



Methanol on Co(0001): XPS, TDS, WF and LEED results

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Abstract

The adsorption and decomposition of methanol on clean Co(0001) was studied as a function of temperature and exposure by means of TDS (thermal desorption spectroscopy), XPS (X-ray photoelectron spectroscopy), WF (work function measurements) and LEED (low energy electron diffraction). Methanol was adsorbed by OH-bond scission as methoxide on the cobalt surface. TD and XP spectra revealed that beside a small amount of molecularly desorbing methanol, it decomposed during heating to the final products: CO and H₂. Desorption of H₂ took place around 356 K and desorption of CO around 390 K. These temperatures are characteristic for desorption of these species on clean cobalt. Work function measurements showed that the adsorption of methanol resulted in a lowering of the WF by 1.1 eV. Heating – and therewith decomposition – led to an increase in the WF of +0.4 eV. After all decomposition products had desorbed, the WF returned to the value for the clean Co(0001) surface. LEED exhibited a combination of two ordered structures: $p(2 \times 2)$ and $(\sqrt{7} \times \sqrt{7})19.1^\circ$. The $(\sqrt{7} \times \sqrt{7})19.1^\circ$ pattern was formed by methoxide or hydrogen and vanished below 340 K. The $p(2 \times 2)$ structure was still found above 380 K and was therefore assigned to CO. © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

In the past decade fuel cell technology became one of the environmentally friendly developments

in the automobile related industry. Liquid methanol is a promising fuel, but the decomposition of methanol on board to CO and hydrogen is an even cleaner and more efficient process [1]. Commonly used catalysts in fuel cells are Ru-based or Pd-based. As these materials are expensive, alternatives with similar capabilities towards the decomposition of methanol are needed; and here cobalt is a promising candidate [2]. The pres-

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ent work gives insight as to why cobalt might successfully replace the traditional materials used in fuel cell catalysts.

The research of cobalt catalysts as a support for methanol decomposition is rather limited. So far, the adsorption of methanol has been studied only on Mo-supported cobalt [3,4]. The results show competition between molecular methanol desorption and O–H bond scission at 210 K. Above that temperature methoxide and hydrogen are found on the surface. Methoxide further decomposes to hydrogen and CO, which desorb at 350 K and 430 K, respectively. C–O bond scission – resulting in atomic carbon and oxygen – is detected but related to presumable defects in the cobalt overlayer enabling methanol adsorption and dissociation on Mo.

Transition metals, which prevent CO bond scission from occurring during CO adsorption, are also believed to retain the C–O bond in the case of methanol adsorption [3]. This holds for Ni(100), Pd(111) and Cu(110) where the CO adsorption as well as methanol adsorption is molecular and for Fe(110) where the adsorption of both species is dissociative. In this respect cobalt should be an interesting material, as dissociation of CO has been detected on open surfaces and surface defects but not on close packed surfaces [5].

Besides these studies, the adsorption of methanol has been investigated on some other metal surfaces, given below in the order of onset of the dissociation temperature. The activation energy for desorption of methanol ranges from 40 kJ/mol on Ag(111) [6] 41 kJ/mol on Cu(100) [7], 45 kJ/mol on Pd(100) [8], 46 kJ/mol on Cu(110) [9], 47 kJ/mol on Pt(111) [7] to 54 kJ/mol on Cu(111) [10].

On Ni(100) methanol starts to dehydrogenate at 160 K to form methoxide species, which further decompose above 240 K to CO adsorbed on the bridge sites [11]. On Pd(111), at low coverages methanol decomposes via methoxide intermediates and then dehydrogenates completely to desorb as CO. At near monolayer coverage the methanolic C–O bond dissociates at 175 K to produce $\text{CH}_{3,\text{ads}}$, which is stable up to 400 K. A stepwise dehydrogenation of $\text{CH}_{3,\text{ads}}$ to form $\text{CH}_{2,\text{ads}}$ (methylene) and CH_{ads} (methylidyne) is observed above 400 K [12].

On Cu(110) annealing causes dissociation into methoxide and formaldehyde around 200 K before all molecular species eventually desorb from the surface [13].

On Al(111) [14] and Fe(110) [15] the adsorption is dissociative already at 100 K. On clean Fe(110) methoxide dehydrogenates around 400 K, yielding gaseous H_2 and CO. The hydroxyl hydrogens leave the surface as H_2 at the slightly lower temperature of 375 K. Carbon–oxygen bond scission competes with CO evolution at 400 K, accounting for about 25% of the CO yield on clean Fe(110).

Our study deals with the adsorption, dissociation and desorption behaviour of methanol on Co(0001). This fundamental study should be helpful in developing new cobalt-based methanol decomposition catalysts.

2. Experimental

All experiments were carried out in an UHV system equipped with facilities for TDS, LEED, XPS and work function measurements. The operating base pressure was of 2×10^{-10} Torr.

The cobalt sample was fixed to the sample holder by 0.25 mm tantalum wires, which in addition served for resistive heating and conducting heat to the liquid-nitrogen-cooled heat sink. The temperature range for the measurements was between 160 K and 690 K. The lower temperature was restricted by the cooling system, the upper by the phase transformation of cobalt from hcp to fcc. The temperature of the sample was monitored continuously by using a chromel–alumel thermocouple spot welded on the sample surface. For a detailed description of the apparatus the reader is referred back to our previously published articles [16–19].

A disc-shaped Co(0001) single crystal with a diameter of 11 mm served as the sample. The initial cleaning procedure was published in an earlier paper [17]. To obtain a clean surface the sample underwent sputtering and subsequent annealing before each experiment. This procedure removed all surface contamination and an atomically smooth vacuum–solid interface was obtained. The cleanliness was controlled by XPS and LEED.

After cleaning, the sample was cooled down to the desired adsorption temperature of 165 K. The methanol gas was admitted in the UHV chamber through a leak valve. The high-purity methanol (99.8%) was additionally purified by repeated freeze–pump–thaw cycles. Subsequently, the purity was controlled by mass spectroscopy.

During XPS measurements the sample was kept at a bias of -25 eV to ensure that the obtained photoelectron signal originated from the crystal and not from the sample holder or supporting structures.

3. Results and discussion

3.1. Thermal desorption

After exposure of 20 L of methanol at 165 K on Co(0001) – corresponding to saturation coverage – the desorption products were analysed by thermal desorption spectroscopy. The obtained spectra are displayed in Fig. 1. A small amount of methanol desorbed from the surface below

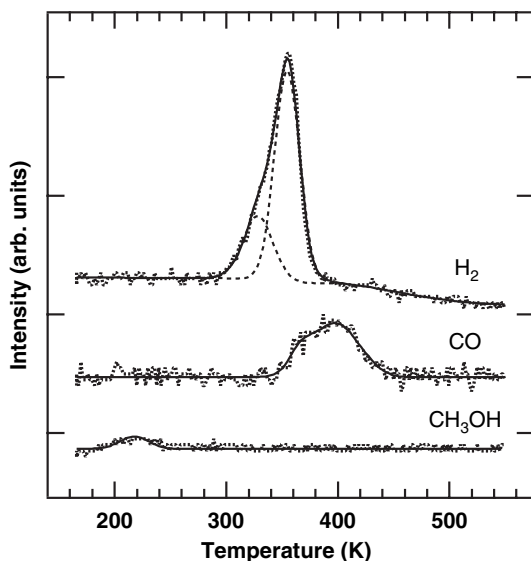


Fig. 1. TD spectra of methanol, CO and H₂ after exposure of 20 L of methanol to a Co(0001) surface at 165 K. The heating rate was 2.6 K/s.

245 K. Between 300 K and 390 K hydrogen desorption was recorded, while CO desorbed at slightly higher temperatures starting at around 350 K and having its peak maximum at 390 K. No other desorption products were found.

In the cases of Ni(100), Fe(110) and Co-covered Mo(110) the same decomposition products – CO and H₂ – were found. Nevertheless these systems showed additionally carbidic contamination which stayed on the Ni(100) surface but recombined and desorbed as CO at high temperatures on Fe(110) and Co-covered Mo.

The temperature values for desorption compare well with the data obtained for CO desorption (~ 400 K) [16] and D₂ desorption (~ 350 K) [20] from clean cobalt as well as for desorption of CO and H₂ originating from dissociated methanol on cobalt-covered molybdenum at 430 K and 350 K, respectively [3].

The analysis of the thermal desorption spectra was used to determine the initial methanol coverage. By comparing the TDS data following methanol exposure, to the TDS peak areas with known coverage of H₂ on Co(0001) and CO on Co(0001) we obtained a saturation coverage of 0.12 ± 0.02 ML. The true coverage is slightly higher since this value does not contain the small fraction of molecularly desorbed methanol.

The hydrogen desorption signal could be fitted with two second-order-desorption peaks, which had an area ratio of 1:3. We explain the two hydrogen desorption states as follows: the hydrogen of the lower desorption state resulted from OH-bond scission during adsorption. The three remaining hydrogen atoms – originating from dehydrogenation of the methoxide – split off later during heating. Due to the second-order-shape, we claim that the remaining hydrogen atoms are attached to the surface prior to H₂ formation.

This kind of desorption for hydrogen following methanol adsorption is in agreement with results in a study on methanol adsorption on Fe(110), exhibiting an asymmetric peak with a leading edge in the TDS spectrum. Isotopic labelling showed that the adsorption of CD₃OH leads to the appearance of three peaks H₂, HD and D₂ with different peak maxima. The H₂ peak at 370 K has its origin in the recombination of hydrogen from O–H bond

scission while the D₂ at 400 K is due to methyl decomposition [15].

The estimated desorption energies for hydrogen and CO – originating from dissociated methanol – were estimated by the Redhead method. For hydrogen an average of both hydrogen states corresponded to a desorption energy of 33 ± 1 kJ/mol, while for CO a value of 110 ± 2 kJ/mol was obtained. These values agreed with the value of 110 kJ/mol for pure CO [16] as well as with 33 kJ/mol for deuterium desorption from Co(0001) [20].

3.2. X-ray photoemission

Remaining traces of atomic carbon or oxygen were not detected in the C1s (Fig. 2 at 450 K) and O1s (not shown) spectra following the TDS experiments. This result is in line with our former studies, which did not show CO bond scission on Co(0001) [16]. In contrast, XPS measurements on cobalt-covered Mo(110) revealed adsorbed atomic carbon and oxygen, recombining and desorbing as CO at temperatures higher than 1000 K [3]. Our study shows that this C–O bond scission must be attributed to the imperfections of the cobalt overlayer, allowing molybdenum sites to be exposed to the surface.

Fig. 2 displays the XP spectra and fitted peaks at 165 K, 230 K, 300 K, 380 K and 450 K. The adsorption temperature was 165 K. Spectra corresponding to higher temperatures were obtained by heating the sample to the indicated temperature and keeping it there during XPS measurements. The temperature accuracy was within ± 5 K.

All the C1s spectra were fitted with two peaks at 287.0–286.4 eV and 286.2 eV. The peak at 286.2 eV diminished during heating and was therefore associated with C–H bonds. As methoxide was observed on cobalt-covered molybdenum [3] we assumed that on Co(0001) the hydrocarbon molecule was methoxide, too. While the amount of methoxide decreased during heating, a steady increase was seen in the peak at higher binding energy. As methoxide was expected to dissociate to CO and hydrogen, the peak at the higher binding energy is ascribed to adsorbed carbon monoxide. At 165 K this peak had a binding energy of

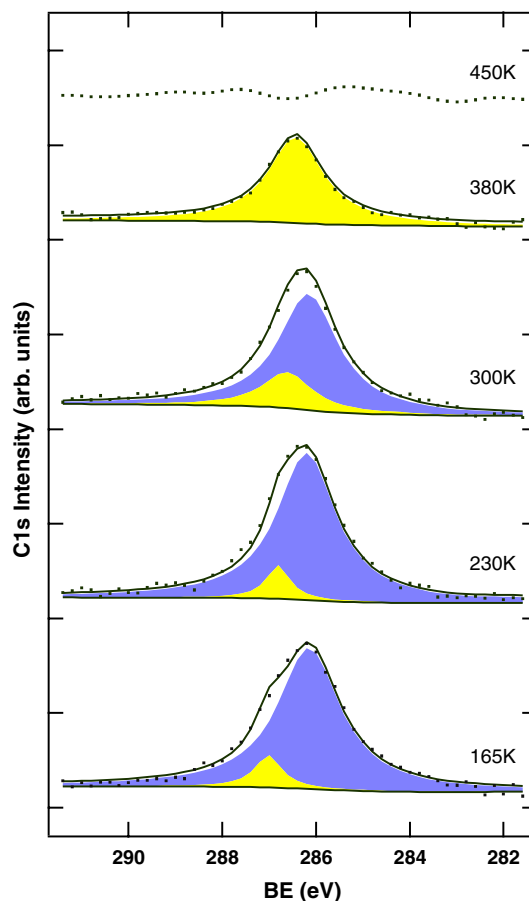


Fig. 2. C1s photoelectron spectra of Co(0001) after pre-exposure to 20 L of methanol at 165 K followed by sequential annealing. The peaks are showing the fitted components at various temperatures between 165 K and 450 K. Methoxide (■) and carbon monoxide (■).

287 eV. Its binding energy decreases with increasing temperature and decreasing amount of undissociated methoxide, until it reaches a binding energy of 286.4 eV. The binding energy of 286.4 eV is close to the value for on-top site adsorption of molecular CO on Co(0001) [16]. A change in the adsorption site of CO was found in the Ni(100) study. The conversion was claimed to be due to the high number of sites available after hydrogen desorption [11].

As these two peaks exhibit close binding energy values and quite large FWHMs we performed a three-peak fit, representing molecular methanol,

methoxide and carbon monoxide at 165 K. The resulting fits showed large FWHMs as well and additionally gave physically unsubstantiated peak-area ratios.

Close binding energy values for methoxide and CO are also found for methanol adsorption on Ni(100) [11] with binding energies of 285.7 eV for methoxide, 285.5 eV for CO on the bridge site and 285.9 eV for CO on top site. Similar binding energies for methoxide and CO are claimed after methanol decomposition on Pd(111), in which the feature at 285.95 eV is ascribed to both decomposition products [21].

We claim therefore that at 165 K methanol is not adsorbing molecularly but as methoxide and hydrogen. Following the XPS fit, a very small amount of methoxide has decomposed to CO and hydrogen at that temperature. We are strengthened in our opinion by the fact that physisorbed methanol desorbs from Cu(110) below 144 K and from Al(111) at 165 K [13,14]. In the case of Cu(110) some methoxide recombines with surface hydrogen upon annealing and is detected as molecular methanol in the TDS spectrum.

The temperature dependence of the carbon-containing surface species is shown in Fig. 3. The XPS data indicated that adsorbed methoxide was the major C-containing component on the surface at low temperatures.

Between 200 K and 245 K – according to the TDS results – a small amount of methoxide recom-

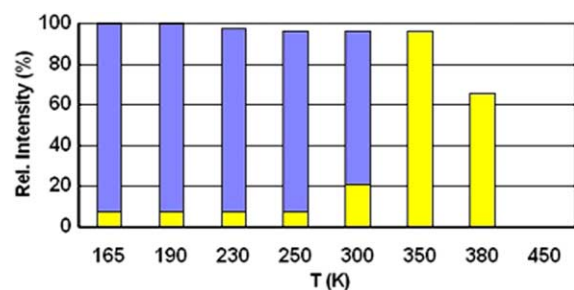


Fig. 3. Relative amount of carbonaceous surface species as a function of temperature derived from fitted XPS data. The pre-exposure was 20 L at 165 K. The values are obtained by comparing the C1s peak area for a particular adsorbate with the total area of the C1s peak at 165 K.

bined with hydrogen and desorbed from the cobalt surface as methanol. Above 280 K adsorbed methoxide starts to decompose to adsorbed CO and adsorbed atomic hydrogen. Around 350 K all methoxide had decomposed.

The total amount of carbon decreased at low temperature due to desorption of molecular methanol. Thereafter it stayed constant below 350 K as carbon from dissociating methoxide remained adsorbed as CO on the surface. After reaching the required temperature for CO desorption, the C1s peak intensity rapidly decreased to zero. Above 440 K no C1s signal was obtained, indicating that no atomic carbon or carbon-containing molecule remained on the cobalt surface.

3.3. Work function

Fig. 4(a) shows the results on the change in the work function (WF) due to methanol exposure: here the value decreased with increasing methanol exposure. The WF for the clean Co(0001) sample was set to zero on the $\Delta\Phi$ scale. For the saturation coverage the change in the WF was -1.1 eV. This value fits well with the value of -1.22 eV for a methanol monolayer on Al(111) [14].

Our reference measurements of coadsorbed CO and D₂ showed an increase in the work function as expected based on the trend for pure CO. For an amount of CO and D₂, corresponding to C- and H-coverages obtained with 0.12 ML methanol; the WF increased by 0.6 ± 0.1 eV. Therefore a dissociation of all methanol to CO and H does not take place. The presence of CO at 165 K on the surface should, of course, increase the work function, but the amount is so small that the total value of the work function is still dominated by the methoxide species.

The dissociation and desorption of the surface species was also followed by the progression of the work function as a function of temperature in Fig. 4(b). With heating, $\Delta\Phi$ increased first to -0.8 eV: the change had its origin in the recombination of methoxide and hydrogen leading to desorption of molecular methanol below 245 K. Between 245 K and 280 K a work function plateau was obtained, as in this temperature range the methoxide stayed on the cobalt surface. Between

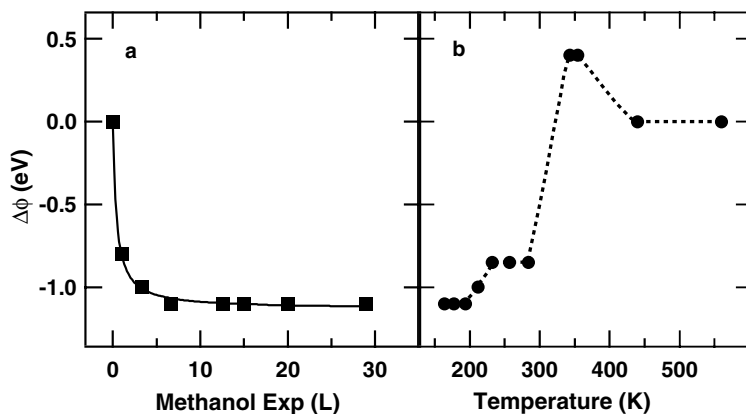


Fig. 4. (a) and (b) WF as a function of exposure (a) and as a function of temperature (b) after exposing Co(0001) to methanol. The lines are drawn to guide the eye.

280 K and 350 K the dehydrogenation of methoxide and the subsequent desorption of hydrogen increased the $\Delta\Phi$ to +0.4 eV. With higher temperatures CO desorbed and the WF decreased to the value for the clean surface, as above 440 K no atomic or molecular compounds were traceable on the surface. A similar work function change as a function of temperature is found for methanol covered Al(111). After methanol desorption and dehydrogenation to methoxide a work function plateau is reached which stretches from 175 K to 400 K. Above 400 K methoxide decomposes and therewith the WF increases [14].

3.4. LEED

The LEED pattern following the admission of methanol at 165 K exhibited a mixture of $p(2 \times 2)$ and $(\sqrt{7} \times \sqrt{7})19.1^\circ$ structures for exposures above 1.6 L. Fig. 5(a) shows a photograph of the LEED pattern at 67 eV and Fig. 5(b) the corresponding schematic pattern. The electron beam easily damaged the ordered structures on the surface and thus the pictures appeared fuzzy. Heating the sample caused the $(\sqrt{7} \times \sqrt{7})19.1^\circ$ structure to disappear below 340 K, but the (2×2) pattern remained. In comparison with the XPS and TDS

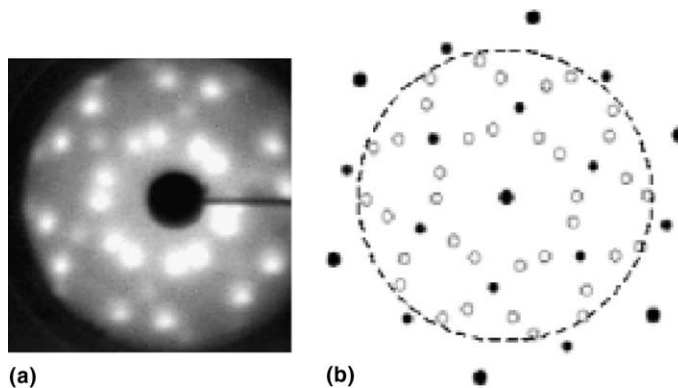


Fig. 5. (a) and (b) LEED pattern of methanol covered Co(0001), exhibiting a $p(2 \times 2)$ and $(\sqrt{7} \times \sqrt{7})19.1^\circ$ structure (a). This pattern was recorded at 160 K with an incident energy of 67 eV. The schematic figure of the LEED pattern is shown in (b). The area inside the circle reflects the exact pattern seen in (a). Big filled circles (●) are used for the cobalt substrate, (●) represents the (2×2) phase and (○) the $(\sqrt{7} \times \sqrt{7})19.1^\circ$ structure.

data, the $(\sqrt{7} \times \sqrt{7})19.1^\circ$ structure was assigned to methoxide or hydrogen induced reconstruction and the $p(2 \times 2)$ structure to CO, as above 380 K only substantial amounts of CO can be found on the sample surface.

The coexistence of two patterns and the wide exposure range, during which these LEED structures are seen, indicate island formation of the adsorbates.

Furthermore the theory of island formation with this system is consolidated by the fact that the $(\sqrt{7} \times \sqrt{7})19.1^\circ$ structure and the $p(2 \times 2)$ structure correspond to nominal coverages of 0.143 ML and 0.25 ML, respectively. Both coverages are too high compared to the estimated coverage of 0.12 ML for CO as would be expected if we have island formation of adsorbates.

A $p(2 \times 2)$ structure for carbon monoxide appears on first sight of utmost surprise, as no such structure was ever found for pure CO adsorption on Co(0001). Nevertheless, a similar discovery has been made with the methanol/Ru(0001) system [22]. Hrbek et al. observed a $p(2 \times 2)$ LEED pattern from CO, which is unknown for pure CO, C + CO or H + CO adsorption on Ru(0001). As small amounts of atomic C and H were seen during their study coadsorption induced restructuring was suggested, but could not be verified, as C + CO and H + CO did not show a (2×2) pattern. Excluding the possibility of coadsorption induced structure change, leaves the reason for this structure change unidentified.

4. Conclusion

In this paper we presented our results on the adsorption, decomposition and desorption of CH₃OH on Co(0001). XPS, TDS, WF measurements and LEED were applied to characterise the adsorbate. Comparison with obtained data for methanol adsorption on cobalt-covered Mo(110) showed good agreement in most results. The main difference was the feature of supported cobalt to dissociate methanol in nameable amounts to atomic carbon and oxygen, which recombined and desorbed between 1000 and 1200 K. Our study as well as studies on CO on Co(0001) do not support

this finding of C–O bond scission. We claim therefore that this is a feature influenced by the supporting material of cobalt.

Although Co(0001) is a model surface, our results show that cobalt might be a suitable alternative as an inexpensive catalytic material in the methanol fuel cell technology. Our following conclusions are:

- (i) The methanol saturation coverage on Co(0001) was estimated to be 0.12 ML.
- (ii) Co(0001) is extremely effective in decomposing methanol to hydrogen and carbon monoxide. Apart from a small low temperature desorption peak from recombined methanol at temperatures below 245 K dehydrogenation leads via methoxide solely to H₂ and CO, which start to desorb at 300 K (hydrogen) and 350 K (CO). No other decomposition products – like atomic carbon or hydrogen – were found. The C–O bond is retained.

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