

## ARTICLE

# Modification of Surface Reactivity by CO: Effects on Decomposition and Polymerization of Acetaldehyde on Ru(0001)<sup>†</sup>

Xiao Chen<sup>a,b</sup>, Fang-liang Li<sup>a,c</sup>, Qing Guo<sup>a\*</sup>, Dong-xu Dai<sup>a</sup>, Xue-ming Yang<sup>a\*</sup>*a. State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Dalian 116023, China**b. University of Chinese Academy of Sciences, Beijing 100049, China**c. ShanghaiTech University, Shanghai 201210, China*

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The adsorption and reaction of acetaldehyde on the clean and CO pre-covered Ru(0001) surfaces have been investigated using temperature programmed desorption method. On the clean Ru(0001) surface, the decomposition of acetaldehyde is the main reaction channel, with little polymerization occurring. However, on the CO pre-covered Ru(0001) surface, the decomposition of acetaldehyde is inhibited considerably with increasing CO coverage. Whereas, the polymerization occurs efficiently, especially at high CO coverage ( $\theta_{\text{CO}} > 0.5$  ML), which is strongly CO coverage dependent. Combined with previous studies, the well-ordered hexagonal structure of CO layer formed on the Ru(0001) surface at high CO coverage that matches the configuration of paraldehyde is likely to be the origin of this remarkable phenomenon.

**Key words:** Acetaldehyde, Polymerization, Temperature programmed desorption, Ru(0001)

## I. INTRODUCTION

The transformations of acetaldehyde ( $\text{CH}_3\text{CHO}$ ) on transition metal surfaces are of significant importance for both applied and fundamental research reasons. From application aspects,  $\text{CH}_3\text{CHO}$  is often viewed as a starting material for the catalytic production of many important chemicals [1]. In the respect of fundamental research, chemisorbed aldehydes have been proposed as key intermediates in the decomposition of primary alcohols on metal surfaces [2–4] and in Fischer-Tropsch synthesis [5]. Among all transition metals, Ruthenium (Ru) is of particular interest for its excellent performance in many catalytic reactions including Fischer-Tropsch synthesis [6, 7], and the decomposition of primary alcohols [8, 9]. Thus, it is necessary for us to gain a deeper insight into the behaviors of  $\text{CH}_3\text{CHO}$  on Ru surfaces.

The transformations of  $\text{CH}_3\text{CHO}$  on transition metal surfaces of Ru [10], Pd [11, 12], Ni [13], Ag [14], Rh [15–17], have been studied with different methods. In general,  $\text{CH}_3\text{CHO}$  adsorbs on metal surfaces by bonding either through the oxygen lone pair electrons in a  $\eta^1(\text{O})\text{CH}_3\text{CHO}$  configuration or in a  $\eta^2(\text{C}, \text{O})\text{CH}_3\text{CHO}$  configuration where both the carbonyl carbon and oxygen

atoms interact with surface metal atoms [10–14]. Usually, electron donation from the oxygen lone pair orbitals in the  $\eta^1(\text{O})\text{CH}_3\text{CHO}$  configuration produces a relatively weak adsorbate-surface bond, while the overlap between the metal d orbitals and the carbonyl  $\pi^*$  orbital in the  $\eta^2(\text{C}, \text{O})\text{CH}_3\text{CHO}$  configuration results in a stronger adsorbate-surface bonding. At low temperature,  $\text{CH}_3\text{CHO}$  adsorbs on metal surfaces in the  $\eta^1(\text{O})\text{CH}_3\text{CHO}$  configuration, which desorbs from the surfaces upon heating and partly converts to the  $\eta^2(\text{C}, \text{O})\text{CH}_3\text{CHO}$  configuration on the surfaces [10–12, 15–17]. Further heating leads to desorption of  $\eta^2(\text{C}, \text{O})\text{CH}_3\text{CHO}$  from metal surfaces. While, the decomposition of  $\eta^2(\text{C}, \text{O})\text{CH}_3\text{CHO}$  into CO,  $\text{H}_2$ , methane and surface carbon species takes place at higher temperature [11, 12, 15–17]. No methane formation is observed on the Ru(0001) surface [10].

In addition to the reactions, the polymerization of  $\text{CH}_3\text{CHO}$  can also occur on metal surfaces [4, 10, 14–18]. For example, on the Ru(0001) surface [10], Henderson and co-workers proposed two kinds of polymerization: two dimensions (2D) polymerization across the surface at low coverage and three dimensions (3D) polymerization above the surface at high coverage. Similar phenomena have been observed on Au(111) [4], Ag(111) [14], Rh(111) [15–17], and Pt(111) [18]. All of these polymerizations show a strong  $\text{CH}_3\text{CHO}$  coverage dependence. Furthermore, the co-adsorbates on metal surfaces have been proven to affect the polymerization of  $\text{CH}_3\text{CHO}$  [13, 17–21]. On the clean Cu(111) surface [19], no polymerization is observed. However, on the

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\*Authors to whom correspondence should be addressed. E-mail: guoqing@dicp.ac.cn, xmyang@dicp.ac.cn

oxygen pre-covered surface,  $\text{CH}_3\text{CHO}$  can react to produce polyacetaldehyde at 190 K. In a similar way, the polymerization of  $\text{CH}_3\text{CHO}$  occurs at about 220 K after the Ni(100) surface is modified by sulfur [13]. In the case of the Ag(111) surface, the surface atomic oxygen on the Ag(111) surface initiates the polymerization of  $\text{CH}_3\text{CHO}$  at about 140 K, which is much lower than the temperature (about 270 K) for the polymerization of  $\text{CH}_3\text{CHO}$  on the clean surface [14, 20]. Whereas, surface carbon adsorbed on the Rh(111) surface is found to reduce the formation of polyacetaldehyde [17].

In this work, we have investigated the effect of CO on the adsorption and polymerization of  $\text{CH}_3\text{CHO}$  on the Ru(0001) surface using a temperature programmed desorption (TPD) method. On the clean Ru(0001) surface, the decomposition of  $\text{CH}_3\text{CHO}$  is the main reaction channel, and little polymerization of  $\text{CH}_3\text{CHO}$  occurs. However, on the CO pre-covered Ru(0001) surface, the decomposition of  $\text{CH}_3\text{CHO}$  is inhibited largely, and the polymerization of  $\text{CH}_3\text{CHO}$  occurs efficiently at high CO coverage.

## II. EXPERIMENTS

TPD experiments were carried out in an ultrahigh vacuum (UHV) chamber with a pressure in the low  $10^{-11}$  Torr range. Details of this TPD apparatus have been described elsewhere [22]. The Ru(0001) single crystal (Princeton Scientific Corp) had a size of  $10\text{ mm} \times 10\text{ mm} \times 1\text{ mm}$  with one side polished. The surface preparation was accomplished by repeated cycles of  $\text{Ar}^+$  sputtering and UHV annealing at 1000 K. Finally, annealing the sample above 1250 K removed the residual oxygen on the surface. The ordering and cleanness of the surface were confirmed by low energy electron diffraction (LEED), Auger spectrometer (LEED/AES optics, Omicron) and CO TPD spectra. TPD signals were collected with a ramping rate of 2 K/s and with the sample facing the mass spectrometer (Extrel).  $\text{CH}_3\text{CHO}$  used in our experiments was purchased from Sigma-Aldrich with a purity of 99.9%. Before use, it was further purified by several freeze-pump-thaw cycles. The surfaces were dosed with different coverages of  $\text{CH}_3\text{CHO}$  ( $1\text{ ML} = 1.58 \times 10^{15}\text{ molecules/cm}^2$ ) using a home-built, calibrated molecular beam doser. Between each TPD experiment, the surface was sputtered by  $\text{Ar}^+$  with a kinetic energy of 1000 eV for 15 min and annealed at 1000 K for 30 min to remove the residual carbon left on the surface.

## III. RESULTS

### A. The adsorption and reaction of $\text{CH}_3\text{CHO}$ on the clean Ru(0001) surface

Before TPD experiments, the surface treatment of Ru(0001) had been accomplished, and subsequently the surface was checked by LEED, AES, and CO TPD spectra. A sharp hexagonal ( $1 \times 1$ ) LEED pattern for

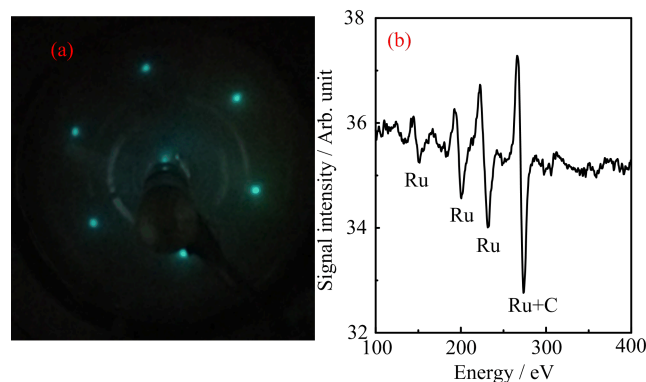


FIG. 1 (a) The LEED (low energy electron diffraction) pattern for Ru(0001) at  $E_{\text{el}} = 100\text{ eV}$  after the surface cleaning process was accomplished. (b) The AES for Ru(0001) after the surface cleaning process was accomplished.

the Ru(0001) surface is shown in FIG. 1(a), confirming the ordering of the surface. While, the AES spectrum displayed in FIG. 1(b) clearly shows the characteristic peaks for Ru at 149, 200, 232, and 274 eV, respectively. Because the characteristic peak for C also appeared at 273 eV, it was hard for us to determine whether residual carbon on the surface had been completely removed. However, our AES spectrum was nearly the same as that collected on the clean Ru(0001) surface by Grant and Haas [23], demonstrating that almost no surface carbon was left after sample preparations. In addition, based on the previous work [24], the adsorption of CO on Ru(0001) was very sensitive to surface oxygen. When the clean Ru(0001) surface was saturated with CO, two main desorption peaks appeared at around 405 and 468 K, with a shoulder peak evolving at about 380 K. Thus, we conducted TPD experiments after adsorbing CO on the Ru(0001) surface to check the existence of surface oxygen. The CO TPD spectra as a function of CO coverage (FIG. 2) were the same as previous results [24, 25], indicating that no surface oxygen remained on the well-prepared surface.

FIG. 3 shows the typical TPD spectra collected at a mass-to-charge ratio ( $m/z$ ) of 29 ( $\text{HCO}^+$ ) after the clean Ru(0001) surfaces were dosed with different coverages of  $\text{CH}_3\text{CHO}$  at 85 K. As the  $\text{CH}_3\text{CHO}$  coverage was  $< 0.13\text{ ML}$ , nearly no  $\text{CH}_3\text{CHO}$  molecules were detected during the TPD process, suggesting that almost all  $\text{CH}_3\text{CHO}$  molecules have been decomposed to other species during the TPD process. Based on previous work done by Henderson *et al.* [10],  $\text{CH}_3\text{CHO}$  molecules were dissociated to produce  $\text{H}_2$ , CO and surface carbon upon heating. With increasing  $\text{CH}_3\text{CHO}$  coverage, three desorption features at 160, 250, 310 K appeared in the TPD spectra, which were due to the desorption of  $\eta^1(\text{O})\text{CH}_3\text{CHO}$ ,  $\text{CH}_3\text{CHO}$  polymers, and  $\eta^2(\text{C}, \text{O})\text{CH}_3\text{CHO}$ , respectively. The intensity of the 310 K peak increased rapidly as the coverage of  $\text{CH}_3\text{CHO}$  increased, and was saturated at about 0.4 ML  $\text{CH}_3\text{CHO}$ .

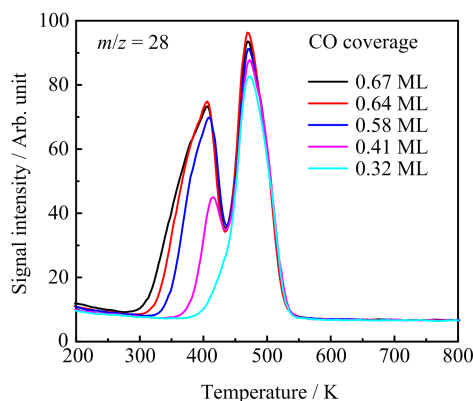


FIG. 2 Typical TPD spectra acquired at  $m/z=28$  ( $\text{CO}^+$ ) after different coverages of CO adsorbed on the Ru(0001) surfaces at 100 K.

coverage, as well as the intensity of the 250 K peak. While, the 250 K peak shifted to 210 K at about 0.4 ML  $\text{CH}_3\text{CHO}$  coverage. As the coverage of  $\text{CH}_3\text{CHO}$  was bigger than 0.4 ML, the 160 K peak increased very fast, and shifted to lower temperature. When  $\text{CH}_3\text{CHO}$  coverage was  $>0.57$  ML, another desorption peak appeared at about 120 K, which was not observed by Henderson and co-workers [10]. According to previous results of  $\text{CH}_3\text{CHO}$  on other metal surfaces [4, 14, 15, 18], this desorption peak was due to the multilayer desorption of  $\text{CH}_3\text{CHO}$ . While, a small peak at about 105 K appeared, and this peak was likely to arise from the desorption of  $\text{CH}_3\text{CHO}$  on the sample holder. Compared with previous results [10], the signal of the desorption feature between 180 and 260 K was attributed to polymerized  $\text{CH}_3\text{CHO}$ , which was much smaller than that observed by Henderson and coworkers [10]. The big difference might be due to the different sample dealing processes.

### B. The adsorption and reaction of $\text{CH}_3\text{CHO}$ on the CO-covered Ru(0001) surface

When the clean surface was predosed with 0.67 ML CO, the TPD spectra of  $\text{CH}_3\text{CHO}$  on the CO-covered Ru(0001) surface changed significantly (FIG. 4), in comparison with that on the clean Ru(0001) surface. As shown in FIG. 4(a), nearly no molecular  $\text{CH}_3\text{CHO}$  desorption was detected on the clean surface after the adsorption of 0.28 ML  $\text{CH}_3\text{CHO}$ . However, on the CO precovered surface, a peak at about 200 K appeared in the TPD spectra of  $\text{CH}_3\text{CHO}$  ( $m/z=29$ ) with a low temperature shoulder at about 140 K with 0.28 ML  $\text{CH}_3\text{CHO}$  adsorption. No decomposition products (such as  $\text{H}_2$ , CO) of  $\text{CH}_3\text{CHO}$  were observed during the TPD process. While, no obvious desorption of  $\eta^2(\text{C}, \text{O})\text{CH}_3\text{CHO}$  at 310 K was observed, indicating that nearly no  $\eta^2(\text{C}, \text{O})\text{CH}_3\text{CHO}$  configuration was formed on the CO-covered Ru(0001) surface. These results suggested that the strongly-bonded CO molecules on

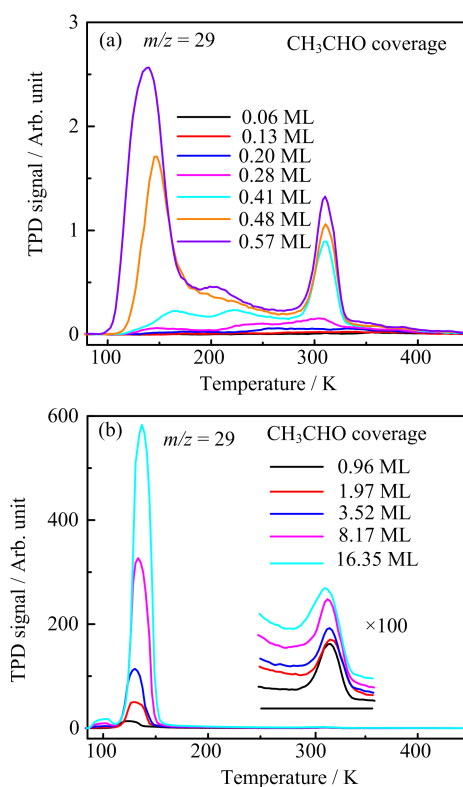


FIG. 3 (a) Typical TPD spectra collected at  $m/z=29$  ( $\text{HCO}^+$ ) after low coverages of acetaldehyde adsorbed on the clean Ru(0001) surfaces at 85 K. (b) Typical TPD spectra collected at  $m/z=29$  ( $\text{HCO}^+$ ) after high coverages of acetaldehyde adsorbed on the clean Ru(0001) surfaces at 85 K.

Ru(0001) not only affected the adsorption structure of  $\text{CH}_3\text{CHO}$  on the surface, but also inhibited the decomposition of  $\text{CH}_3\text{CHO}$ . Usually, the adsorption energy of CO on Ru(0001) is much larger than that of  $\text{CH}_3\text{CHO}$ , therefore the competitive adsorption between CO and  $\text{CH}_3\text{CHO}$  could decrease the adsorption energy of  $\text{CH}_3\text{CHO}$  molecules on the surface, leading to the desorption of  $\text{CH}_3\text{CHO}$  at lower temperature ( $<160$  K). Whereas, the desorption of  $\text{CH}_3\text{CHO}$  at 200 K on the CO-covered Ru(0001) surface implied that  $\text{CH}_3\text{CHO}$  molecules either reacted to form more stable species or adopted a more stable adsorption configuration through the attractive interactions with surface-bound CO molecules, namely, the 200 K TPD peak might arise from the desorption of more stable  $\text{CH}_3\text{CHO}$  or other products.

As the  $\text{CH}_3\text{CHO}$  coverage increased from 0.28 ML to 16.35 ML, the 200 K peak grew very fast and gradually shifted to higher temperature (FIG. 4(b)). Meanwhile, the multilayer desorption peak at about 120 K increased rapidly. Then, we calculated the amounts of  $\text{CH}_3\text{CHO}$  desorbed at 120 and 200 K at different  $\text{CH}_3\text{CHO}$  coverages, as shown in FIG. 5. The amount of  $\text{CH}_3\text{CHO}$  desorbed at 200 K increased very fast, and was larger

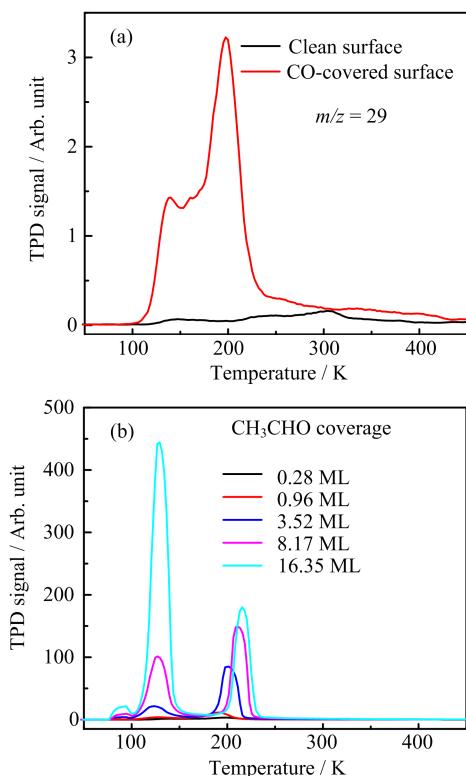


FIG. 4 (a) Typical TPD spectra collected at  $m/z=29$  ( $\text{HCO}^+$ ) after 0.28 ML  $\text{CH}_3\text{CHO}$  adsorbed on the clean Ru(0001) surface (black line) and the 0.67 ML CO pre-covered Ru(0001) surface (red line) at 85 K. (b) Typical TPD spectra collected at  $m/z=29$  ( $\text{HCO}^+$ ) after different coverages of  $\text{CH}_3\text{CHO}$  adsorbed on the 0.67 ML CO pre-covered Ru(0001) surfaces at 85 K.

than that at the 120 K when the coverage of  $\text{CH}_3\text{CHO}$  was  $< 8.17$  ML. With increasing  $\text{CH}_3\text{CHO}$  coverage, the amount of  $\text{CH}_3\text{CHO}$  desorbed at 200 K reached about 4.7 ML, and was nearly saturated. This value was much larger than the coverage of CO (0.67 ML) on the Ru(0001) surface, suggesting that the 200 K peak was not likely from the desorption of more stably adsorbed  $\text{CH}_3\text{CHO}$  molecules which was induced by the attractive interactions between CO and  $\text{CH}_3\text{CHO}$  molecules.

In order to confirm this desorption product, a series of TPD spectra at different masses (FIG. 6) were acquired after adsorption of 8.17 ML  $\text{CH}_3\text{CHO}$  on the 0.67 ML CO covered Ru(0001) surface. From the TPD traces of  $m/z=29$ , 44, and 45, it was clearly shown that the 120 K peak was from the desorption of  $\text{CH}_3\text{CHO}$  molecules. However, the 200 K peak was also observed in the TPD traces of  $m/z=89$  and 117. The presence of these fragments indicated that the 200 K peak was not from  $\text{CH}_3\text{CHO}$  monomers. Similar phenomena have been observed on other surfaces, such as Rh(111) [17], S/Ni(100) [14],  $(\text{WO}_3)_3/\text{Pt}(111)$  [21]. On the Rh(111) surface, both dimers and trimers of  $\text{CH}_3\text{CHO}$  could be detected at about 225 K. While, on the S/Ni(100) and

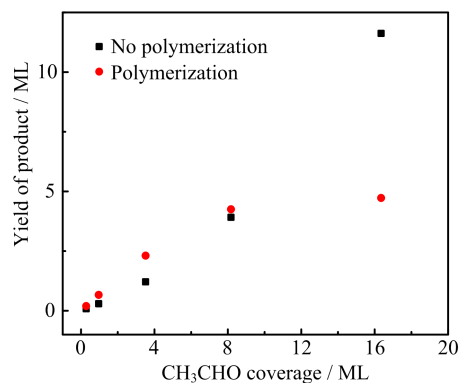
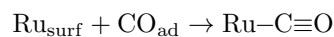


FIG. 5 Yields of  $\text{CH}_3\text{CHO}$  that desorbs at about 140 K and polymerizes at about 200 K on the 0.67 ML CO pre-covered Ru(0001) surfaces as a function of  $\text{CH}_3\text{CHO}$  coverage, respectively. Data were obtained from FIG. 4.

$(\text{WO}_3)_3/\text{Pt}(111)$  surfaces, a cyclic polymer, was observed in their experiments. Usually, the most stable oligomer with such a cracking pattern was considered as paraldehyde, the cyclic  $(\text{CH}_3\text{CHO})_3$  trimer [14, 21]. Therefore, this desorption feature at 200 K was likely attributed to the desorption of  $\text{CH}_3\text{CHO}$  polymers, especially paraldehyde. While, by considering the detecting efficiency of our mass spectroscopy at different masses, the ratio of the intensity at  $m/z=45$ , 89, and 117 is close to the standard mass spectroscopy of paraldehyde in NIST database, suggesting that the 200 K product is likely to be paraldehyde.

#### IV. DISCUSSION

Based on previous studies about  $\text{CH}_3\text{CHO}$  polymerization on O/Cu(111) [19] and O/Ag(111) [20],  $\text{CH}_3\text{CHO}$  was subjected to nucleophilic attack by the surface O adatoms that initiated polymerization into polyacetaldehyde at low temperature. Here, due to the effect of pre-covered CO, the  $\eta^2(\text{C}, \text{O})\text{CH}_3\text{CHO}$  configuration on Ru(0001) nearly disappeared on the surface, and  $\text{CH}_3\text{CHO}$  molecules probably adsorbed on the CO layer rather than the surface after adsorbing high coverage of CO. Generally, CO molecules adsorbed onto the surface with C atoms bound to surface Ru atoms, leaving O atoms upward [26]. So in this case, the  $\text{CH}_3\text{CHO}$  molecules adsorbed on the CO layer had the opportunity to be subjected to nucleophilic attack by the O atoms of CO molecules. Sequentially, more  $\text{CH}_3\text{CHO}$  molecules underwent nucleophilic addition by the O end in carbonyl group of the propagating oligomer, leading to the production of a polymeric chain like polyacetaldehyde  $((\text{CH}_3\text{CHO})_x)$ . The process may be as follows:



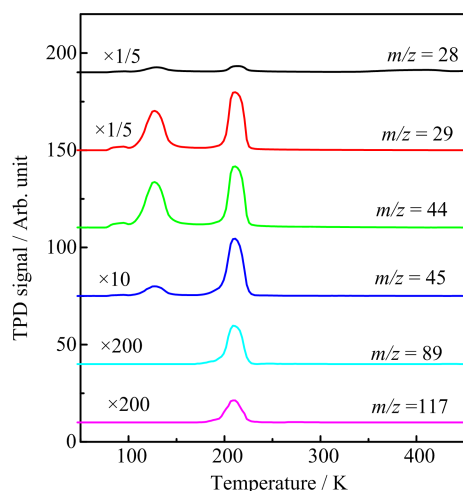
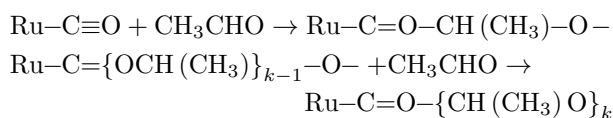
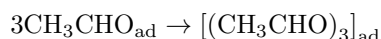


FIG. 6 Typical TPD spectra collected at  $m/z=28, 29, 44, 45, 89, 117$  after 8.17 ML  $\text{CH}_3\text{CHO}$  adsorbed on the 0.67 ML CO pre-covered Ru(0001) surface at 85 K.



In addition, as reported previously [14, 21], well-ordered structures might initiate the polymerization, leading to the formation of paraldehyde. For example, the deposition of sulphur on the Ni(100) created a  $p(2\times 2)$  S structure, which facilitated the formation of paraldehyde [14]. Similarly, the ordered  $(\text{WO}_3)_3$  ( $3\times 3$ ) structure deposited on the Pt(111) surface also resulted in the formation of paraldehyde on the  $(\text{WO}_3)_3/\text{Pt}(111)$  surface by the adsorption of  $\text{CH}_3\text{CHO}$  on W sites [21]. According to previous studies of CO adsorption on the Ru(0001) surface [27–30], a hexagonal adsorption structure could be also formed in the CO layer on the Ru(0001) surface, which might perfectly match the configuration of paraldehyde. So the polymerization of  $\text{CH}_3\text{CHO}$  might proceed as follows:



To identify the possible mechanisms for the polymerization of  $\text{CH}_3\text{CHO}$  on Ru(0001), the TPD measurements were carried out after different coverages of CO pre-covered Ru(0001) surfaces were dosed with 8.17 ML  $\text{CH}_3\text{CHO}$  (FIG. 7). At 0.32 ML CO coverage, only one desorption peak at about 125 K was observed. No obvious signals of  $\text{CH}_3\text{CHO}$  polymerization and  $\eta^2(\text{C}, \text{O})$   $\text{CH}_3\text{CHO}$  adsorption were detected. Even at 0.51 ML CO coverage, the 230 K peak from depolymerization of  $\text{CH}_3\text{CHO}$  polymers was still very small. With increasing CO coverage from 0.51 ML to 0.67 ML, the 125 K peak decreased very fast. Concomitant to the decrease of the 125 K peak, the peak at 230 K increased rapidly and shifted to 210 K with increasing CO coverage. It was clearly shown that the amount of  $\text{CH}_3\text{CHO}$

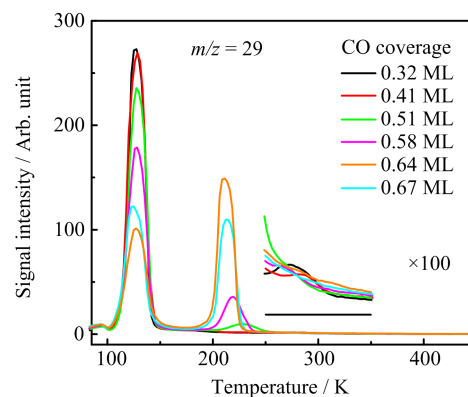


FIG. 7 Typical TPD spectra collected at  $m/z=29$  ( $\text{HCO}^+$ ) after 8.17 ML of  $\text{CH}_3\text{CHO}$  adsorbed on the CO-covered Ru(0001) surfaces as a function of CO coverage at 85 K.

taking part in polymerization increased slowly at low CO coverages ( $<0.51$  ML) (FIG. 8), and rose dramatically when the CO coverage was larger than 0.51 ML. At 0.67 ML CO coverage, the amount of  $\text{CH}_3\text{CHO}$  that took part in polymerization increased to  $\sim 4$  ML. The nonlinear relationship between the CO coverage and the yield of  $\text{CH}_3\text{CHO}$  polymers suggested that the polyacetaldehyde formation via nucleophilic attack of  $\text{CH}_3\text{CHO}$  molecules adsorbed on the CO layer by the O atoms of CO molecules was nearly impossible, because of the negligible yield of  $\text{CH}_3\text{CHO}$  polymers at low CO coverages ( $<0.51$  ML).

Conversely, the nonlinear relationship between the CO coverage and the yield of  $\text{CH}_3\text{CHO}$  polymers indicated the well-ordered structures might act as the initiators for the polymerization. As mentioned previously [27–30], at low CO coverage ( $\theta_{\text{CO}} \leq 0.33$  ML), only the  $(\sqrt{3}\times\sqrt{3})R30^\circ$  structure existed on the Ru(0001) surface. As the CO coverage increased from 0.33 ML to 0.67 ML,  $(\sqrt{3}\times\sqrt{3})R30^\circ$  structure gradually disappeared, and the  $(2\sqrt{3}\times 2\sqrt{3})R30^\circ$  structure began to be formed and developed. Although a hexagonal adsorption structure of CO in the CO layer could be also found on the 0.33 ML CO covered Ru(0001) surface, all the CO molecules adsorbed on the top sites, and the distance between neighbouring CO molecules in a hexagonal structure was much larger than the bond length of C–O in the paraldehyde. As the  $(2\sqrt{3}\times 2\sqrt{3})R30^\circ$  structure of CO was formed, the arrangement of the CO molecules became more densely packed, and the distance between neighbouring CO molecules in a hexagonal structure would thus be much shorter than that in the  $(\sqrt{3}\times\sqrt{3})R30^\circ$  structure [28]. Based on the work of  $\text{CH}_3\text{CHO}$  polymerization on  $(\text{WO}_3)_3/\text{Pt}(111)$  surface [21], structures of  $(\text{WO}_3)_3$  on the Pt(111) surface that matched the configuration of paraldehyde would initiate the polymerization of  $\text{CH}_3\text{CHO}$ . Therefore, the well-ordered hexagonal adsorption structure of CO on Ru(0001) at high CO coverage might initiate polymer-



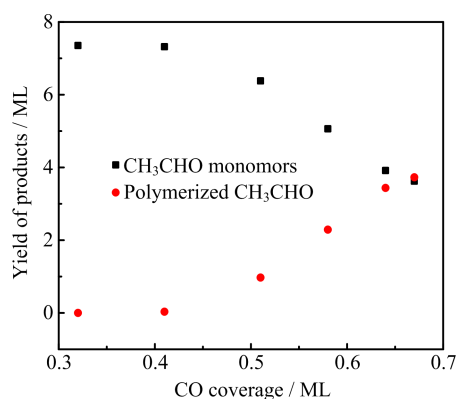


FIG. 8 Yields of CH<sub>3</sub>CHO monomers and polymerizes after 8.17 ML of CH<sub>3</sub>CHO adsorbed on the CO covered Ru(0001) surface as a function of CO coverage, data were obtained from FIG. 7.

ization when this adsorption structure matched the configuration of paraldehyde. Although paraldehyde was the most possible polymerization product, the possibility of the formation of a polymeric chain and 2D or 3D polymerization could not be ruled out completely.

## V. CONCLUSION

In summary, we have investigated the adsorption and reaction of CH<sub>3</sub>CHO on the CO pre-covered Ru(0001) surfaces using a TPD method. Experimental results show that the transformations of CH<sub>3</sub>CHO on the Ru(0001) surface can be affected greatly by the presence of surface CO molecules. With high coverage of CO pre-adsorption, the formation of  $\eta^2(\text{C}, \text{O})$  CH<sub>3</sub>CHO configuration was precluded, and the decomposition of CH<sub>3</sub>CHO was consequently inhibited greatly. Whereas, the polymerization of CH<sub>3</sub>CHO could occur efficiently, which shows a strong CO coverage dependence. Only when the CO coverage is larger than 0.51 ML, an apparent polymerization can be observed. Upon heating, paraldehyde simultaneously decomposes and desorbs in the form of monomers and oligomers at around 230 K. The formation of a well-ordered hexagonal adsorption structure of CO layer on Ru(0001) that matches the configuration of paraldehyde is most likely the reason for the polymerization.

## VI. ACKNOWLEDGEMENTS

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