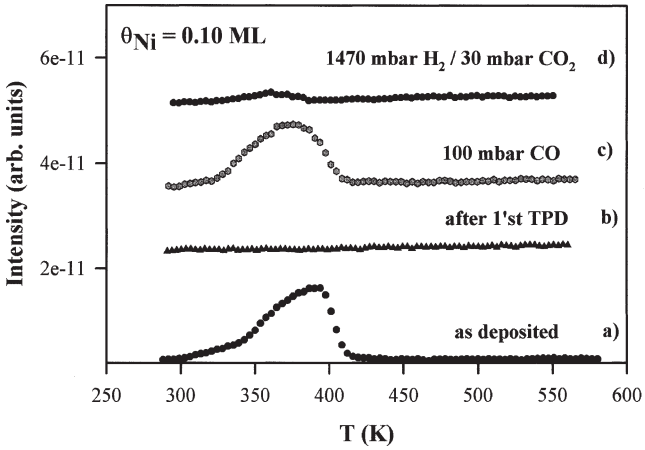

Figure 4. CO TPD spectra obtained from 0.10 ML Ni/Cu(100) after exposures to (a) 10 L CO at RT (as deposited), (b) 10 L CO at RT (post TPD), (c) 100 mbar CO for $\Delta t = 15$ min at $T = 320$ K (post TPD), and (d) 1470 mbar H_2 and 30 mbar CO_2 for $\Delta t = 15$ min at $T = 320$ K (post TPD).

order for the promotional effect to be fully active, while an increase in pressure above this point only has very little influence on the rate. This is taken as an additional support for the idea that CO has a promotional effect rather than a role as a reactant in the present system. Thus, both the rate dependence of the CO and CO_2 partial pressure strongly indicate that it is the reaction between CO_2 and H_2 which is responsible for the activity of the Ni/Cu(100) system, and that the role of CO is promoting.

In order to explain the promoting role of CO we turn to an investigation by TPD of the adsorbed species present after given gas exposures. Unfortunately, it is not possible to investigate the surface at the reaction temperature since the adsorbed species desorb as the gas is pumped out (TPD spectra obtained after cooling the sample in the reaction mixture will be discussed in [18]). Instead we have obtained a series of TPD spectra after exposures at lower temperatures ($T = 300$–320 K).

Figure 4(a) shows the CO TPD spectrum obtained after exposing 10 L CO to a freshly deposited 0.1 ML Ni/Cu(100) sample at RT. We observe a CO-related peak at $T = 390$ K. Since CO does not adsorb on Cu(100) at RT this is attributed to CO bonding to Ni [13]. After the TPD and cooling to RT this treatment was then followed by an additional dose of 10 L CO in UHV. This did not result in adsorption of detectable amounts of CO (figure 4(b)) or any other species as probed by TPD. This means that annealing of the sample at 543 K during the TPD results in removal of all Ni from the surface. However, if a post-TPD sample (0.1 ML Ni/Cu(100)) is transferred to the high pressure cell and exposed to 100 mbar CO for 15 min at $T = 320$ K (figure 4(c)) we obtain a CO TPD peak quite similar to the one obtained for the initial CO dose. This means that elevated pressures of CO is capable of extracting essentially all of the initially deposited Ni to the surface. Finally, figure 4(d) shows the TPD spectrum obtained after exposing a post-TPD surface to a mixture of 30 mbar CO_2 and 1470 mbar H_2 for 15 min. This exposure results only in very little CO uptake ($\sim$7% of the uptake obtained after the initial exposure). In the last case a small CO_2 desorption peak ($\sim$3% of the maximum CO signal) was also detected. It originates from decomposition of formate but considering the small intensity it is of no significance to the interpretation of the data.

The results of the sequence are understood as follows. After the first TPD Ni is no longer present at the surface. This finding is obviously connected to the annealing of the sample during the first TPD and is in accordance with the results of Hernnäs et al. [20], who found that extensive migration of Ni into subsurface sites takes place upon annealing at the final temperature of the TPD experiment (543 K). The reason for the migration not taking place already at RT is most probably due to kinetics (the bulk diffusion lengths are of the order of 0.05 Å/h at 300 K and 10 Å/s at 540 K [21]). Though the Ni obviously is removed from the surface upon annealing at the reaction temperature figure 4(c) emphasizes that high exposures of CO may restore the initially deposited Ni. This is obviously not the case for the H_2/CO_2 mixture used in figure 4(d) which only extracts a small fraction of the deposited Ni. The fraction, which is extracted, is attributed to CO_2 dissociating on the surface resulting in a non-zero coverage of CO, which is able to extract a small amount of Ni. The driving force behind the surface segregation of Ni is the energy gain obtained by chemisorption of CO. Thus, the amount of Ni which one will extract depends both on CO partial pressure (as shown in figure 4) and temperature.

Having both Ni and CO present at the surface one could also expect disproportionation reactions to occur. No carbon build-up beyond the low level always observed on the clean copper crystal (less than 5% of a monolayer graphite and dependent on the overall cleanliness of the cell) was observed in the post-reaction XPS investigation. On the other hand, a weak increase of the methane signal could be observed at the highest Ni coverages. It was unfortunately

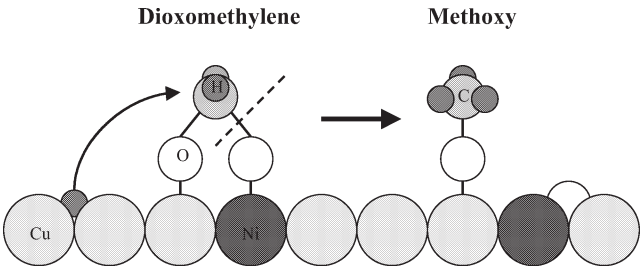

Figure 5. Proposed mechanism for the rate-limiting step in the synthesis of MeOH from CO_2 and H_2. It is suggested that the presence of Ni at the surface lowers the reaction barrier by stabilizing one of the products (adsorbed oxygen).

not possible to quantify this signal as it was obscured by a high and constant background of methane independent of the status of the crystal. The weak dependency indicates that isolated Ni atoms in the low coverage regime are not capable of dissociating CO whereas this possibility increases when bigger ensembles of Ni become possible at the high coverage.

From the above discussion it is then clear that an important effect of adding CO to the reaction mixture is to create a chemical potential for Ni to stay at the surface. Considering that the reactivity measurements strongly imply that CO acts as a promoter in the present system it is most probably the enrichment of Ni at the surface that leads to the increase in methanol formation. There are several reasons why this indeed should be the case. It has been observed that formate is formed under UHV conditions in the case of coadsorption of H_2 and CO_2 on Ni(110) [22] whereas elevated pressures are needed in the case of Cu(100) [15]. This means that a higher rate of formate formation could be anticipated for the Ni/Cu(100) system. On the other hand, a Ni surface is also more reactive towards disproportionation of formate [22] meaning that an increase in formate coverage for the Ni/Cu(100) system by no means is given. Another possibility is that Ni affects the rate-limiting step, which has been suggested to be the hydrogenation of dioxymethylene into methoxy and adsorbed oxygen (figure 5) [16,24]. Recent theoretical investigations indicate that final-state effects are dominating in case of reactions at (transition) metal surfaces [25]. That is, if the products of a reaction are stabilized (for instance, by coadsorption of another metal) then the barrier for reaction is lowered (by a proportional amount). It could then be speculated that the larger oxygen affinity of Ni compared to Cu increases the rate of the reaction step shown in figure 5 since a stabilization of the final state (in this case adsorbed oxygen) and thereby a lowering of the reaction barrier most probably occurs. This argument could, we believe, also account for a similar increase in the methanol rate from CO_2/H_2 mixtures observed for the Zn/Cu(111) system [26] since Zn, like Ni, has a larger affinity towards oxygen compared to Cu.

The present results clearly illustrate that the influence of the chemical potential of the gas phase on the surface structure and composition can be very significant. For the high-area $Cu/ZnO/Al_2O_3$ methanol catalyst similar reversible changes in morphology [27] and activity [28] as a function of the reduction potential of the gas phase have indeed been observed. The latter has mainly been ascribed to an area effect. Another effect of an increase in the reduction potential of the gas phase over the high-area catalyst could be a reduction of the surface of the ZnO particles and subsequent alloying of Zn into the surface of the Cu particles. This idea is supported by recent IR data obtained for the high-area catalyst [29] which shows a relatively low CO stretching frequency at reducing conditions. According to the authors [29] this could be obtained by alloying Zn into Cu(111) facets as it was done in [26]. Further investigation is obviously needed in order to clarify this matter.

4. Conclusion

We have performed reactivity studies of methanol formation over Cu(100) and Ni/Cu(100) from various mixtures of CO, CO_2 and H_2. While CO does not influence the rate of MeOH formation from CO_2 and H_2 over Cu(100), a strong increase is found in the case of Ni/Cu(100). The influence of the partial pressures of CO and CO_2 on the rate indicates that the role of CO is strictly promoting. From TPD spectra it follows that the surface concentration of Ni depends critically on the CO partial pressure. In this way we attribute the increase in reactivity to a CO-induced structural promotion introduced by the stronger bonding of CO to Ni as compared to Cu. The fact that the gas responsible for the structural change does not participate in the reaction only emphasizes the dynamical aspect of the promotion. We believe that this finding could be of importance in existing real catalytical systems (as, for example, the Cu-based MeOH catalysts) but it is perhaps even more relevant in the development of new and improved bimetallic catalysts.

Acknowledgement

We gratefully acknowledge discussions with and suggestions by I. Alstrup, B.S. Clausen and J.K. Nørskov. This work was financed by the Danish Research Councils through the Center for Surface Reactivity. The Center for Atomic-scale Materials Physics is sponsored by the Danish National Research Foundation.

References

[1] G.A. Somorjai, *Surface Chemistry and Catalysis* (Wiley, New York, 1994).
[2] W.H. Sachtler and R. van Santen, Adv. Catal. 26 (1977) 69.
[3] V. Ponec, Adv. Catal. 32 (1983) 149.
[4] J.H. Sinfelt, *Bimetallic Catalysts* (Wiley, New York, 1983).
[5] L.P. Nielsen, F. Besenbacher, I. Stensgaard, E. Lægsgaard, C. Engdahl, P. Stoltze, K.W. Jacobsen and J.K. Nørskov, Phys. Rev. Lett. 71 (1993) 754.
[6] P.M. Holmblad, J.H. Larsen and I. Chorkendorff, J. Chem. Phys. 104 (1996) 7289.

[7] P.M. Holmblad, J.H. Larsen, I. Chorkendorff, L.P. Nielsen, F. Besenbacher, I. Stensgaard, E. Lægsgaard, P. Kratzer, B. Hammer and J.K. Nørskov, Catal. Lett. 40 (1996) 131.
[8] F. Besenbacher, I. Chorkendorff, B.S. Clausen, B. Hammer, A. Molenbroek, J.K. Nørskov and I. Stensgaard, Science 279 (1998) 1913.
[9] DK patent application 0683/97 (1997).
[10] A. Christensen, A.V. Ruban, P. Stoltze, K.W. Jacobsen, H.L. Skriver, J.K. Nørskov and F. Besenbacher, Phys. Rev. B 56 (1997) 5822.
[11] V. Ponec, Surf. Sci. 80 (1979) 352.
[12] D. Tomànek, S. Mukherjee, V. Kumar and K.H. Bennemann, Surf. Sci. 114 (1982) 11.
[13] K.Y. Yu, D.T. Ling and W.E. Spicer, J. Catal. 44 (1976) 373.
[14] A.V. Ruban, I.A. Abrikosov, D.Ya. Kats, D. Gorelikov, K.W. Jacobsen and H.L. Skriver, Phys. Rev. B 49 (1994) 11383.
[15] S. Quannasser, L.T. Wille and H. Dreyssé, Phys. Rev. B 55 (1997) 14245.
[16] P.B. Rasmussen, M. Kazuta and I. Chorkendorff, Surf. Sci. 318 (1994) 267.
[17] I. Chorkendorff and P.B. Rasmussen, Surf. Sci. 248 (1991) 35.
[18] J. Nerlov, J. Wambach and I. Chorkendorff, in preparation.
[19] J. Yoshihara and C.T. Campbell, J. Catal. 161 (1996) 776.
[20] B. Hernnäs, M. Karolewski, H. Tillborg, A. Nilsson and N. Mårtensson, Surf. Sci. 302 (1994) 64.
[21] D.R. Buytymowitz, J.R. Manning and M.E. Read, J. Phys. Chem. Ref. Data 2 (1973) 643.
[22] J. Wambach, G. Illing and H.-J. Freund, Chem. Phys. Lett. 184 (1991) 239.
[23] P.A. Taylor, P.B. Rasmussen, C.V. Ovesen, P. Stoltze and I. Chorkendorff, Surf. Sci. 261 (1992) 191.
[24] P.B. Rasmussen, P.M. Holmblad, T. Askgaard, C.V. Ovesen, P. Stoltze, J.K. Nørskov and I. Chorkendorff, Catal. Lett. 26 (1991) 373.
[25] M. Mavrikakis, L.B. Hansen, J.J. Mortensen, B. Hammer and J.K. Nørskov, Symposium Series, Am. Chem. Soc. to be published.
[26] T. Fujitani, I. Nakamura, T. Uchijima and J. Nakamura, Surf. Sci. 383 (1997) 285.
[27] B.S. Clausen, G. Steffensen, B. Fabius, J. Villadsen, R. Feidenhans'l and H. Topsøe, Topics Catal. 1 (1994) 367.
[28] M. Muhler, E. Törnqvist, L.P. Nielsen, B.S. Clausen and H. Topsøe, Catal. Lett. 25 (1994) 1.
[29] N.-Y. Topsøe and H. Topsøe, J. Mol. Catal. (1998), submitted.