

CO-Free Methyl Formate from Methanol: the Control of the Selectivity of the Process on Cu-Based Catalysts

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Abstract

The influence of the structure and composition of precursor (which is used as support after treatment) and the structure of copper particles formed in the course of activation of copper containing catalysts by hydrogen on their catalytic properties in methanol dehydrogenation and reactivity towards hydrogen adsorption has been studied. The reactivity of catalyst towards hydrogen adsorption was investigated by means of Thermal Desorption Spectroscopy (TDS). Two catalysts preserving the structure of their precursor-oxide after reduction (CuZnSi and CuCr) and having strong bonds of metal particles with the surface are characterized by hydrogen adsorption at elevated temperatures. This type of adsorption is not observed for usual unsupported metal copper and for two other catalysts Cu/SiO₂ and Cu/Cr₂O₃. Methanol dehydrogenation proceeds via successive reactions $2\text{CH}_3\text{OH} = \text{CH}_3\text{OOCH} + 2\text{H}_2$ (I) and $\text{CH}_3\text{OOCH} = 2\text{CO} + 2\text{H}_2$ (II). The catalyst activity in reaction (II) greatly depends on the state of metal copper in the catalyst. It was assumed that catalyst activity in methylformate conversion to CO and H₂ and, hence, the selectivity of methanol dehydrogenation in respect to methylformate at moderate methanol conversion depends on the character of interaction between metal copper particles and catalyst oxide surface, which is determined by the composition and structure of oxide precursor

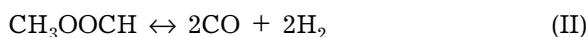
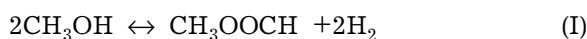
INTRODUCTION

The wide use of Cu-containing catalysts determines the intent attention to their active surface formation. Earlier it was shown that the activation temperature has crucial influence on the catalytic behaviour of copper hydroxosilicates [1] and copper chromite [2] in ester hydrogenolysis and acetone hydrogenation, respectively. Phase transformations of copper hydrosilicates [3] and copper chromite [4] under the hydrogen activation were thoroughly studied. It was shown that the composition of these compounds depends on the reduction temperature.

The present work is devoted to the study of the influence of the structure and composition of precursor (used as support after treatment) and the structure of copper particles formed in the course of hydrogen activation

on the adsorption and catalytic properties of copper containing dehydrogenation catalysts.

Copper hydroxosilicate of Chrisocolla structure, zinc-copper hydroxosilicate of Zincsilite structure and copper chromite of tetragonally distorted spinel structure were chosen for investigation. The reactivity towards hydrogen adsorption and catalytic behaviour of reduced samples in practically important process of methanol dehydrogenation were studied. The peculiarity of the process consists in its consecutive mechanism through the formation of intermediate product – methyl formate:



The selectivity on methyl formate depends on the ratio of the rates of reaction (I) and (II) [5].

The direct methyl formate production from methanol has the advantage over the other

methods because it doesn't demand to store and use of environmentally hazard carbon monoxide.

EXPERIMENTAL

Catalyst preparation

The samples of copper hydroxysilicate with Cu : Si = 0.14 : 0.86 (Cu/SiO₂) and copper-zinc hydroxysilicate with Cu : Zn : Si = 0.13 : 0.30 : 0.57 (CuZnSi) were prepared by the deposition-precipitation method at a gradually increasing pH from the appropriate mixtures of aqueous solutions of copper and zinc nitrates with aerosil suspended in urea, and calcined at 723 K in flowing air [6].

The copper chromite sample CuCr₂O₄ was prepared via thermal decomposition of coprecipitated copper-chromium hydroxycarbonate carried out in air at 1173 K (CuCr and Cu/Cr₂O₃).

The catalysts were then reduced in flowing hydrogen at the following temperatures: 653 K for copper hydroxysilicate (Cu/SiO₂) and copper-zinc hydroxysilicate (CuZnSi); and 573 K for copper chromite (CuCr) and 773 K for Cu/Cr₂O₃.

The characteristics of the catalysts are given in the Table 1.

Catalysts characterization

Thermal analysis (STA), infrared spectroscopy (IRS), X-ray diffraction analysis (XRD), and electron microscopy (EM) were used at every preparation step to control the conformity of the obtained samples' composition and structure to that for the catalysts obtained

under the given conditions in the previous studies.

Adsorption measurements. A vacuum-adsorption apparatus [7] supplied with a system of reaction gas circulation was used for adsorption studies. A sample (3–5 g, the grain size 0.25–0.5 mm) was placed into a microreactor, designed so that a gas flow might be directly injected into the sample layer to provide its fluidization.

The sample was reduced in pure hydrogen at static conditions under gas circulation; the initial hydrogen pressure 8 10⁴ Pa was decreased to 4–6 10⁴ Pa during the reduction. The reduction temperature was raised at the rate 2 K/min to desired value and then maintained constant for 2 h.

Thermal desorption spectroscopy (TDS) experiments were performed using argon as a carrier gas and a thermal conductivity detector. The apparatus sensitivity to hydrogen was estimated from calibration tests as 3.1 10⁻¹⁹ mV min/molecule.

Catalytic properties. The catalytic properties of the samples were studied by the continuous flow method at atmospheric pressure and 473 K. Catalyst grains of size 0.25–1.0 mm, mixed with the quartz particles, were loaded in the reactor.

Before the reaction, the initial samples were activated in a hydrogen flow at the temperatures indicated above. The temperature was elevated at the rate of 2 K/min, and then the catalyst was kept in hydrogen flow for 2 h at a specified temperature. After the activation, the initial mixture, containing 0.14–0.16 molar fractions of methanol in helium, was fed to the catalyst. The temperature of the experiment was set, and after an hour the composition of the reaction mixture at the reactor outlet was

TABLE 1
Copper metal characteristics of the samples

Sample	T_{red} , K	Cu ⁰ surface area, m ² /g catalyst*	Size of Cu particles, Å
Cu/SiO ₂	653	26	30–50
CuZnSi	653	8	30–70
CuCr	573	6	50 × 100 × 100
Cu/Cr ₂ O ₃	773	4	300–500

*Copper surface area was determined by N₂O titration.

successively analyzed several times till its constant value was reached. The concentrations of methanol, C_m^0 (in the initial mixture) and C_m (in the reactor outlet mixture), of methyl formate, C_{mf} , and carbon monoxide, C_{CO} , were determined chromatographically and expressed in terms of their molar fractions. No substantial amounts of other carbon-containing products were found in the experiments. The analysis was made with a flame-ionization detector and a thermal conductivity detector. No analytic measurement of the hydrogen concentration C_{H_2} was made, it was calculated from the methyl formate and carbon monoxide concentrations on the basis of stoichiometric ratios according to eq. (1):

$$C_{H_2} = 2C_{mf} + 2C_{CO} \quad (1)$$

Conversion degree (X) and selectivity (S) were calculated by eqs. (2) and (3), respectively:

$$X = \frac{(2C_{mf} + C_{CO})}{C_m^0 (1 - C_{mf} - 2C_{CO})} \quad (2)$$

$$S = \frac{2C_{mf}}{2C_{mf} + C_{CO}} \quad (3)$$

Contact time (t) was determined as a ratio between the catalyst volume loaded to the reactor (v) and adjusted to normal conditions volume of the initial steam-gas mixture fed in a unit time (V):

$$t = v/V \quad (4)$$

Changing the amount of catalyst loaded and the rate of steam-gas mixture feeding allowed to vary the contact time from 0.02 to 3 s. The catalyst' volume was determined as the ratio of the catalyst mass to its bulk weight.

The reaction rates were calculated from the expression, which follows from the differential material balance for the gas flow. In the case of low concentrations of the reaction mixture components it may be represented by the following approximation:

$$W = \frac{aN_A}{V_m \rho} \frac{dC}{dt} \quad (5)$$

where W is the reaction rate, molecule/g s; a is the stoichiometric coefficient; C is the concentration of component being consumed or formed, molar fraction; N_A is the Avogadro

number; $V_m = 2.24 \cdot 10^4 \text{ cm}^3/\text{mol}$ is the volume of 1 mol gas under the normal conditions; ρ is the catalyst bulk weight, g/cm^3 ; t is the contact time, s. Note that, despite the presence of the catalyst bulk weight in eq. (5), the calculated rate values are actually independent of ρ and relate to the catalyst weight unit, since implicitly ρ enters also into the denominator of the t value.

RESULTS AND DISCUSSION

Samples characterization

According to IRS data the Cu/SiO₂ sample precursor has the structure of Chrisocola mineral. In accordance with [8] it represents copper particles of 30–50 Å in size on the silica surface after reduction at 653 K. Copper metal surface according to the N₂O titration is 26 m²/g.

The CuZnSi sample is copper-zinc hydroxosilicate of Zincsilite structure according to IRS data. Zincsilite has a layered structure, zinc ions are located in two positions: (1) octahedral positions of the layers formed by [Si₄O₁₀] tetrahedrons, and (2) at tetrahedrons in water interlayer. Copper ions partially substitute zinc ions in each structural position, being distributed among the 'layer' and 'interlayer' in a 2 : 1 ratio [3, 8]. Zincsilite is represented by the formula: Zn_{*x*}(Zn_{3-*x*}□_{*x*})[Si₄O₁₀](OH)₂ · *n*H₂O, where Zn_{3-*x*} are the zinc ions located at octahedral positions of the layers formed by [Si₄O₁₀] tetrahedrons, Zn_{*x*} are the zinc ions located in water interlayer, and □_{*x*} are the vacancies [9]. The IRS, XRD, and EM studies of the CuZnSi sample, obtained in the present work, showed the sample after reduction at 653 K to be copper-zinc hydroxosilicate of Zincsilite structure with metal copper particles of size 30–70 Å located at its surface. The extent of copper reduction is about 66 %. According to the results of N₂O titration, the surface area of metal copper amounted 8.0 m²/g for the CuZnSi sample.

The sample CuCr has a spinel-like structure with tetragonal distortion of the lattice ($a = 8.537 \text{ \AA}$ and $c = 7.792 \text{ \AA}$). In accordance with [10] after the reduction at 573 K the CuCr sample represents the plane metal copper particles linked epitaxially with the acidic copper

chromite surface of spinel structure. The extent of copper reduction for the sample reduced at 573 K is less than 60 %. N_2O titration of the sample showed the surface area of copper to be $6.0 \text{ m}^2/\text{g}$.

The $\text{Cu}/\text{Cr}_2\text{O}_3$ sample was obtained by decomposition of the spinel structure as a result of high temperature (773 K) reduction of copper chromite. The sample represents the copper metal particles of roundish shape at the surface of chromia ($\alpha\text{-Cr}_2\text{O}_3$). Copper metal surface area is $4 \text{ m}^2/\text{g}$ according to N_2O titration.

So, the samples Cu/SiO_2 and $\text{Cu}/\text{Cr}_2\text{O}_3$ represent the round shaped copper particles weakly bound to the surface of supporting oxides SiO_2 and Cr_2O_3 , respectively. Two other catalysts CuZnSi and CuCr represent copper metal particles at the surface of precursors (the oxide phases of variable composition) keeping their structure after the reduction. Copper metal particles in reduced copper chromite have the plate form and are epitaxially bounded to the spinel surface that indicates the strong bonding between copper particles and surface. It is shown [7] that the copper chromite reduction with copper metal formation occurs without destruction of the structure *via* red-ox substitution of copper ions by protons yielding copper hydrochromite. The form of copper particles in the reduced CuZnSi sample of zincsilite structure has not been studied, but the fact that 66 % of copper reduce without zincsilite structure destruction makes it possible to propose the similarity of the mechanism of its reduction with copper chromite.

Adsorption properties of the catalysts

The hydrogen adsorption was studied at temperatures 160–650 K and $4\text{--}8 \cdot 10^4 \text{ Pa}$.

Two series of experiments were carried out for each sample. In the first one the hydrogen adsorption took place during the activation of precursors at 653 K for Cu/SiO_2 and CuZnSi and at 573 K for CuCr and $\text{Cu}/\text{Cr}_2\text{O}_3$. The sample was cooled at first to the room temperature and kept not less than 18 h, then to 160 K and kept 1 h. After such a treatment the hydrogen thermodesorption was carried out.

The second series of experiments included only the low temperature hydrogen adsorp-

tion on the surface free of chemisorbed hydrogen during the reduction. The conditions of the low temperature hydrogen adsorption were as in the first series: chemisorption at the room temperature for more than 18 h and at 160 K for 1 h.

The first series of the experiment allowed to reveal the whole set of adsorbed hydrogen states, the second – the hydrogen adsorbed at low temperatures with low activation energy of adsorption. The results have shown that the properties of the Cu/SiO_2 sample are close to the $\text{Cu}/\text{Cr}_2\text{O}_3$ and of the CuZnSi – to the CuCr . Between these two groups the essential difference in adsorption properties is observed. At the surface of the first group of samples the low temperature hydrogen adsorption, mainly, takes place. At the surface of the second group of the samples the low temperature adsorption is also observed, but mainly the adsorption occurs at elevated temperatures.

The typical thermal desorption spectrum of hydrogen for the Cu/SiO_2 sample in both series of experiments is shown in the Fig. 1, *a*. One can see that the main amount of hydrogen is desorbed at near room temperature and the fewer amounts – at the higher temperature, about 400 K. The similar spectrum was observed for the $\text{Cu}/\text{Cr}_2\text{O}_3$ sample in both series of experiments. In general the spectrum is similar to the one typical for the unsupported metal copper [11, 12]. For copper not bounded with the support it is shown [13, 14] that the dissociative adsorption is characterized by the heat of adsorption 40–50 kJ/mol and activation energy of adsorption up to 50 kJ/mol. So, it may be concluded that the dissociative adsorption takes place at the room and lower temperatures on the surface of the first group of the samples with the characteristics mentioned above.

Figure 1, *b* shows the thermal hydrogen desorption spectrum obtained in the first series of experiments for the CuCr sample. One can see that hydrogen is desorbed, mainly, at elevated temperatures. The portion of low temperature desorbed hydrogen is very small. The thermal desorption spectrum obtained in the second series of the experiments has the only low temperature peak of weak intensity. The spectrum in low temperature field is similar to

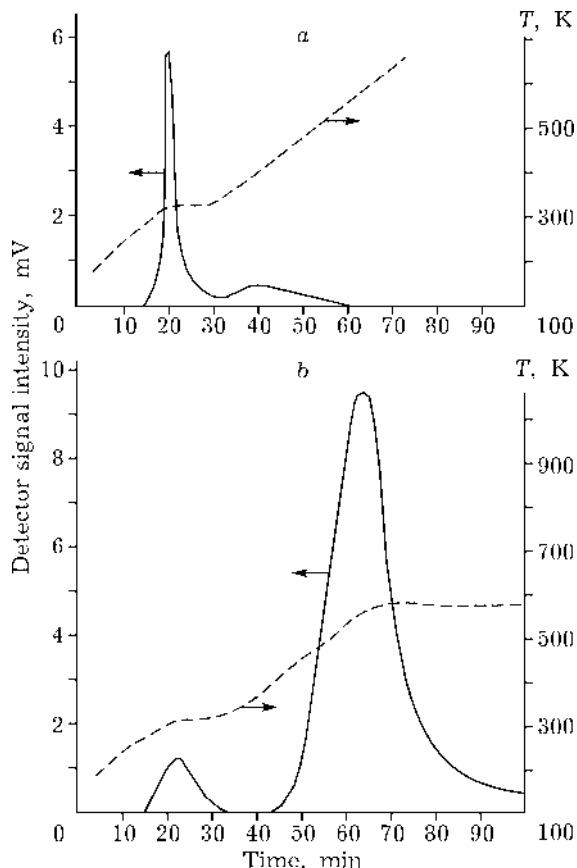


Fig. 1. Thermal hydrogen desorption spectra for the Cu/SiO₂ (a) and CuCr (b) catalysts: a – after the reduction of the precursor by hydrogen at 653 K and keeping in hydrogen at room temperature and 160 K; b – after the reduction of the precursor CuCr₂O₄ by hydrogen at 573 K and keeping in hydrogen at room temperature and 160 K.

one for the first group samples and for unsupported copper. So, the hydrogen adsorption on the CuCr sample surface proceeds to the most extent at elevated temperatures and is characterized, as it was shown earlier [7], by the heat of adsorption about 80 kJ/mol and activation energy of adsorption about 70 kJ/mol.

The similar general picture is obtained for the CuZnSi catalyst. Hence, at the surface of the second group of catalysts (CuCr and CuZnSi) the hydrogen adsorption proceeds, in the main, at elevated temperatures and is characterized by the heat and activation energy of adsorption significantly higher than those parameters for the first group of the catalysts and for copper free of support.

So, hydrogen adsorption properties of copper metal particles weakly bounded to the oxide-support in the Cu/SiO₂ and Cu/Cr₂O₃ catalysts are similar to adsorption properties of cop-

per metal. Adsorption properties of copper metal particles epitaxially bounded to the precursor oxide (acid copper chromite and acid copper-zinc hydroxosilicate of variable composition) in the CuCr and CuZnSi samples differ significantly. On the main part of their surface the adsorption occurs at elevated temperature and is characterized by appreciably higher heat and activation energy of adsorption.

Catalytic behaviour

Catalytic behaviour in the methanol dehydrogenation was studied. In the special experiment it was shown that the samples reveal the activity only after the reduction of precursors. The catalysts were preliminary activated: Cu/SiO₂ and CuZnSi at 653 K; CuCr at 573 K and Cu/Cr₂O₃ at 773 K. The typical kinetic curves are shown in Fig. 2.

At very short contact time, the methanol consumption is accompanied by methyl formate accumulation with no CO formation. Thus, the selectivity of methyl formate formation approaches unity. As the contact time increases, so does the methyl formate concentration. Then, after reaching its maximum, it decreases to a rather low value. CO formation becomes noticeable at certain values of contact time, which differ with the catalysts, and the CO concentration increases with increasing contact time. This function has an inflection point at

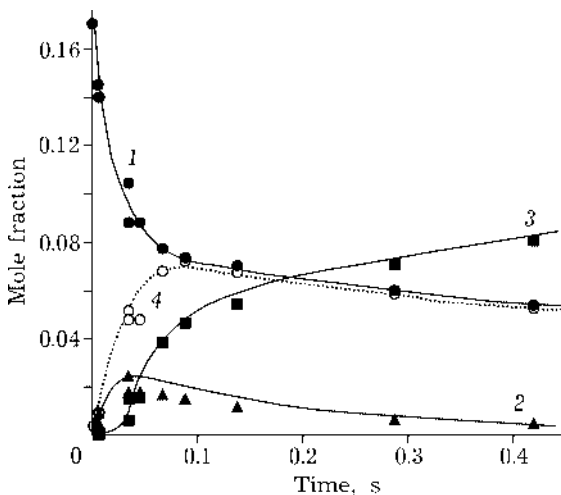


Fig. 2. The contact time dependencies of methanol (1), methyl formate (2) and carbon monoxide (3) concentrations in the reactor outlet mixture and virtual methanol concentration (4) at 473 K for the Cu/SiO₂ catalyst.

TABLE 2

Catalysts activity in methanol dehydrogenation at 473 K

Activity	CuCr	CuZnSi	Cu/Cr ₂ O ₃	Cu/SiO ₂
W_1 , molecules/(m ² s)	1.3 10 ¹⁸	4.7 10 ¹⁷	4.5 10 ¹⁸	9.7 10 ¹⁷
W_2 , molecules/(m ² s)	1.3 10 ¹⁷	2.3 10 ¹⁶	1.4 10 ¹⁸	4.2 10 ¹⁷
W_1/W_2	~10	~20	~3	~2

the maximal concentration of methyl formate. Thus, for all the catalysts studied, the kinetic regularity typical for successive reactions is observed: the inflection point for the contact time function of the end product (CO) corresponds to the maximum of the intermediate product (methyl formate) on the concentration curve. Hence, methanol dehydrogenation proceeds stepwise through intermediate product methyl formate formation.

The C_m^* values were found as methanol virtual pressures, P_m^* , from the expression for equilibrium constant of reaction (I) for methyl formate and hydrogen concentrations obtained in the experiments. The curve obtained is marked with dotted line in Fig. 2. This relationship shows how closely reaction (I) approaches its equilibrium under the conditions of successive occurrence of reaction (II). The virtual concentration of methanol increases rapidly in the range of short contact times and low methanol conversions, and attains a value close to the experimental concentration of methanol at $t = 0.1-0.5$ s for various catalysts. Further, with increasing contact time, its value closely follows the experimentally observed dependence of methanol concentration on the contact time. It means that at contact times more than 0.1–0.5 s the process proceeds not far from the equilibrium (1).

The catalysts' activity in reaction was characterized by the maximal rate of methyl formate production and consumption. The results of study are summarized in Table 2. It may be seen that the rate of methyl formate formation W_1 (reaction (I)) in the series the studied catalysts is varying in the limits of one order. The rate of methyformate decomposition W_2 (reaction (II)) differs significantly – up to the two orders, but the considerable difference is observed in the value of W_1/W_2 ratio. This va-

lue determines the selectivity of the process in methyl formate production only in the field of the middle extents of methanol conversion, because at low conversion the contribution of reaction (II) in the total reaction is too small, and at high conversions the reaction (I) proceeds not far from its equilibrium, so, the selectivity is low and decreases in the same way for all the catalysts with increase of conversion. It means that the field of the middle extent of methanol conversions is the most interesting for comparison of different catalysts' behavior.

As it follows from the Table 2 the best selectivity to methyl formate is achieved at the CuZnSi and CuCr catalysts. The W_1/W_2 ratio is 20 and 10, respectively. The lower selectivity is obtained at the Cu/Cr₂O₃ и Cu/SiO₂ catalysts having W_1/W_2 ratio 3 and 2, respectively.

The increasing of the W_1/W_2 ratio, and therefore the selectivity to methyl formate formation is achieved as a result of decreasing the activity in methyl formate decomposition by the reaction (II). The substantial decreasing of the rate of the reaction (II) occurs at the CuZnSi and CuCr catalysts, *i. e.* those having metal copper particles at the precursor surface, formed through red-ox substitution of copper ions by hydrogen. Those copper metal particles preserve the bonding to the precursors' surface. The rates of reactions (I) and (II) are close for the Cu/Cr₂O₃ and Cu/SiO₂ catalysts having copper particles weakly bonded at the oxide-support surface.

CONCLUSION

So, both hydrogen adsorption properties and catalytic behavior in methyl formate transformation to CO and H₂ (hence, the selectivity in methanol dehydrogenation) of copper metal

particles of different texture and character of bonding to the oxide surface differ significantly. The obtained results don't allow elucidating the direct influence of the character of hydrogen adsorption on the catalytic properties. The additional research is necessary to solve this question. But the obtained results evidence unambiguously the influence of the structure and composition of precursor and its activation on the state of metal copper particles, consequently on their adsorption and catalytic properties.

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REFERENCES

- 1 D. S. Brands, E. K. Poels and A. Bliek, *Stud. Surf. Sci. Catal.*, 101B (1996) 1085.
- 2 O. V. Makarova, T. M. Yurieva, G. N. Kustova *et al.*, *Kinetika i kataliz*, 34 (1993) 681.
- 3 T. M. Yurieva, G. N. Kustova, T. P. Minyukova *et al.*, *Mat. Res. Innov.*, 5 (2001) 3.
- 4 T. M. Yurieva, L. M. Plyasova, O. V. Makarova and T. A. Krieger, *J. Mol. Catal.*, 113 (1996) 455.
- 5 T. P. Minyukova, I. I. Simentsova, A. V. Khasin *et al.*, *Appl. Catal. A: General*, 237 (2002) 171.
- 6 C. J. G. Van der Grift, P.A. Elberse, A. Mulder and J.W. Geus, *Ibid.*, 59 (1990) 275.
- 7 I. I. Simentsova, L. P. Davydova, A. V. Khasin and T. M. Yurieva, *React. Kinet. Catal. Lett.*, (2002), in press.
- 8 T. M. Yurieva, T. P. Minyukova, G. N. Kustova *et al.*, *Mat. Res. Innov.*, 5 (2001) 74.
- 9 Minerals, The Layered Silicates, Nauka, Moscow, 1992, vol. IV, issue 2 (in Russian).
- 10 L. M. Plyasova, L. P. Solovieva, T. A. Krieger *et al.*, *Kinetika i kataliz.*, 37 (1996) 622.
- 11 G. Anger, A. Winkler and R. D. Rendulic, *Surf. Sci.*, 220 (1989) 1.
- 12 J. Tabatabaei, B. H. Sakahini, M. J. Watson and K. C. Waugh, *Catal. Lett.*, 59 (1999) 143.
- 13 C. S. Alexander and J. Pritchard, *J. Chem. Soc. Faraday I*, 68 (1972) 202.
- 14 P. B. Rasmussen, P. M. Holmblad, H. Christoffersen *et al.*, *Surf. Sci.*, 287/288 (1993) 79.