

# 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

**H**YDROCARBONS 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  $\text{CH}_2$  insertion mechanism as dominant for FTS. However, oxygenates are hardly feasible via  $\text{CH}_2$  insertion mechanism. Routes of oxygenates formation seem complicated. In order to explain both hydrocarbons and oxygenates formation, Dry [1] proposed a mechanism involves both  $\text{CH}_2$  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

and proposed mechanism of “CO associating-ketene-ethylene oxide-ethanol”. Tamaru, in accordance with the results of Somorjai [3], concluded that hydrocarbons and  $\text{C}_2$  oxygenates have a common hydrocarbonated  $\text{C}_1$  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  $\text{C}_2$  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 2h under atmospheric pressure by pure hydrogen at 547K ( $30\text{ml}\cdot\text{min}^{-1}$ ,  $1\text{K}\cdot\text{min}^{-1}$ ). Then the reactor was flushed by pure nitrogen again (573K, 30min). Vacuum was then applied. Vacuum degree was better than  $10^{-4}\text{Pa}$ .  $10^5\text{Pa}$  1.05%  $\text{CH}_3\text{CHO}/\text{He}$  or  $10^5\text{Pa}$  gaseous methanol carried by pure nitrogen was introduced at room temperature on reduced samples. In-situ reaction studies were performed after activation.  $\text{H}_2/\text{CO}$  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  $4\text{cm}^{-1}$  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  $\text{CH}_3\text{OH}$  or  $\text{CH}_3\text{I}$  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

Wanyu Mao, Hongfang Ma, Haitao Zhang, and WeixinQian are with Engineering Research Center of Large Scale Reactor Engineering and Technology, Ministry of Education, State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237 China (e-mail: cat.tou@163.com, zht@ecust.edu.cn).

WeiyongYing is with Engineering Research Center of Large Scale Reactor Engineering and Technology, Ministry of Education, State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237 China (corresponding author; phone: 86-21-64252193; fax: 86-21-64252192; e-mail: wyying@ecust.edu.cn).

$\text{cm}^{-1}$  could be ascribed to CO which formed by decomposition of methanol. Bands at 3006, 2944, 2838 and  $1458\text{cm}^{-1}$  could be attributed to methoxy species ( $\nu_{\text{a}}\text{CH}_3$  3006 and  $2944\text{cm}^{-1}$ ,  $\nu_{\text{s}}\text{CH}_3$  2838 $\text{cm}^{-1}$ ,  $\delta\text{CH}_3$  1458 $\text{cm}^{-1}$ ) [7]-[9]. Bands at 2931 ( $\nu_{\text{a}}\text{CH}_3$ ), 2868 (Fermi resonance  $2\delta\text{CH}_3$  and  $\nu_{\text{s}}\text{CH}_3$ ), 2824 ( $\nu_{\text{s}}\text{CH}_3$ ) and  $1054\text{cm}^{-1}$  ( $\nu\text{C-O}$ ) were probably that of a bidentatemethoxy species on surface [10]. It can be seen from Fig. 1 that band at  $3661\text{cm}^{-1}$  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  $3400\text{cm}^{-1}$  (O-H---O stretching superimposed at  $3661\text{cm}^{-1}$ ). By heating, the band at  $1350\text{cm}^{-1}$  broadened and was shifted to  $1368\text{cm}^{-1}$  which corresponded to CH rocking frequency ( $\rho\text{CH}$ ). Zamboni, et al. [11] assigned these bands (2974,  $1368\text{cm}^{-1}$ ) 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  $1197\text{cm}^{-1}$  at low temperature (298K), whose intensity weakened with temperature, would be discussed in the following section.

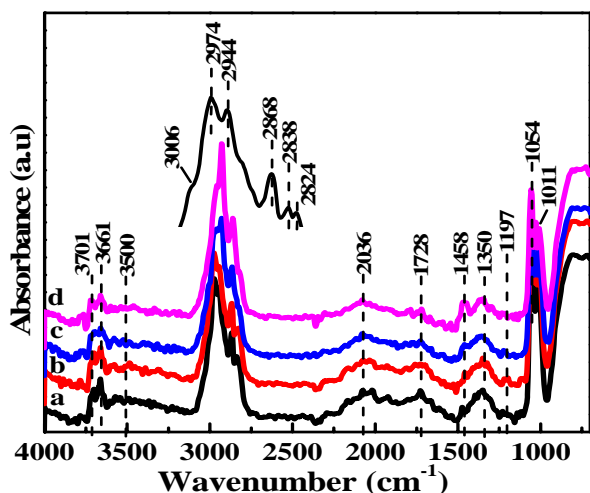


Fig. 1 Infrared spectra of  $\text{CH}_3\text{OH}$  adsorption on precipitated iron-based catalysts: a-298 K; b-333 K; c-393 K; d-453 K

#### 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  $2731\text{cm}^{-1}$ , as well as in the lower frequency region at 1760, 1443, 1371, 1120 and  $1058\text{cm}^{-1}$ . These bands were corresponded to  $\nu\text{CH}_3$  and  $\nu\text{CH}$ . A strong carbonyl band at  $1738\text{cm}^{-1}$  could be observed which can be assigned to physisorbed molecules [12]. Band at  $1760\text{cm}^{-1}$  corresponded to  $\text{C=O}$  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  $1710\text{cm}^{-1}$  could be observed which corresponded to monomeric carbonylic species. Strong absorptions in the  $\text{C=O}$  stretching region showed that acetaldehyde could be both physically ( $1729\text{cm}^{-1}$ ) and

chemically ( $1584\text{cm}^{-1}$ ) adsorbed on precipitated iron-based high temperature catalyst. Major acetaldehyde adsorbed on this catalyst chemically according to Fig. 2. Bands at 2946 and  $1412\text{cm}^{-1}$  were assigned to polymers of formaldehyde on hematite [14]. With temperature increasing, the intensity of bands at 2981, 1443, 1120, 1058 and  $1004\text{cm}^{-1}$  decreased apparently. Anton, et al. [15] studied adsorption of formaldehyde on Ru(001) and thought that these bands were attributed to adsorbed  $\text{CH}_3\text{CHO}$  in  $\eta^2(\text{C,O})\text{CH}_3\text{CHO}$  configuration ( $\nu_{\text{a}}\text{CH}_3$ ,  $\delta\text{CH}_3$ ,  $\omega\text{CH}_3$ ,  $\nu\text{C-O}$  and  $\rho\text{CH}_3$ ). Moreover, the intensity of band at  $1666\text{cm}^{-1}$  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.

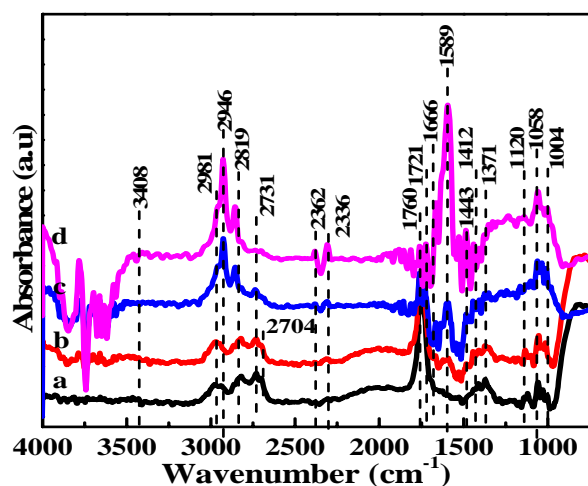


Fig. 2 Infrared spectra of acetaldehyde adsorption on precipitated iron-based catalysts: a-298K; b-333K; c-393K; d-453K

#### 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  $2871\text{cm}^{-1}$  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  $2116\text{cm}^{-1}$ . Bands at  $1648\text{cm}^{-1}$  and  $1060\text{cm}^{-1}$  were that of carboxylate group ( $\nu_{\text{s}}\text{O-C-O}$ ) and bidentatemethoxy species ( $\nu\text{C-O}$ ) respectively. Fig. 3 showed that  $\text{CO}_2$  adsorption with characteristic bands at 2364 and  $2327\text{cm}^{-1}$  were dominant at higher temperature. Moreover, intensity of band around  $1441\text{cm}^{-1}$  which was assigned to surface methoxy species increased upon heating. These species may arise from formate reduction in the presence of hydrogen or dioxymethylene decomposition upon heating [17]. The

intensities of bands at 1534 and 1247 $\text{cm}^{-1}$  gradually increased until a stationary state of FTS reaction was reached.

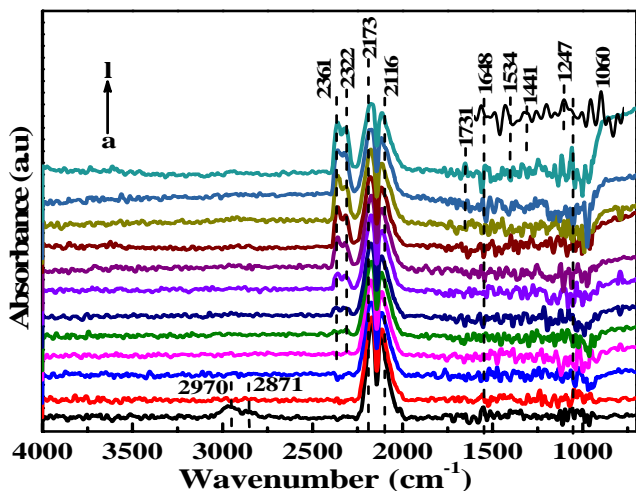


Fig. 3 Infrared spectra of surface species arising from CO + H<sub>2</sub> interaction with reduced precipitated iron-based catalysts at different temperatures: a-323 K; b-423 K; c-523 K; d-543 K; e-553 K; f-563 K; g-573 K; h-583 K; i-593 K; j-603 K; k-613 K; l-623 K

#### 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 2855 $\text{cm}^{-1}$  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 C<sub>2</sub> intermediates were observed at 1450, 1392 and 1343 $\text{cm}^{-1}$  when the pressure increased. Moreover, intensity of the bands at 2304, 2378 $\text{cm}^{-1}$  and 3016 $\text{cm}^{-1}$  rapidly increased with pressure. This result showed that higher pressure enhanced oxygenates formation and formation of CO<sub>2</sub> and CH<sub>4</sub> 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.

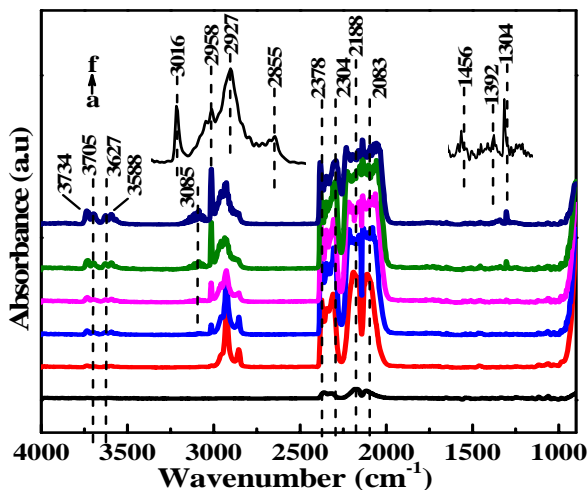


Fig. 4 Infrared spectra of surface species arising from CO + H<sub>2</sub> interaction with reduced precipitated iron-based catalysts under different pressures: a-0.1 MPa; b-0.5 MPa; c-1.0 MPa; d-1.5 MPa; e-2.0 MPa; f-2.5 MPa.

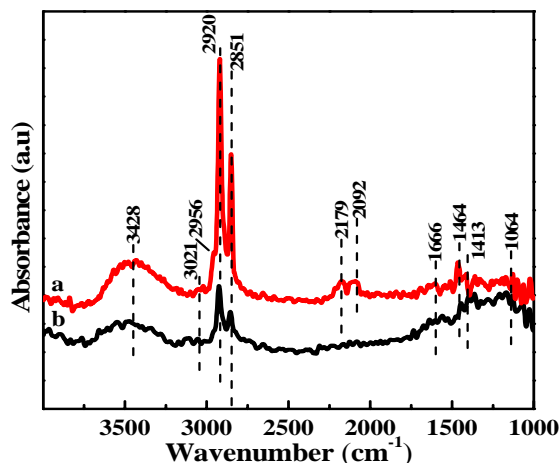


Fig. 5 Infrared spectra of surface species arising from CO + H<sub>2</sub> interaction with reduced precipitated iron-based catalysts: a-0.1 MPa, 623 K, N<sub>2</sub>, 30min; b-spectra after switching to pure H<sub>2</sub>.

By replacing syngas (623 K, 2.5 MPa) with pure H<sub>2</sub> (1 atm) at 623K (after purged by N<sub>2</sub> for 30 min), as shown in Fig. 5, one could observe an immediate decrease of the bands in the region of 3000-2800 $\text{cm}^{-1}$ . However, the bands did not disappear completely. This indicated that bands in this region were assigned to two species, one being sensitive to H<sub>2</sub> (ν<sub>s</sub>CH<sub>3</sub> of a monoxide acetate justified by the band at 3021 $\text{cm}^{-1}$  which disappeared as soon as CO was switched off), the other being insensitive to H<sub>2</sub> (CH<sub>3</sub>-O-Support species justified by the band at 2920 and 2851 $\text{cm}^{-1}$  whose intensity kept constant after the system was flushed for 15min) [19]. This indicated that CH<sub>3</sub>-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 1500-1200 $\text{cm}^{-1}$ , which decreased rather slowly on treatment with H<sub>2</sub>, were assigned to abidentate acetate. Band around 1666 $\text{cm}^{-1}$  was attributed to

acetyl species whose intensity decreased continuously on treatment with  $H_2$ . 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  $C_2^+$  oxygenates synthesis[20]. The CO insertion mechanism consumes alkyl species. Two reactions had been studied including  $CH_3OH + CO$  and  $CH_3I + H_2 + CO$  to study the route for oxygenates formation.

#### 1. $CH_3OH + CO$

Upon heating, characteristic bands of adsorbed CO and methoxy species which were observed at 2170, 2119 $cm^{-1}$  and 2948, 2865, 2828, 1054, 1011 $cm^{-1}$  diminished. This indicated that chemical trapping occurred on the surface. The contact with  $CH_3OH + CO$  vapor immediately caused the disappearance of band at 3706 $cm^{-1}$  which corresponding to the free OH and the appearance of a broad adsorption toward lower frequencies. This showed that  $CH_3OH$  reacted with surface OH $^-$  ions to form  $H_2O$  molecules. A condensation mechanism was proposed. Small amount of acetate were also formed ( $\nu_aCH_3$ : 3005, 2973 $cm^{-1}$ ,  $\delta_aCH_3$ : 1455 $cm^{-1}$ ,  $\nu_aC-C$ : 1209 $cm^{-1}$ ). Similar results were found by Ichikawa, et al. [4], who found a minor part of ethanol or acetaldehyde in  $CO + H_2$  reaction incorporated  $^{13}C$  by addition of  $^{13}CH_3OH$ .

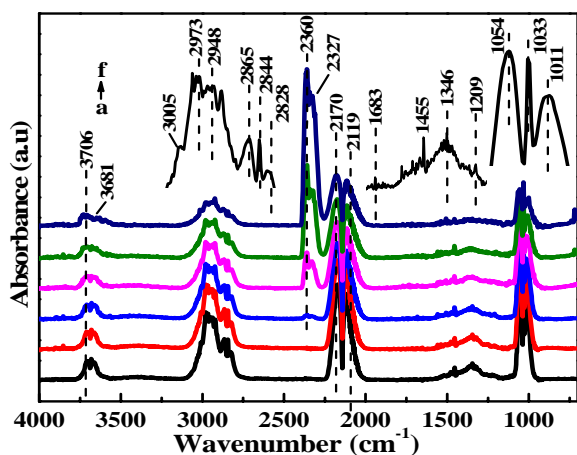


Fig. 6 Infrared spectra of  $CH_3OH + CO$  adsorbed on precipitated iron-based catalysts: a-298 K; b-333 K; c-393 K; d-453 K; e-513 K; f-573 K

#### 2. $CH_3I + H_2 + CO$

Fig. 7 showed an immediate reduction of bands of chemisorbed CO at 2179 and 2105 $cm^{-1}$  after  $CH_3I$  was added to the stable system. Chemical trapping on the surface was indicated. Moreover, a band decreased with time at 1666 $cm^{-1}$  together with bands at 2900, 2874, 1418, 1104 and 942 $cm^{-1}$ . Forster assigned these bands to an acetyl formed by the reaction of  $CH_3I$  and syngas ( $\nu_{CH_3}$ : 2964 and 2900 $cm^{-1}$ ,  $\nu_{C=O}$ : 1667 $cm^{-1}$ ,  $\delta_sCH_3$ : 1409 $cm^{-1}$ ,  $\delta_aC-C$ : 1054 $cm^{-1}$ ) [21]. The  $\nu_{C=O}$

vibration of an acetone was located at 1615 $cm^{-1}$ . It was thought to be formed through chemical trapping of an acetyl species by a surface  $CH_3$  entity. This confirmed the presence of acetyl species. Chateau observed methyl acetate by introducing  $CH_3I$  in large excess after syngas contact [22]. Methyl acetate was thought to be formed by the reaction of an acetate species with a surface  $CH_3$ . However, no obvious characteristic bands for methyl acetate were found in this paper. This may due to lack of  $CH_3$  on the catalytic surface.

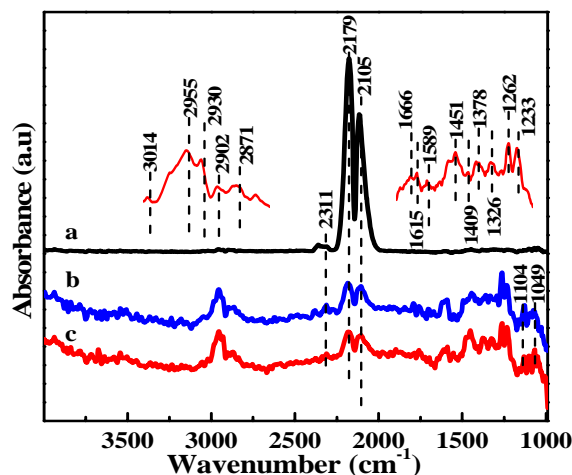


Fig. 7 Infrared spectra of  $CH_3I + H_2 + CO$  adsorbed on precipitated iron-based catalysts at 623 K: a- $H_2 + CO$ ; b- $CH_3I + H_2 + CO$ , 36s; c- $CH_3I + H_2 + CO$ , 72s.

Acetyl as a key intermediate for oxygenates was observed by investigation of  $CH_3OH + CO$  and  $CH_3I + CO + H_2$ . It gave characteristic band at 1666 $cm^{-1}$  ( $C=O$  stretching mode). They were thought to be formed by continuous hydrogenation of formates.

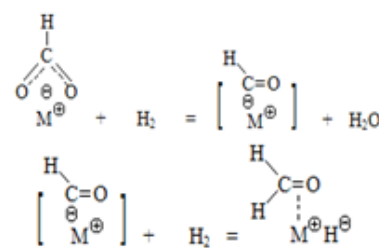


Fig. 8 Continuous hydrogenation of formates

Lavelley observed acetyl species by studying adsorption of  $CO/H_2$  below 298K [23]. Moreover, results of  $CH_3I$  tracer experiments confirmed the presence of acetyl species [24].

It can be seen from Fig. 6 that characteristic bands of alcohols (near 1064 $cm^{-1}$ ) had a positive correlation with bands of acetyl. This confirmed the conclusion that acetyl was a key intermediate for  $C_2^+$  oxygenates.

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

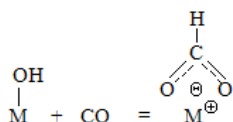


Fig. 9 CO insertion into a metal-hydroxy bond

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  $^{13}\text{C}$ -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.

#### ACKNOWLEDGMENT

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