

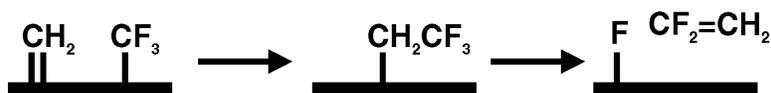
Communication

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 Reaction between CH(a) and CF(a) on Ag(111)**

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Direct Spectroscopic Evidence of the Cross-Coupling Reaction between CH₂(a) and CF₃(a) on Ag(111)

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The formation of carbon–carbon bonds catalyzed by transition metals is a central and challenging subject in catalytically important reactions, e.g., Fischer–Tropsch (FT) synthesis,¹ and Zeigler–Natta polymerization.² Previous UHV studies^{3–14} show that the carbon–carbon bond formation reactions via alkyl coupling on metal surfaces are reaction controlled, i.e., reaction products desorb promptly. Thus, no spectroscopic characterization of proposed adsorbed reaction intermediates can be obtained. Very recently, the desorption of CF₂=CH₂ was observed during heating coadsorbed CD₂(a) and CF₃(a) on Ag(111).^{15,16} The formation of CF₃CH₂(a) via migratory methylene insertion into Ag–CF₃(a) was proposed as the reaction intermediate (Scheme 1). However, no direct spectroscopic evidence was reported. In this communication, we combined reflection–adsorption infrared spectroscopy (RAIRS) and temperature-programmed reaction spectroscopy (TPRS) to study the cross-coupling reaction between CH₂(a) and CF₃(a) on Ag(111). We report for the first time the direct spectroscopic evidence of reaction intermediate (CF₃CH₂(a)) of the carbon–carbon bond formation reaction. Furthermore, our results show that the methylene insertion reaction is so facile that it occurs at cryogenic temperatures (120 K). Since sequential methylene insertion into metal–carbon bonds is a widely accepted mechanism for FT synthesis,¹⁷ our results provide new fundamental insights into understanding this important catalytic reaction.

Our experiments were performed in a two-level UHV chamber with a base pressure of $1\sim 2 \times 10^{-10}$ Torr.¹⁸ The Ag(111) sample was cleaned by repeated cycles of sputtering and annealing until AES could detect no contaminants. The adsorbates, diiodomethane (CH₂I₂, 99%, Aldrich), trifluoromethyl iodide (CF₃I, 99%, Aldrich), and 2,2,2-trifluoroethyl iodide (CF₃CH₂I, 99%, Lancaster) were used without further purification except for removal of dissolved gases in CH₂I₂ and CF₃CH₂I by several cycles of freeze–pump–thaw prior to the experiments. The exposures are given in unit of langmuir (1 langmuir = 1×10^{-6} Torr sec).

Following the adsorption of 0.2 langmuir CH₂I₂ at 90 K, we found only ethylene desorption (monitored as C₂H₃⁺, *m/e* = 27) at 134 K with a shoulder at 113 K, as indicated in the TPR spectra of Figure 1a. In agreement with ref 19, the results indicate that CH₂I₂ initially dissociates into CH₂(a) and I(a), and TPR of CH₂(a) leads to self-coupling and ethylene evolution. TPRS after a 0.5 langmuir CF₃I dose gives rise to CF₃ radical ejection (monitored as CF₂⁺, *m/e* = 50) near 351 K (Figure 1c), consistent with a previous report.²⁰

Figure 1b illustrates the TPRS of 0.5 langmuir CF₃I and 0.2 langmuir CH₂I₂ coadsorption on Ag(111) at 90 K and clearly differs from those for the molecules adsorbed individually. In addition to dramatically reduced intensity of both C₂H₄ and CF₃, C₂H₄ desorbs at 134 and 172 K, while the CF₃ radical desorption peak shifts down to 323 K, effects attributed to the increased I(a) coverage. The most interesting change is the emergence of new desorption

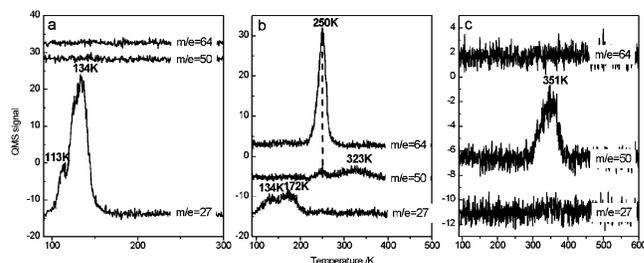


Figure 1. TPRS spectra following (a) 0.2 langmuir CH₂I₂, (b) 0.5 langmuir CF₃I + 0.2 langmuir CH₂I₂, and (c) 0.5 langmuir CF₃I on Ag(111) at 90 K. Ramping rate is 1 K/s.

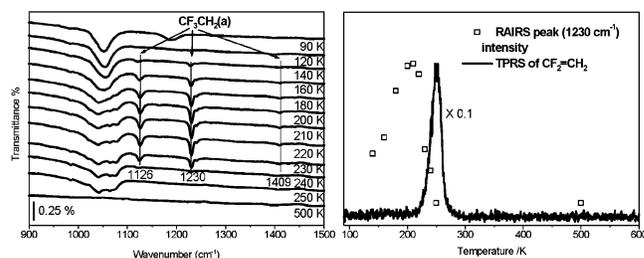
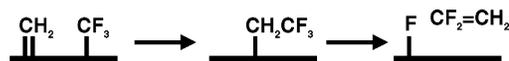


Figure 2. Left: RAIRS of 0.5 langmuir CF₃I + 0.2 langmuir CH₂I₂ dosing on Ag(111) at 90 K followed by annealing at the indicated temperature for 2 min. All spectra were recorded at 90 K. Right: Comparison, as reaction temperature increases, of the evolution of the RAIRS peak at 1230 cm⁻¹ and CF₂=CH₂ desorption.

Scheme 1



peak at 250 K of *m/e* = 50 (CF₂⁺) and 64 (C₂H₂F₂⁺) that we attribute to CF₂=CH₂. These TPRS results indicate that heating of CH₂(a) and CF₃(a) coadsorbed on Ag(111) leads to cross-coupling surface reactions.

We employed RAIRS to study in detail the formation mechanism of CF₂=CH₂. Following coadsorption of 0.5 langmuir CF₃I and 0.2 langmuir CH₂I₂ at 90 K, two vibrational peaks are observed at 1052 and 1192 cm⁻¹, Figure 2a, corresponding to the symmetric and asymmetric CF stretch of CF₃I(a). CH₂(a) shows a CH₂ stretch vibrational peak at 2914 cm⁻¹ (results not shown). The disappearance of the peak at 1192 cm⁻¹ upon annealing at 120 K indicates the complete dissociation of CF₃I(a) into CF₃(a). After the surface was annealed at 140 K, three distinct new vibrational peaks emerge at 1126, 1230, and 1409 cm⁻¹, indicating the occurrence of surface reaction between CH₂(a) and CF₃(a). With increasing annealing temperature, these new features vary simultaneously, first growing and then attenuating, implying that they belong to the same surface species. These peaks completely disappear after annealing at 250 K, and only a mode corresponding to the remaining CF₃(a) is

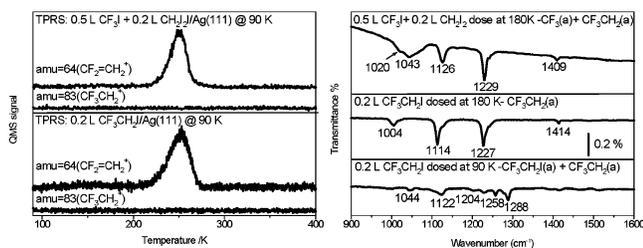


Figure 3. Direct evidence showing the formation of $\text{CF}_3\text{CH}_2(\text{a})$ via the migratory methylene insertion into $\text{Ag}-\text{CF}_3$ on $\text{Ag}(111)$.

Table 1. Assignment of Observed Vibrational Frequencies (cm^{-1}) of $\text{CF}_3\text{CH}_2\text{I}(\text{a})$ and $\text{CF}_3\text{CH}_2(\text{a})$ on $\text{Ag}(111)$

	$\text{CF}_3\text{CH}_2\text{I}(\text{a})$	$\text{CF}_3\text{CH}_2(\text{a})$	$\text{CF}_3\text{CH}_2\text{I}(\text{l})$ (from ref 22)
CF stretch a'	1044	1004	1049
CF stretch a'	1122	1114	1114
CH_2 wag a'	1204		1211
CH_2 deformation a'	1258	1227	1257
CH_2 twist a''	1288		1288
CF stretch a''		1409	1423

observed close to 1052 cm^{-1} . No peaks are observed after the surface is annealed at 500 K.

The evolution of the new surface species with the reaction temperature, represented by the feature at 1230 cm^{-1} , was plotted and compared with the TPRS of $\text{CF}_2=\text{CH}_2$, as shown in Figure 2b. Clearly, the new species forms between 140 and 210 K and disappears sharply above 210 K. We note that the loss of the new species on the surface coincides exactly with the desorption of $\text{CF}_2=\text{CH}_2$. Since no other new species was observed either on the surface by RAIRS or in the gas phase by mass spectroscopy, the desorption of $\text{CF}_2=\text{CH}_2$ clearly originates from the reaction of the new surface species on $\text{Ag}(111)$.

By direct comparison of these data with that of $\text{CF}_3\text{CH}_2(\text{a})$, prepared by dosing $\text{CF}_3\text{CH}_2\text{I}$ on $\text{Ag}(111)$, we identify the new species to be $\text{CF}_3\text{CH}_2(\text{a})$ formed via the migratory insertion of $\text{CH}_2(\text{a})$ into $\text{Ag}-\text{CF}_3$. The results are shown in Figure 3. The TPRS after adsorption of 0.5 langmuir CF_3I and 0.2 langmuir CH_2I_2 at 90 K is the same as that after adsorption of 0.2 langmuir $\text{CF}_3\text{CH}_2\text{I}$ (Figure 3, left panel). Both only give rise to the desorption of $\text{CF}_2=\text{CH}_2$ at about 250 K with no intensity of $m/e = 83$ ($\text{C}_2\text{H}_2\text{F}_3^+$). The results are in good agreement with the work of Gellman et al.,²¹ that $\text{CF}_3\text{CH}_2(\text{a})$ on $\text{Ag}(111)$ does not self-couple or desorb as a radical but instead decomposes via β -fluoride elimination, yielding $\text{CF}_2=\text{CH}_2$ at about 250 K as the sole gas-phase product. The TPRS results strongly infer that the reaction product between $\text{CH}_2(\text{a})$ and $\text{CF}_3(\text{a})$ is $\text{CF}_3\text{CH}_2(\text{a})$.

Direct evidence comes from spectroscopic results (Figure 3, right panel). $\text{CF}_3\text{CH}_2\text{I}$ (0.2 langmuir) dosed at 90 K shows seven bands, which are assigned to two different surface species, 1044, 1122, 1204, 1258, and 1288 cm^{-1} , to molecular chemisorbed $\text{CF}_3\text{CH}_2\text{I}$, while 1114 and 1227 cm^{-1} are assigned to $\text{CF}_3\text{CH}_2(\text{a})$. The detailed assignment is presented in Table 1. The same dose at 180 K only produces $\text{CF}_3\text{CH}_2(\text{a})$ on $\text{Ag}(111)$, which shows four peaks at 1004, 1114, 1227, and 1414 cm^{-1} , corresponding to CF asymmetric stretch, CF symmetric stretch, CH_2 deformation, and CF asymmetric stretch vibrations, respectively. Following adsorption of 0.5 langmuir CF_3I and 0.2 langmuir CH_2I_2 at 180 K, five vibrational peaks are observed at 1020, 1043, 1126, 1129, and 1409 cm^{-1} . By

comparison with the RAIRS spectra of $\text{CF}_3\text{CH}_2(\text{a})$, the four bands at 1020, 1126, 1129, and 1409 cm^{-1} can be unambiguously assigned to $\text{CF}_3\text{CH}_2(\text{a})$, while the remaining one at 1053 cm^{-1} is assigned to unreacted $\text{CF}_3(\text{a})$. These RAIRS results directly prove the formation of $\text{CF}_3\text{CH}_2(\text{a})$ via the migratory $\text{CH}_2(\text{a})$ insertion into $\text{Ag}-\text{CF}_3$ on $\text{Ag}(111)$.

Since both $\text{CF}_3\text{CH}_2\text{I}(\text{a})$ and $\text{CF}_3\text{CH}_2(\text{a})$ have C_s symmetry, a simple symmetry analysis shows that they have different orientations on $\text{Ag}(111)$. As shown in Figure 3, $\text{CF}_3\text{CH}_2\text{I}(\text{a})$ shows the most intense RAIRS peak at 1288 cm^{-1} corresponding to CH_2 twist with a'' symmetry; however, the strongest vibrational peaks of $\text{CF}_3\text{CH}_2(\text{a})$ at 1114 and 1227 cm^{-1} correspond to CF symmetric stretch and CH_2 deformation, both of which possess a' symmetry. On the basis of the surface selection rule,²³ we conclude that the molecular plane of $\text{CF}_3\text{CH}_2(\text{a})$ tilts more away from the $\text{Ag}(111)$ surface than that of $\text{CF}_3\text{CH}_2\text{I}(\text{a})$. The orientation of $\text{CF}_3\text{CH}_2(\text{a})$ may result from the interaction between Ag and one fluorine atom of $\text{CF}_3\text{CH}_2(\text{a})$. Obviously, this kind orientation would facilitate subsequent β -fluoride elimination of $\text{CF}_3\text{CH}_2(\text{a})$.

We found that the migratory methylene insertion into $\text{Ag}-\text{CF}_3$ is a very facile reaction. By directly dosing CF_3I and CH_2I_2 on $\text{Ag}(111)$ at different temperatures, RAIRS results show that $\text{CF}_3\text{CH}_2(\text{a})$ is formed at cryogenic temperatures as low as 120 K. This finding indicates that the chain propagation via sequential methylene insertion may not be the rate-limiting step in FT synthesis.

In summary, we have successfully clarified the reaction mechanism of $\text{CH}_2(\text{a})$ and $\text{CF}_3(\text{a})$ coadsorbed on $\text{Ag}(111)$. $\text{CF}_3\text{CH}_2(\text{a})$ is spectroscopically identified as the reaction intermediate via migratory methylene insertion reaction. This UHV study points to a better understanding of practical catalytic FT synthesis.

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