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Influence of co-adsorbates on the methylene coupling reaction on Ag(1 1 1)

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Abstract

The influence of co-adsorbates on the methylene coupling reaction on Ag(1 1 1) was investigated by means of reflection–absorption infrared spectroscopy (RAIRS) and temperature-programmed reaction spectroscopy (TPRS). Generated by thermal decomposition of adsorbed CH_2I_2, CH_2(a) selectively self-couples to form ethylene. The desorption of ethylene resulted from methylene coupling reaction shows an interesting coverage-dependent, which on basis of the RAIRS and TPD results, is attributed to both the existence of co-adsorbates on the surface and the coverage-dependent C–I rupture of CH_2I_2(a). The reaction kinetics of methylene coupling reaction is also affected by the co-existence of CF_3I(a) on the surface. It is the migration and/or assembly of methylene on the surface, not the actual methylene coupling reaction, which is influenced by the co-adsorbates.

Keywords: Temperature-programmed reaction spectroscopy; Reflection–absorption infrared spectroscopy; Methylene coupling reaction; Silver

1. Introduction

Reactivity of alkyl fragments over transitional metals is an issue of great importance in heterogeneous catalysis. Depending on the metal, alkyls will undergo dehydrogenation, hydrogenation, or coupling reaction, the last of which results in the carbon chain propagation reaction, so that higher hydrocarbons can be produced from simple reactants, for example, the famous Fischer–Tropsch synthesis [1]. Fundamental understanding of this issue still mostly comes from the surface science studies of model catalysts. Numerous researchers, using thermal, photochemical, or electron-impact dissociation of alkyl halides under ultra-high-vacuum (UHV) conditions, have generated alkyl groups on single crystal metal surfaces to study carbon chain propagation via alkyl coupling [2–4]. Most metal surfaces preferentially dehydrogenate adsorbed alkyls, however, the coinage metals, copper, silver, and gold allows adsorbed alkyls to selectively undergo the coupling reaction because of their relative inertness.

The coupling of alkyl fragments on metal surfaces is quite complicated. As Zheng et al. pointed out [5], the coupling of alkyl fragments on metal surfaces to form carbon–carbon bonds consists of several steps: chemisorption, migration, assembly of fragments prior to reaction, and finally, actual coupling, and desorption; the kinetics is determined primarily by the step having the largest activation barrier. When alkyl halides are used to generate alkyl groups, we have to consider the effect of co-adsorbates (halogen atoms, etc.) on the rupture of the carbon–halide bond and the coupling reaction. Zhou et al. compared the chemistry of vinyl and phenyl groups on Ag(1 1 1) formed by: (a) thermal dissociation of the corresponding iodides (CH_2CHCl and C_6H_5I) and (b) electron-induced dissociation of the corresponding hydrocarbon (C_2H_4 and C_6H_6) and found that the effect of the halogen on coupling of these unsaturated hydrocarbon fragments was to lower the coupling activation energy by several kcal/mol [6]. Paul and Bent reported that co-adsorbing $P(CH_3)_3$ with methyl groups on Au(1 0 0) inhibited the methyl coupling reaction so that methyl radical desorption was observed [7]. These previous works show that co-adsorbates do affect the coupling reaction of hydrocarbon fragments on transitional metals.

In the present paper, we investigated the influence of co-adsorbates on the methylene coupling reaction on Ag(1 1 1) by means of reflection–absorption infrared spectroscopy (RAIRS) and temperature-programmed reaction spectroscopy (TPRS).

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We chose this reaction because methylene coupling reaction proceeds most facile on Ag(1 1 1) among coinage metals so that the effect of co-adsorbates on this reaction can be relatively easily observed. Although the methylene coupling reaction on Ag(1 1 1) were previously reported [8,9], the effect of co-adsorbates on the methylene coupling reaction has not been discussed.

2. Experimental

We conducted our experiments in a two-level stainless steel ultra-high-vacuum chamber [10]. The upper level is equipped with a Nicolet Magna-IR 860 spectrometer for RAIRS, a SRS RGA 200 for residual gas analysis (RGA), and an ion sputtering gun; the lower level comprises a UTI-100C mass analyzer for TPRS, and a single-pass cylindrical mirror analyzer for Auger electron spectroscopy (AES). Turbo-molecular pumps brought the chamber to a base pressure from 1.0×10^{-10} to 2.0×10^{-10} Torr.

The Ag(1 1 1) sample was mounted on a tungsten loop attached to rectangular cross-section copper bars that were electrically isolated from a hollow copper block filled with liquid nitrogen. Resistive heating of the sample was achieved through a high current power supply connected to the tungsten loop. Sample temperatures between 80 and 1000 K were managed using a commercial temperature-controller and the surface temperature measured with a type *K* thermocouple inserted into a hole at the crystal's edge.

We cleaned the Ag(1 1 1) surface initially by repeated cycles of Ar^+ sputtering and annealing, until no contaminants were detected in AES. After each experiment, the surface was cleaned again by heating to 960 K, to desorb atomic iodine and AgF [8]. Diiodomethane (CH_2I_2, 99% purity, Aldrich) was used as-received except that we removed dissolved gases by several cycles of freeze–pump–thaw prior to experiments. The gaseous compound trifluoromethyl iodide (CF_3I, 99% purity, Aldrich) was used as-received. All purities were verified by RGA.

A pre-set leak valve ending in a capillary-array doser was used to dose adsorbates. During dosing, the doser tube ended 2 mm in front of the sample; after dosing, it was retracted 25 mm. A fixed pressure of adsorbate was added to a vessel behind a closed butterfly valve connected by an evacuated tube to the leak valve. The leak valve was pre-set to obtain a chamber pressure rise of 3.0×10^{-10} Torr at a chamber surface temperature of 300 K. With the substrate cooled to the desired temperature, the butterfly valve was opened to initiate the dose. The dose was terminated by evacuating the gas behind the leak valve with a turbo-molecular pump rather than closing the leak valve—a procedure that yielded excellent experimental reproducibility (±2%) of TPD spectra. Because careful calibration indicates that the surface exposure is 30× that obtained by backfilling the chamber, we have multiplied by 30 the reported exposures in Langmuir ($1L = 1.0 \times 10^{-6}$ Torr s), i.e. (exposure in $L = 30 \times 3 \times 10^{-10} \times t$), where *t* is the dose time (s).

RAIRS spectra were collected, using a mercury–cadmium telluride (MCT) detector, by co-adding 1500 scans at $4\,cm^{-1}$ resolution; RAIRS for clean Ag(1 1 1) served as the reference. TPRS spectra were collected at a ramp rate of $1\,K\,s^{-1}$, with a maximum of eight different *m*/*e* values recorded for each experiment.

3. Results and discussion

CH_2I_2 was used to generate $CH_2(a)$ on Ag(1 1 1). Fig. 1 displays the TPRS spectra of $C_2H_3^+$ ($m/e = 27$, representing C_2H_4) following various exposures of CH_2I_2 at 90 K. Atomic iodine, monitored by I^+, desorbs from the surface above 800 K (spectra not shown). The molecular desorption peak of CH_2I_2 appears at 179 K only after dosing 1.5 L CH_2I_2 (the insert in Fig. 1), below which dose C_2H_4, formed by self-coupling of $CH_2(a)$, is the only product detected during TPRS experiments. The results shows that $CH_2(a)$ selectively self-couples to form C_2H_4 on Ag(1 1 1). The evolution of C_2H_4, controlled by the self-coupling of $CH_2(a)$, shows an interesting dose-dependence. The lowest dose (0.2 L) gives rising to the C_2H_4 peak at 134 K with a shoulder at 113 K. As the dose increases to 0.5 L, these two peaks disappear and instead an intense peak arises at 142 K. Further dosing causes continuous attenuation of the peak at 142 K and the growth of a new peak at much higher temperatures—initially centered at 214 K, then moving to and remaining at 227 K.

The corresponding RAIRS spectra are presented in Fig. 2. A dose of 0.2 L CH_2I_2 yields one vibrational feature at $2914\,cm^{-1}$. With further dosing, the peak first intensifies (up to 0.5 L CH_2I_2) and then attenuates. Two new features emerge at 2981 and $3051\,cm^{-1}$ following dosing of 0.7 L CH_2I_2, and they grow as the dosing continues. We assign the peak at $2914\,cm^{-1}$ to the CH_2 asymmetric stretch of $CH_2(a)$ and those at 2981 and $3051\,cm^{-1}$, respectively, to the CH_2 symmetric and asymmet-

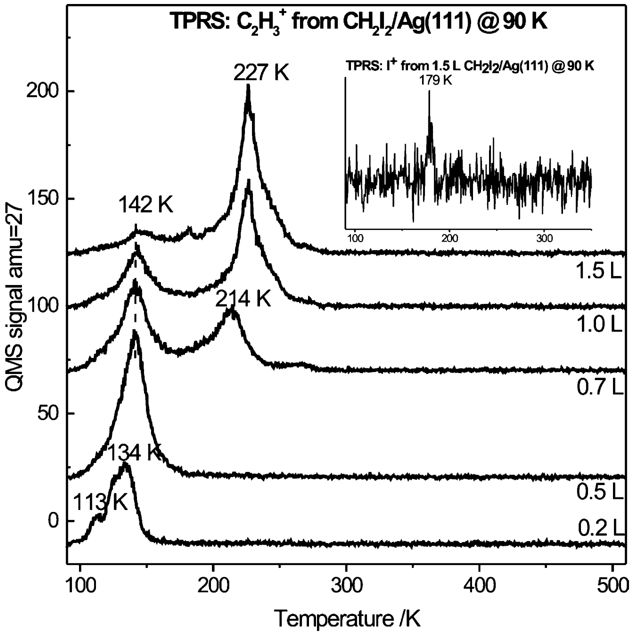

Fig. 1. Evolution of C_2H_4 (represented by $C_2H_3^+$) from Ag(1 1 1) following CH_2I_2 dosing at 90 K monitored by TPRS. The insert indicates the molecular desorption of CH_2I_2 at 179 K.

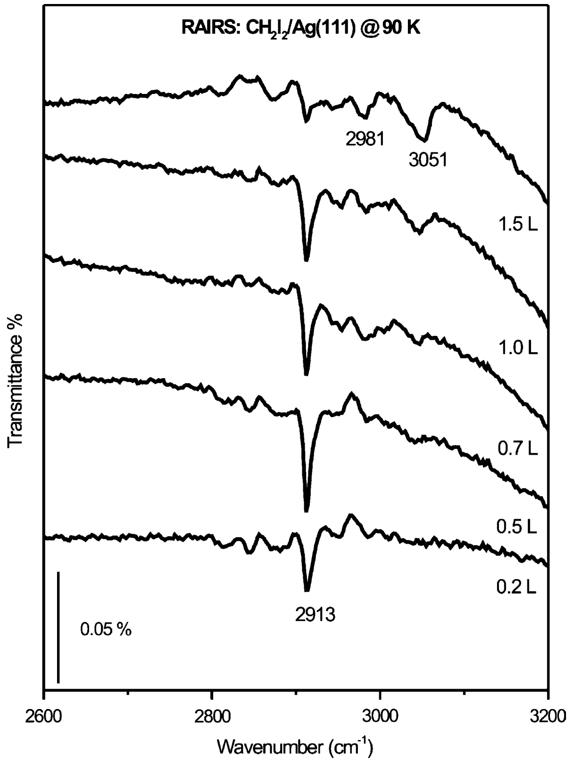

Fig. 2. RAIRS spectra following CH_2I_2 dosing at 90 K. Spectra recorded at 90 K.

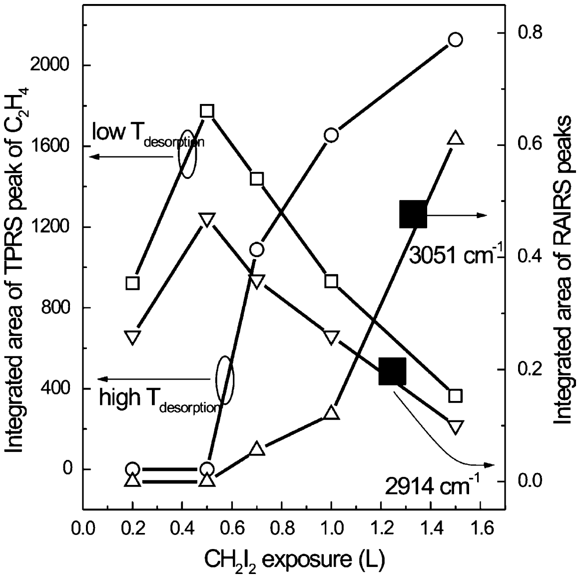

Fig. 3. Comparison between the yields of C_2H_4 formed via CH_2(a) self-coupling at low and high temperature (derived from Fig. 1), and surface coverages of CH_2(a) and CH_2I_2(a) following various doses of CH_2I_2 (derived from Fig. 2) at 90 K on Ag(1 1 1).

ric stretch of CH_2I_2(a). Similar assignments have been made for CH_2I_2 adsorption on other single crystal surfaces [9,11,12]. The RAIRS results clearly show that CH_2I_2 preferentially dissociates on Ag(1 1 1) at low coverages but tends to molecularly adsorb with surface crowding at 90 K. The fact that only CH_2 asymmetric stretch of CH_2(a) was observed by RAIRS indicates that the C_2 axis of CH_2(a) orients parallel with the Ag(1 1 1) surface. Thus, only CH_2 asymmetric stretch vibration produces a transition dipole moment that is perpendicular to the substrate surface, which on basis of the surface infrared selection rule [13], is detectable by RAIRS.

Above results suggest that when generated by thermal dissociation of CH_2I_2, the reaction kinetics of the CH_2(a) self-coupling reaction is dependent on the coverage of CH_2I_2 (Fig. 1). Roughly, using the molecular desorption of CH_2I_2(a) at 180 K as a reference, the C_2H_4 evolution can be divided into two regions: low temperature desorption below 180 K that dominates at low coverages and high temperature desorption above 180 K that prevails at high coverages.

The coverage-dependent evolution of C_2H_4 can be first attributed to the coverage-dependent C–I rupture of CH_2I_2(a) on Ag(1 1 1). As revealed by RAIRS, at 90 K, CH_2I_2 dissociates to produce CH_2(a) on Ag(1 1 1) at low exposures, while it molecularly adsorbs at high exposures. Fig. 3 shows the relationship between the desorption amounts of the low and high temperature C_2H_4 desorption peaks from the surface, and the surface coverages of CH_2(a) (represented by the peak at 2914 cm^{-1}) and CH_2I_2(a) (represented by the peak at 3051 cm^{-1}). Clearly, the low and high temperature C_2H_4 desorption peaks vary with the CH_2(a) and CH_2I_2(a) coverages on the surface upon CH_2I_2 dosing at 90 K, respectively, suggesting that the low temperature C_2H_4 desorption peak comes from the self-coupling of CH_2(a) formed upon CH_2I_2 dosing and the high desorption peak from the self-coupling of CH_2(a) formed by the dissociation of CH_2I_2(a) upon heating. The observed coverage-dependent C–I rupture of CH_2I_2(a) on Ag(1 1 1) at 90 K, can be roundly explained by a site blocking model. At low coverage, CH_2I_2(a) dissociates on Ag(1 1 1), which needs surface sites for incorporating three fragments, 2I(a) and CH_2(a). With the surface crowding, the surface sites are not available for the dissociation so that CH_2I_2 tends to molecular adsorption at 90 K, which undergoes C–I bond rupture after free surface sites are liberated by CH_2I_2(a) thermal desorption around 180 K.

Second, the coverage-dependent evolution of C_2H_4 arises from the effect of co-adsorbing surface species, such as iodine and CH_2I_2(a), on the methylene coupling reaction. We found that even the evolution of C_2H_4 in the low temperature region is still coverage-dependent, as shown in Fig. 1. A dose of 0.2 L CH_2I_2 produces C_2H_4 at 134 K with a shoulder at 113 K, while higher doses produce C_2H_4 at 142 K. It was demonstrated that ethylene desorbs from Ag(1 1 1) pre-saturated with I(a) around 115 K [9]. Thus, it is not clear whether the ethylene desorption peak at 113 K may be methylene coupling reaction-controlled or ethylene desorption-controlled, but the ethylene desorption peaks at 134 and 142 K must be methylene coupling reaction-controlled. It is noteworthy that the ethylene desorption peak at 113 K is *not* due to methylene coupling reaction on the surface defective sites, in which we would expect saturation of the desorption peak with higher doses. Instead, with increased dosing of CH_2I_2, the peak disappears rather than saturates. This observation indicates that the methylene coupling reaction proceeds with a lower barrier after a dose of 0.2 L CH_2I_2 than that after

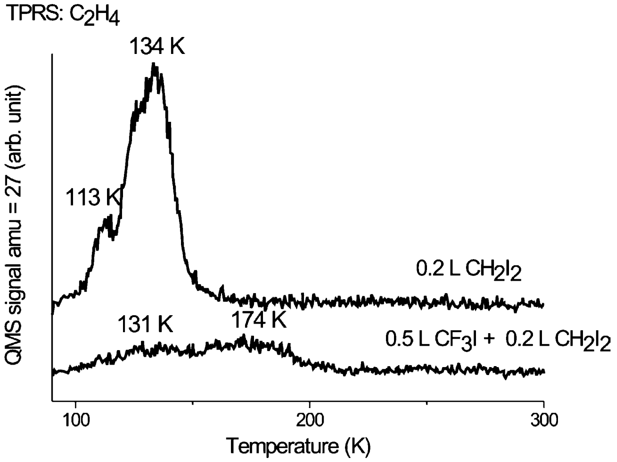

Fig. 4. Evolution of C_2H_4 (represented by $C_2H_3^+$) from Ag(1 1 1) following a dose of 0.2 L CH_2I_2 and a co-adsorption of 0.5 L CF_3I + 0.2 L CH_2I_2 at 90 K. Ramping rate was 1 K s^{-1}.

higher CH_2I_2 doses on Ag(1 1 1) at 90 K. The low temperature ethylene desorption peak is due to coupling reaction of methylene formed upon CH_2I_2 dosing (RAIRS results), and thus, the C–I rupture is not involved. Comparing the environments of CH_2(a) on Ag(1 1 1) following various CH_2I_2 dosing at 90 K, the only difference is that overall coverage of co-adsorbates (I(a) and CH_2I_2(a)) increases with increasing dosing. Thus, the co-adsorbates increase the apparent activation energy of methylene coupling reaction on Ag(1 1 1).

Co-adsorption with CF_3I(a) also affects the kinetics of methylene coupling reaction. Following co-adsorption of 0.5 L CF_3I and 0.2 L CH_2I_2, C_2H_4 desorption occurs at 131 and 174 K, much higher than the desorption temperatures of 113 and 134 K for the individual dosing of 0.2 L CH_2I_2 (Fig. 4). The decreasing amount of C_2H_4 is due to the existence of another coupling reaction between CH_2(a) and CF_3(a) [14,15].

As mentioned above, the coupling of alkyl fragments on metal surfaces consists of several steps: chemisorption, migration, assembly of fragments prior to reaction, and finally, actual coupling, and desorption. Increasing the barrier of any step may eventually affect the kinetic of the coupling reaction. We believe that co-adsorbates hinder methylene coupling reaction on Ag(1 1 1) in two possible ways. One is the electronic effect. Charge transfer may locally occur between co-adsorabte (particularly iodine) and the silver substrate, resulting in the $Ag^{\delta+}$, which generally binds with hydrocarbon more strongly than Ag [16]. The strengthening of Ag–CH_2 bond will increases the barrier for CH_2(a) coupling reaction. The other is geometric effect. Previous TPRS studies suggested that the coupling reactions of adsorbed alkyl groups on Ag(1 1 1) typically follow first-order kinetics rather than the second-order kinetics expected for a bimolecular recombination reaction [17,18]. Although there is no direct evidence on Ag, this is ascribed to islanding of alkyl groups, supporting this model is strong LEED and STM evidence for islanding of methyl radicals on Cu(1 1 1) [19,20]. The methylene coupling reaction on Ag(1 1 1) seems also following first-order kinetics beyond the dose of 0.5 L CH_2I_2, as reflected by the independence of the maximum of the C_2H_4 desorption peak at 142 K on the exposure. Prior to the coupling reaction, CH_2(a) migrates and assembles to form islands on the surface. Therefore, co-adsorbates may increase the migration barrier of CH_2(a) on Ag(1 1 1), eventually leading to the apparent activation energy increasing of methylene coupling reaction.

Although without direct evidence, we believe that it is the migration and/or assembly of CH_2(a) on the surface, not the actual methylene coupling reaction that is influenced by the co-existing surface species. In other words, geometric effect instead of electronic effect dominates the influence of co-adsorbates on the methylene coupling reaction on Ag(1 1 1). Indirect evidence comes from the observation of the independence of ethylene desorption peak at 142 K, which is due to the coupling reaction of methylene formed upon exposure at 90 K, on the iodine coverage. The reaction pathways of CH_3(a) on Cu(1 1 1) and Au(1 0 0) were observed to change when surface iodine and $P(CH_3)_3$ co-existed on the surfaces [7,21]. Co-existing with high coverages of I(a) or $P(CH_3)_3$(a), CH_3(a) desorbs as radicals instead of coupling to produce higher hydrocarbons. The effect of co-adsorbates was assumed to inhibit the coupling reaction of CH_3(a), not to alter the metal–CH_3 bond. Thus, one conceivable possibility is that the co-adsorbates increase the barrier for CH_3(a) migration, thereby increasing the apparent barrier of the coupling reaction, and thus, favoring CH_3(a) desorption as radicals. In our recent publication [22], we also established that fluorine substitution substantially decreased the mobility of alkyl fragments on the Ag(1 1 1) surface and thus, switched the reaction pathway of ethyl on Ag(1 1 1) from selective coupling reaction (CH_3CH_2(a)) to selective β-defluorination reaction (CF_3CH_2(a)). The β-elimination rates of alkyl fragments on Cu(1 0 0) and Cu(1 1 0) were also reported to be dramatically inhibited by high iodine coverage due to cages of immobile iodine atoms that surround the alkyl groups and prohibit hydrogen transfer to the surface [23]. This influence also belongs to the geometric effect.

No matter which step, methylene coupling reaction or ethylene desorption, controls the ethylene desorption peak at 113 K, the observation of this peak indicates a very low activation barrier for the methylene coupling reaction on Ag(1 1 1). The actual activation barrier could be even lower, provided that CH_2(a) could be prepared without co-existing surface species on Ag(1 1 1). This experimental finding is consistent with theoretical calculations suggesting that two neighboring methylenes will self-couple spontaneously or with a very low energy barrier on metal surfaces [5,24].

The effect of co-adsorbates on the methylene coupling reaction has only been observed on Ag(1 1 1). Desorption of ethylene from Cu(1 0 0) and Cu(1 1 0) resulted from methylene coupling reaction show single peaks with first-order kinetics at 220 and 300 K on surface, respectively [25]. This observation implies that the rate-controlling step of methylene coupling reaction on copper does not switch as it does on Ag(1 1 1). A likely explanation is that the activation barriers among various elementary steps of methylene coupling reaction are comparable on Ag(1 1 1). Free of co-adsorbates, the actual methylene coupling reaction is the rate-controlling step on Ag(1 1 1), which gives the ethylene desorption at 113 K (this desorption peak may also be ethylene desorption-controlled); with the increasing coverage of co-adsorbates, the activation barrier of migration and/or assembly of methylene prevails, and thus, the rate-controlling step is the migration and/or assembly of methylene on the surface.

Our conclusion on the influence of co-adsorbates on the methylene coupling reaction on Ag(1 1 1) is only preliminary, the complete understanding of this issue depends on developing the novel and direct method of CH_2(a) preparation without any co-adsorbates. Recently, Chuang's group studied the reactivity of methyl fragment free of co-adsorbates on copper single crystals generated by the pyrolysis of azomethane and observed different product distribution and desorption kinetics from the coupling reaction of methyl fragment generated by CH_3I dissociation [26,27]. The difference was attributed to the influence of surface halogen atoms.

4. Conclusions

Employing TPRS and RAIRS, we have studied the influence of co-adsorbates on the methyllene coupling reaction on Ag(1 1 1). For the coupling reaction of methylene generated upon CH_2I_2 exposure at 90 K, the reaction kinetics is still coverage-dependent, which is attributed to the influence of co-adsorbates (surface iodine and CH_2I_2). We believe that it is the migration and/or assembly of methylene on the surface, not the actual methylene coupling reaction, which is influenced by the co-adsorbates.

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