

An Infrared Investigation on Surface Species over Iron-Based Catalysts: Implications for Oxygenates Formation

Wanyu Mao, Hongfang Ma, Haitao Zhang, WeixinQian, and Weiyong Ying

Abstract—The nature of adsorbed species on catalytic surface over an industrial precipitated iron-based high temperature catalyst during FTS was investigated by in-situ DRIFTS and chemical trapping. The formulation of the mechanism of oxygenates formation and key intermediates were also discussed. Numerous oxygenated precursors and crucial intermediates were found by in-situ DRIFTS, such as surface acetate, acetyl and methoxide. The results showed that adsorbed molecules on surface such as methanol or acetaldehyde could react with basic sites such as lattice oxygen or free surface hydroxyls. Adsorbed molecules also had reactivity of oxidizing. Moreover, acetyl as a key intermediate for oxygenates was observed by investigation of $\text{CH}_3\text{OH} + \text{CO}$ and $\text{CH}_3\text{I} + \text{CO} + \text{H}_2$. Based on the nature of surface properties, the mechanism of oxygenates formation on precipitated iron-based high temperature catalyst was discussed.

Keywords—Iron-based catalysts, intermediates, oxygenates, in-situ DRIFTS, chemical trapping.

I. INTRODUCTION

HYDROCARBONS synthesis from coal or natural gas via syngas due to its good application as alternative fuel, namely Fischer-Tropsch synthesis (FTS), has resulted in significant research. Iron has high olefin selectivity, excellent stability and low cost when FTS is considered. A multicomponent mixture of hydrocarbons and oxygenates can be obtained on iron-based catalysts. As oxygenates have often been considered as unimportant by-products, literature related to the study of mechanism on oxygenates formation appears to be scarce. At present, many authors favor CH_2 insertion mechanism as dominant for FTS. However, oxygenates are hardly feasible via CH_2 insertion mechanism. Routes of oxygenates formation seem complicated. In order to explain both hydrocarbons and oxygenates formation, Dry [1] proposed a mechanism involves both CH_2 and CO as active intermediates. Katzer [2] studied distribution of the labeled atoms in the reaction products by using labeled CO and indicated that methanol is not the precursor of ethanol. He suggested an isomeric structure of ketene and ethylene oxide

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and proposed mechanism of “CO associating-ketene-ethylene oxide-ethanol”. Tamaru, in accordance with the results of Somorjai [3], concluded that hydrocarbons and C_2 oxygenates have a common hydrocarbonated C_1 intermediate. Ichikawa, et al. [4] and Pijolat [5] suggested that alcohols were formed by CO insertion. However, many questions remain unanswered in the mechanism of oxygenates formation. With the advent of surface analytical instrumentation and chemical trapping studies, it is accepted by many researchers now that higher alcohols are formed by reaction of oxygenated C_2 species with a carbonic type hydrocarbonated species, which can contain several carbon atoms [6].

The aim of the present study was to study the nature of adsorbed species on catalytic surface over an industrial precipitated iron-based high temperature catalyst during FTS. The formulation of the mechanism of oxygenates formation and key intermediates were also discussed based on the results. For that purpose, in-situ DRIFTS technique and chemical trapping were applied.

II. EXPERIMENTAL

In-situ DRIFTS was carried out with a spectrometer (Nicolet 6700, MCT detector, Thermo, USA), fitted with an in situ cell equipped with ZnSe windows. The catalyst was reduced in situ for 2 h under atmospheric pressure by pure hydrogen at 547 K ($30\text{ml}\cdot\text{min}^{-1}$, $1\text{K}\cdot\text{min}^{-1}$). Then the reactor was flushed by pure nitrogen again (573 K, 30 min). Vacuum was then applied. Vacuum degree was better than 10^{-4}Pa . 10^5Pa 1.05% $\text{CH}_3\text{CHO}/\text{He}$ or 10^5Pa gaseous methanol carried by pure nitrogen was introduced at room temperature on reduced samples. In-situ reaction studies were performed after activation. H_2/CO gases with a 2/3 ratio were introduced and the spectra were recorded with the increasing temperature and pressure.

All spectra were recorded with a resolution of 4cm^{-1} and accumulation of 32 scans.

The device used for chemical trapping experiments was the same to that used in in-situ DRIFTS analysis. The species were trapped by introducing CH_3OH or CH_3I to CO or syngas ($\text{H}_2/\text{CO} = 2/3$).

III. RESULTS AND DISCUSSION

A. Infrared Spectra of Methanol Adsorption

Fig. 1 showed the infrared spectra of adsorbed methanol on precipitated iron-based high temperature catalyst. Band at 2036

cm^{-1} could be ascribed to CO which formed by decomposition of methanol. Bands at 3006, 2944, 2838 and 1458 cm^{-1} could be attributed to methoxy species ($\nu_a\text{CH}_3$ 3006 and 2944 cm^{-1} , $\nu_s\text{CH}_3$ 2838 cm^{-1} , δCH_3 1458 cm^{-1}) [7]-[9]. Bands at 2931 ($\nu_a\text{CH}_3$), 2868 (Fermi resonance 2 δCH_3 and $\nu_s\text{CH}_3$), 2824 ($\nu_s\text{CH}_3$) and 1054 cm^{-1} ($\nu\text{C-O}$) were probably that of a bidentate methoxy species on surface [10]. It can be seen from Fig. 1 that band at 3661 cm^{-1} which was assigned to free surface hydroxyls irreversible disappeared on surface. This may due to production of methoxy species. Methanol always acted as proton donor on catalyst surface which could be identified through the bands near 3400 cm^{-1} (O-H---O stretching superimposed at 3661 cm^{-1}). By heating, the band at 1350 cm^{-1} broadened and was shifted to 1368 cm^{-1} which corresponded to CH rocking frequency (ρCH). Zamboni, et al. [11] assigned these bands (2974, 1368 cm^{-1}) to linear or cyclic polymeric compounds, whose stability were determined by multiple hydrogen bondings with surface OH's. The assignment of the bands at 1728 and 1197 cm^{-1} at low temperature (298K), whose intensity weakened with temperature, would be discussed in the following section.

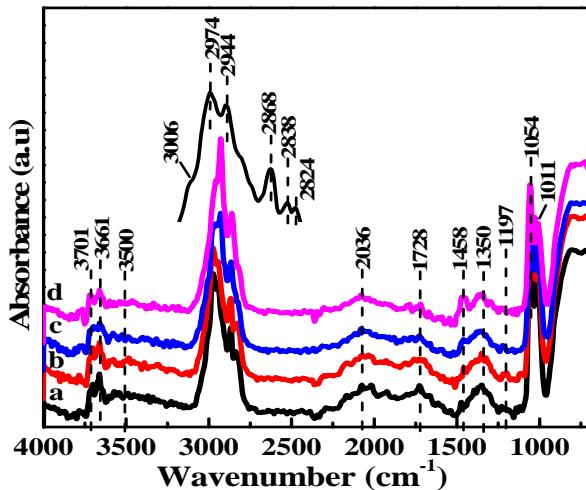


Fig. 1 Infrared spectra of CH_3OH adsorption on precipitated iron-based catalysts: a-298 K; b-333 K; c-393 K; d-453 K

B. Infrared Spectra of Acetaldehyde Adsorption

Fig. 2 showed the infrared spectra of adsorbed acetaldehyde on precipitated iron-based high temperature catalyst. Bands were observed at 2981, 2819 and 2731 cm^{-1} , as well as in the lower frequency region at 1760, 1443, 1371, 1120 and 1058 cm^{-1} . These bands were corresponded to νCH_3 and νCH . A strong carbonyl band at 1738 cm^{-1} could be observed which can be assigned to physisorbed molecules [12]. Band at 1760 cm^{-1} corresponded to C=O stretching vibration of vapor-phase acetaldehyde. Similar species had also been detected by adsorption of formaldehyde [13]. In the case of formaldehyde adsorption, only a weak band at 1710 cm^{-1} could be observed which corresponded to monomeric carbonylic species. Strong absorptions in the C=O stretching region showed that acetaldehyde could be both physically (1729 cm^{-1}) and

chemically (1584 cm^{-1}) adsorbed on precipitated iron-based high temperature catalyst. Major acetaldehyde adsorbed on this catalyst chemically according to Fig. 2. Bands at 2946 and 1412 cm^{-1} were assigned to polymers of formaldehyde on hematite [14]. With temperature increasing, the intensity of bands at 2981, 1443, 1120, 1058 and 1004 cm^{-1} decreased apparently. Anton, et al. [15] studied adsorption of formaldehyde on Ru(001) and thought that these bands were attributed to adsorbed CH_3CHO in $\eta^2(\text{C},\text{O})\text{CH}_3\text{CHO}$ configuration ($\nu_a\text{CH}_3$, δCH_3 , ωCH_3 , $\nu\text{C-O}$ and ρCH_3). Moreover, the intensity of band at 1666 cm^{-1} weakened apparently upon heating. Demri et al.[16] assigned this band to $\nu\text{C=O}$ vibration of an $\eta^1(\text{C})$ formyl species. This indicated that $\eta^1(\text{C})$ formyl species were not very stable and appeared only as a transient entity during heating up.

Infrared spectra of adsorbed methanol and acetaldehyde on catalyst surface gave useful information for DRIFTS studies. Some similarities of surface properties were observed: adsorbed molecules on surface such as methanol could react with basic sites such as lattice oxygen or free surface hydroxyls. Adsorbed molecules had reactivity of oxidizing.

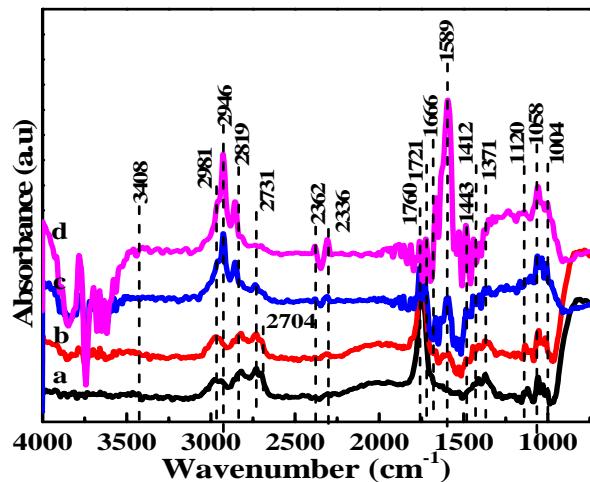


Fig. 2 Infrared spectra of acetaldehyde adsorption on precipitated iron-based catalysts: a-298K; b-333K; c-393K; d-453K

C. Infrared Spectra of in-situ Reaction at Different Temperatures

Fig. 3 showed the infrared spectra of in-situ reaction at different temperatures on precipitated iron-based high temperature catalyst. Weak bands at 2970 and 2871 cm^{-1} which appeared at low temperature (323K) were possibly assigned to $\nu(\text{CH}_3)$ and $\nu(\text{CH}_2)$ of surface hydrocarbons and oxygenates. Band typical of gaseous CO and CO linear stretching mode were detected at 2173 and 2116 cm^{-1} . Bands at 1648 cm^{-1} and 1060 cm^{-1} were that of carboxylate group ($\nu_s\text{O-C-O}$) and bidentate methoxy species($\nu\text{C-O}$) respectively. Fig. 3 showed that CO_2 adsorption with characteristic bands at 2364 and 2327 cm^{-1} were dominant at higher temperature. Moreover, intensity of band around 1441 cm^{-1} which was assigned to surface methoxy species increased upon heating. These species may arise from formate reduction in the presence of hydrogen or dioxygen-methylene decomposition upon heating [17]. The

intensities of bands at 1534 and 1247cm⁻¹ gradually increased until a stationary state of FTS reaction was reached.

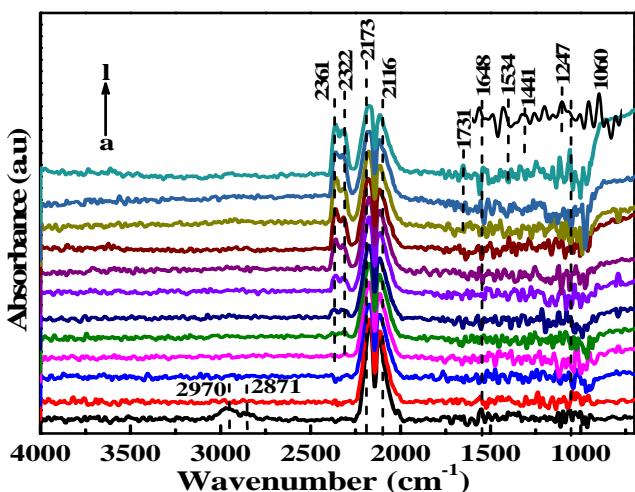


Fig. 3 Infrared spectra of surface species arising from CO + H₂ interaction with reduced precipitated iron-based catalysts at different temperatures: a-323 K; b-423 K; c-523 K; d-543 K; e-553 K; f-563 K; g-573 K; h-583 K; i-593 K; j-603 K; k-613 K; l-623 K

D. Infrared Spectra of In-situ Reaction under Different Pressures

Fig. 4 showed the infrared spectra of in-situ reaction at 623K under different pressures. A slight increase was observed at 2927 and 2855cm⁻¹ when the pressure increased from 0.1 to 2.5 MPa. This indicated that carbene could reach a saturated extent of adsorption even at low pressure. Apparent bands of C₂ intermediates were observed at 1450, 1392 and 1343cm⁻¹ when the pressure increased. Moreover, intensity of the bands at 2304, 2378cm⁻¹ and 3016cm⁻¹ rapidly increased with pressure. This result showed that higher pressure enhanced oxygenates formation and formation of CO₂ and CH₄ simultaneously. It was well known that the total volume reduced in FTS [18]. Thus pressure enhanced the equilibrium conversion rate. Results above showed that pressure also enhanced oxygenates formation. As a result, pressure was an important factor that affected the reaction path.

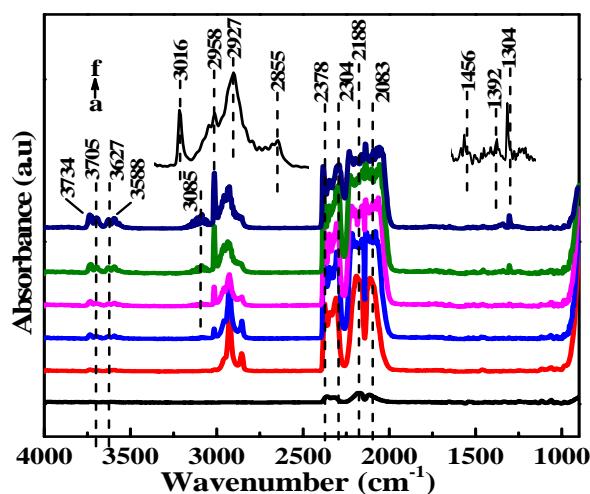


Fig. 4 Infrared spectra of surface species arising from CO + H₂ interaction with reduced precipitated iron-based catalysts under different pressures: a-0.1 MPa; b-0.5 MPa; c-1.0 MPa; d-1.5 MPa; e-2.0 MPa; f-2.5 MPa.

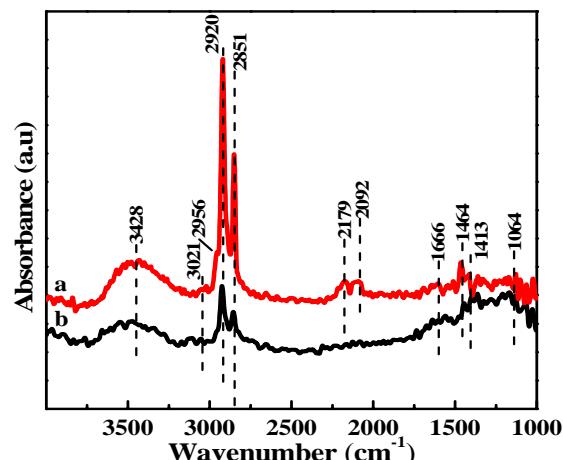


Fig. 5 Infrared spectra of surface species arising from CO + H₂ interaction with reduced precipitated iron-based catalysts: a-0.1 MPa, 623 K, N₂, 30min; b-spectra after switching to pure H₂.

By replacing syngas (623 K, 2.5 MPa) with pure H₂ (1 atm) at 623K (after purged by N₂ for 30 min), as shown in Fig. 5, one could observe an immediate decrease of the bands in the region of 3000-2800cm⁻¹. However, the bands did not disappear completely. This indicated that bands in this region were assigned to two species, one being sensitive to H₂ (ν_s CH₃ of a monoxide acetate justified by the band at 3021cm⁻¹ which disappeared as soon as CO was switched off), the other being insensitive to H₂ (CH₃-O-Support species justified by the band at 2920 and 2851cm⁻¹ whose intensity kept constant after the system was flushed for 15min) [19]. This indicated that CH₃-O-Support species which were stable and hard to desorb occupied a large part of surface and reduced the reactivity of the catalyst. The Bands in the region of 1500-1200cm⁻¹, which decreased rather slowly on treatment with H₂, were assigned to abidentate acetate. Band around 1666cm⁻¹ was attributed to

acetyl species whose intensity decreased continuously on treatment with H₂. This indicated a hydrogenation reaction on the surface.

E. Chemical Trapping

Infrared spectra of in-situ reaction at different reaction conditions indicated that acetyl was a key intermediate for oxygenates. Mark, et al. also reported that CO insertion into an alkyl-metal bond to form acetyl species was the key step in C₂⁺ oxygenates synthesis[20]. The CO insertion mechanism consumes alkyl species. Two reactions had been studied including CH₃OH + CO and CH₃I + H₂ + CO to study the route for oxygenates formation.

1. CH₃OH + CO

Upon heating, characteristic bands of adsorbed CO and methoxy species which were observed at 2170, 2119cm⁻¹ and 2948, 2865, 2828, 1054, 1011cm⁻¹ diminished. This indicated that chemical trapping occurred on the surface. The contact with CH₃OH + CO vapor immediately caused the disappearance of band at 3706cm⁻¹ which corresponding to the free OH and the appearance of a broad adsorption toward lower frequencies. This showed that CH₃OH reacted with surface OH⁻ ions to form H₂O molecules. A condensation mechanism was proposed. Small amount of acetate were also formed (v_aCH₃: 3005, 2973cm⁻¹, δ_aCH₃: 1455cm⁻¹, v_aC-C: 1209cm⁻¹). Similar results were found by Ichikawa, et al. [4], who found a minor part of ethanol or acetaldehyde in CO + H₂ reaction incorporated ¹³C by addition of ¹³CH₃OH.

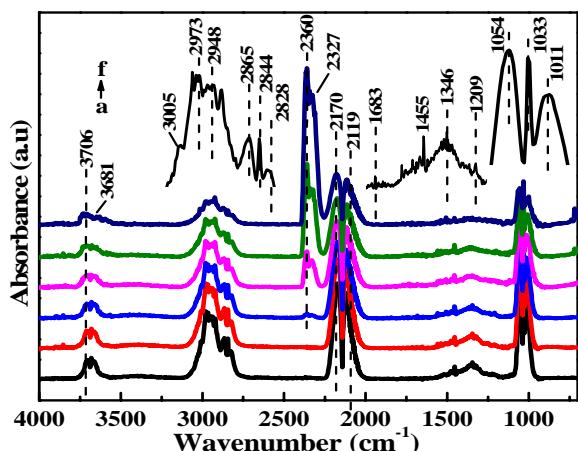


Fig. 6 Infrared spectra of CH₃OH + CO adsorbed on precipitated iron-based catalysts: a-298 K; b-333 K; c-393 K; d-453 K; e-513 K; f-573 K

2. CH₃I + H₂ + CO

Fig. 7 showed an immediate reduction of bands of chemisorbed CO at 2179 and 2105cm⁻¹ after CH₃I was added to the stable system. Chemical trapping on the surface was indicated. Moreover, a band decreased with time at 1666cm⁻¹ together with bands at 2900, 2874, 1418, 1104 and 942cm⁻¹. Forster assigned these bands to an acetyl formed by the reaction of CH₃I and syngas (vCH₃: 2964 and 2900cm⁻¹, vC=O: 1667cm⁻¹, δ_sCH₃: 1409cm⁻¹, δ_aC-C: 1054cm⁻¹) [21]. The vC=O

vibration of an acetone was located at 1615cm⁻¹. It was thought to be formed through chemical trapping of an acetyl species by a surface CH₃ entity. This confirmed the presence of acetyl species. Chateau observed methyl acetate by introducing CH₃I in large excess after syngas contact [22]. Methyl acetate was thought to be formed by the reaction of an acetate species with a surface CH₃. However, no obvious characteristic bands for methyl acetate were found in this paper. This may due to lack of CH₃ on the catalytic surface.

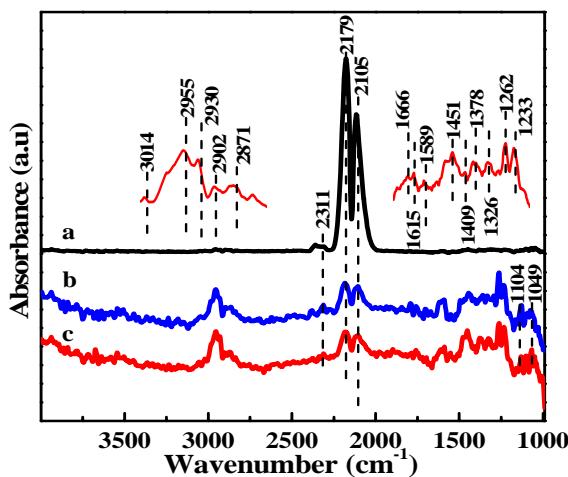


Fig. 7 Infrared spectra of CH₃I + H₂ + CO adsorbed on precipitated iron-based catalysts at 623 K: a-H₂ + CO; b-CH₃I + H₂ + CO, 36s; c-CH₃I + H₂ + CO, 72s.

Acetyl as a key intermediate for oxygenates was observed by investigation of CH₃OH + CO and CH₃I + CO + H₂. It gave characteristic band at 1666cm⁻¹ (C=O stretching mode). They were thought to be formed by continuous hydrogenation of formates.

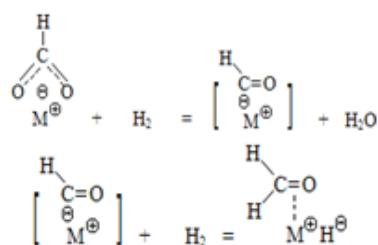


Fig. 8 Continuous hydrogenation of formates

Lavelley observed acetyl species by studying adsorption of CO/H₂ below 298K [23]. Moreover, results of CH₃I tracer experiments confirmed the presence of acetyl species [24].

It can be seen from Fig. 6 that characteristic bands of alcohols (near 1064cm⁻¹) had a positive correlation with bands of acetyl. This confirmed the conclusion that acetyl was a key intermediate for C₂⁺ oxygenates.

Thus route for oxygenates should involve the formation of formates: CO insertion into a metal-hydroxy bond.

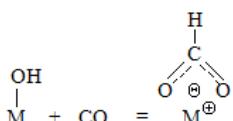


Fig. 9 CO insertion into a metal-hydroxy bond

Johnston and Joyner [25] proposed the involvement of surface hydroxyl species in the formation of oxygenated product compounds.

In-situ reaction and chemical trapping had proved that large amounts of methoxy and formate species were produced on catalyst surface. It was thought that methoxy species were formed by reaction of formates and hydrogen at high temperature [17].

Vedage, et al. [26] conducted ^{13}C -tracer experiments on a Cu/ZnO catalyst, which had been treated with $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$, and observed high concentrations of $^{13}\text{C}^{18}\text{O}$ and $^{12}\text{C}^{16}\text{O}$ in the product. This provided experimental evidence for Fig. 9.

Chain growth occurred through a condensation reaction between adsorbed alcohols under elimination of water. Termination of the chain growth process or desorption yielded oxygenates. The formation of acids in the Fischer-Tropsch synthesis was postulated as a secondary reaction of primarily formed aldehydes as a result of Cannizzaro reactions. Acids reacting with an alcohol yielded esters.

IV. CONCLUSION

Adsorption of methanol and acetaldehyde provided spectroscopic evidence on the different surface species of the precipitated iron-based high temperature catalyst. Numerous oxygenated precursors and crucial intermediates were found by in-situ DRIFTS, such as surface acetate, acetyl and methoxide. The results showed that adsorbed molecules on surface such as methanol or acetaldehyde could react with basic sites such as lattice oxygen or free surface hydroxyls. Adsorbed molecules also had reactivity of oxidizing. Moreover, acetyl as a key intermediate for oxygenates was observed by investigation of $\text{CH}_3\text{OH} + \text{CO}$ and $\text{CH}_3\text{I} + \text{CO} + \text{H}_2$. The formulation of the mechanism of oxygenates formation and key intermediates were also discussed based on the intermediates observed on the catalytic surface and the similarities of surface properties.

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