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Computational Study on Thermodynamic Properties of Fischer-Tropsch Synthesis Process

Hong-kun Zhu, Guo-liang Song*, Zhen-hua Li*

Shanghai Key Laboratory of Molecular Catalysis & Innovative Materials, Department of Chemistry, Fudan University, Shanghai 200438, China

Using the highly accurate G4 method, we computed the thermodynamic data of 1287 possible reaction products under a wide range of reaction conditions in the Fischer-Tropcsh synthesis (FTS) process. These accurate thermodynamic data provide basic thermodynamic quantities for the actual chemical engineering process and are useful in analyzing product distribution because FTS demonstrates many features of an equilibrium-controlled system. Our results show that the number of thermodynamically allowed products to increase when lowering temperature, raising pressure, and raising H_2/CO ratio. At low temperature, high pressure and high H_2/CO ratio, many products are thermodynamically allowed and the selectivity of product has to be controlled by kinetic factors. On the other hand, high selectivity of lighter products can be realized in thermodynamics by raising temperature and lowering pressure. We found that the equilibrium product yield will reach a maximum and remain unchanged when lowering temperature, raising pressure, and raising H_2/CO ratio to some limits, implying that optimizing reaction conditions has no effect on equilibrium product yields beyond these limits. The thermodynamic analysis is also useful in designing and evaluating FTS reaction mechanisms. We found that reaction pathways through formaldehyde should be discarded because of its extremely low equilibrium yield. Recently, in the FTS process using metal-oxide-zeolite catalysts for the highly selective production of C_2-C_4 olefins and aromatic hydrocarbons, there are several guesses on the possible reaction intermediates entering the zeolite channel. Our results show that ketene, methanol, and dimethyl ether are three possible reaction intermediates.

Key words: Fischer-Tropsch synthesis, Thermodynamics, G4 Method, Product distribution, Reaction mechanism

I. INTRODUCTION

With the decreasing of global-oil reserving and increasing of petroleum price, Fischer-Tropsch synthesis (FTS), which converts synthesis gas (mixing gas of hydrogen and carbon monoxide) to a series of useful chemical products such as C_2-C_4 olefins, methanol, aromatic hydrocarbons *etc.*, nowadays has become the focus of numerous researches [1−6]. Because synthesis gas can be obtained from a variety of sources, such as coal, natural gas and biomass, FTS does not rely on crude oil supplies [7, 8]. Therefore, FTS has drawn intensive worldwide academic and industrial attentions, especially in those coal-rich but lean-oil countries.

Because of the strong covalent bonds in CO and H_2, FTS has to be a catalytic process. In the past, Fe- and Co-based catalysts were often used [2, 9−11]. How-

ever, selectivities of these catalysts are not very satisfactory. As we know, the product distribution of a catalytic process is affected by both thermodynamic and kinetic factors. Some studies show that the FTS process demonstrates many features of an equilibrium-controlled system. However, the thermodynamic properties of the FTS process have not been thoroughly studied [12, 13]. These thermodynamic properties are the basis for understanding the product distribution of FTS and provide basic thermodynamic quantities for the actual chemical engineering process. Smith *et al.* and Anderson *et al.* [14, 15] studied the product distribution from a thermodynamic approach. They used a free-energy minimization technique and concluded that methane is the most probable product in FTS. Norval *et al.* [16, 17] considered the local equilibriums in FTS and carried out a preliminary exploration. All these studies relied on the accurate thermodynamic data of various possible products. Unfortunately, accurate thermodynamic data for all the products especially those less stable ones are not always available. Some data were estimated from empirical formula such as the Benson

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*Authors to whom correspondence should be addressed. E-mail: lizhenhua@fudan.edu.cn, guoliangsong@fudan.edu.cn

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group contribution method and ABWY method, and they had large uncertainties [12, 18, 19].
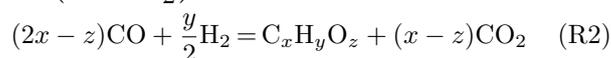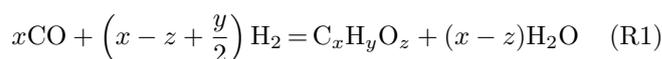
Thermodynamic data can be useful in designing and examining the reaction mechanism of FTS, and in identifying rate-controlling processes. When designing possible reaction mechanisms, we can discard some pathways based on thermodynamic considerations. For example, if there is a very unstable intermediate in a reaction pathway, this pathway is probably a less possible one. In recent years, bi-functional catalysis, in which physically mixed metal oxides and zeolites were used as FTS catalysts, could reach high selectivity of C_2-C_4 olefins [20−22] and aromatic hydrocarbons [23, 24]. For these bi-functional catalysts, the intermediates from the FTS process on the metal oxides entered the zeolite channels and there highly selective C_2-C_4 olefins and aromatic hydrocarbons were synthesized. There were several guesses on the possible intermediates that entered the zeolite channels, such as ketene, methanol, or dimethyl ether. From thermodynamic considerations, we can provide some useful information to judge which guess is more reasonable and to help the experiments to design more plausible reaction mechanisms.

Owing to the limitation of experimental technology, it is difficult to obtain the accurate thermodynamic data for those unstable intermediates and products. Nowadays, accurate thermodynamic data with chemical accuracy (with a mean absolute deviation (MAD) less than 1 kcal/mol) or sub-chemical accuracy (with an MAD less than 0.5 kcal/mol) for small molecules can be computed routinely using highly accurate theoretical methods, such as the Gn-type models of Curtiss *et al.* [25] and the Wn-type procedures of Martin *et al.* [26−29]. The G4 method is the most accurate composite method of the Gn family. For the 38 hydrocarbons in the G3/05 test, it has an MAD of just 0.48 kcal/mol on heats of formation [25]. G4 is more accurate than G3 but is more expensive. G3 has an MAD of 0.68 kcal/mol on the same test set [25]. On the other hand, G4 is less accurate than the Wn-type procedures but is much less expensive. In a recent study, Martin *et al.* compared G3 and G4 families with the Wn-families on 183 atomization energies of molecules composed of first-row and second-row elements and they found that G4 has a RMSD (root mean square deviation) of just 0.98 kcal/mol [28]. On the other hand, G3 and CBS-QB3 have RMSDs of 1.88 kcal/mol and 2.35 kcal/mol, respectively. W1 and W2 are slightly better, with RMSDs of 0.74 kcal/mol and 0.57 kcal/mol, respectively. We selected G4 as a compromise between accuracy and efficiency because the molecules computed exceed 1000. In this study, we used the G4 method to systematically investigate the thermodynamic properties of 1287 possible intermediates and products in FTS. Trends in these thermodynamic properties and their implications on the product distribution and reaction mechanism were discussed.

II. COMPUTATIONAL DETAILS

All the computations were carried out with the Gaussian 09 software package [30]. The thermodynamic properties of all the molecules were computed at the G4 level of theory. The computed molecules are the possible reaction products of the FTS process, which can be expressed as $C_xH_yO_z$, including 1229 molecules with $1 \leq x \leq 4$ and $0 \leq z \leq 2$, and 58 stable hydrocarbons (alkanes, alkenes, alkynes, and aromatics) with five to ten carbon atoms.

Using the G4 method, we computed the reaction enthalpy ($\Delta_r H$s) and Gibbs free-energy changes ($\Delta_r G$s) of the following two important reactions in the FTS process:

$$x\mathrm{CO} + \left(x - z + \frac{y}{2}\right)\mathrm{H_2} = \mathrm{C}_x\mathrm{H}_y\mathrm{O}_z + (x-z)\mathrm{H_2O} \quad \text{(R1)}$$

$$(2x - z)\mathrm{CO} + \frac{y}{2}\mathrm{H_2} = \mathrm{C}_x\mathrm{H}_y\mathrm{O}_z + (x-z)\mathrm{CO_2} \quad \text{(R2)}$$

R1 is the major reaction on metal surfaces while R2 is the major reaction on metal oxide surfaces recently used in the bi-functional catalysts to directly synthesize aromatics from syngas. R2 can be viewed as the coupling of R1 with the water gas shift reaction ($\mathrm{CO} + \mathrm{H_2O} = \mathrm{CO_2} + \mathrm{H_2}$). To compute $\Delta_r H$s and $\Delta_r G$s, we followed the detailed procedure of the G4 method [25] to compute the enthalpy (H_T) and Gibbs free energy (G_T) of every specie involved in reactions R1 and R2 at temperature T, where H_T and G_T are computed as:

$$H_T = E_e(\mathrm{G4}) + \mathrm{ZPE} + \Delta H_{0 \to T} \quad (1)$$

$$G_T = E_e(\mathrm{G4}) + \mathrm{ZPE} + \Delta G_{0 \to T} \quad (2)$$

where E_e (G4), ZPE, $\Delta H_{0 \to T}$, and $\Delta G_{0 \to T}$ are the potential energy computed by the G4 method, zero-point vibrational energy, enthalpy change from 0 to T, and Gibbs free-energy change from 0 to T, respectively.

Although the G4 method is very accurate in computing the thermodynamic properties of organic molecules, we found large errors in the computed $\Delta_r H$s and $\Delta_r G$s for 31 molecules with accurate experimental values and the error increases with the size of the molecule (Tables S1 and S2 in supplementary materials). A detailed analysis revealed that the error was caused by the small but systematic errors of the computed thermodynamic properties of CO, H_2, CO_2, and H_2O. Although the errors are small for the four molecules individually, they cumulate with the size of $C_xH_yO_z$. To obtain accurate $\Delta_r H$ and $\Delta_r G$ values, we used a thermodynamic cycle to derive the accurate "experimental" energies of CO, H_2, CO_2, and H_2O at 0 K (see supplementary materials for details). These four "experimental" energies at 0 K were used to compute $\Delta_r H$s and $\Delta_r G$s for all the 1287 molecules. After the correction, the MADs of $\Delta_r H$s and $\Delta_r G$s for reaction R1 dropped from 5.08 kcal/mol and 5.21 kcal/mol to just 0.23 kcal/mol and
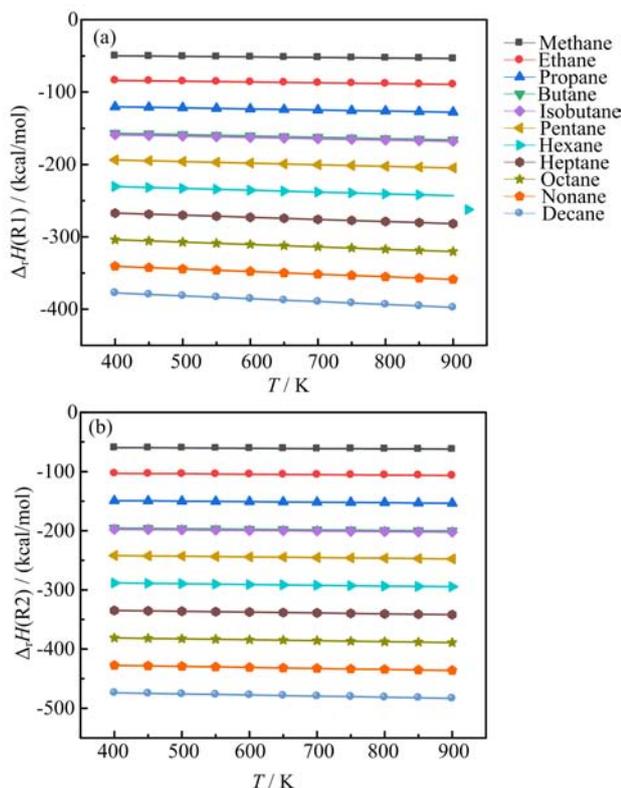
FIG. 1 (a) $\Delta_{\mathrm{r}}H$(R1) and (b) $\Delta_{\mathrm{r}}H$(R2) of alkanes at different temperatures.

FIG. 2 $\Delta_{\mathrm{r}}H$(R1) and $\Delta_{\mathrm{r}}H$(R2) of alkanes, alkenes, and alkynes (C_1-C_{10}) at 600 K.
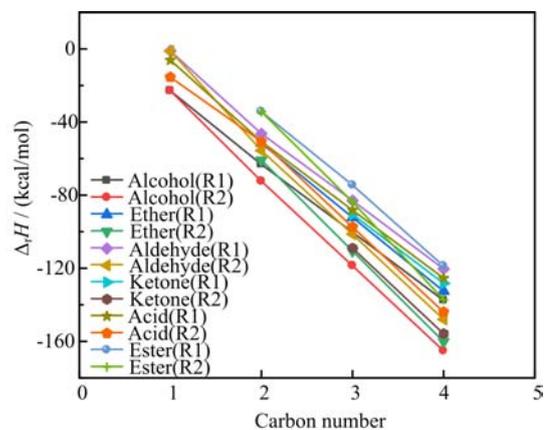
FIG. 3 $\Delta_{\mathrm{r}}H$(R1) and $\Delta_{\mathrm{r}}H$(R2) of normal oxygenated products (C_1-C_4) at 600 K.

0.36 kcal/mol, respectively, for the 31 molecules (Table S1 in supplementary materials). For reaction R2 the MADs of $\Delta_{\mathrm{r}}H$ and $\Delta_{\mathrm{r}}G$ dropped from 3.66 and 3.85 kcal/mol to just 0.23 and 0.42 kcal/mol, respectively, for the 31 molecules (Table S2 in supplementary materials).

III. RESULTS AND DISCUSSION

A. Reaction enthalpy change ($\Delta_{\mathrm{r}}H$) in FTS

Here we discuss the reaction enthalpy changes of reaction R1 ($\Delta_{\mathrm{r}}H$(R1)) and R2 ($\Delta_{\mathrm{r}}H$(R2)).

1. Alkanes, alkenes, and alkynes

The trends in $\Delta_{\mathrm{r}}H$s with respect to temperature are similar for different types of products and therefore only those of hydrocarbons are discussed in detail. The temperature dependences of $\Delta_{\mathrm{r}}H$(R1) and $\Delta_{\mathrm{r}}H$(R2) are plotted in FIG. 1 (a) and 1(b), respectively, for alkanes. FIG. 1 shows that all the reactions are exothermic and $\Delta_{\mathrm{r}}H$(R1) and $\Delta_{\mathrm{r}}H$(R2) are not sensitive to temperature. It is worth mentioning that isomers, such as butane and isobutane have very close $\Delta_{\mathrm{r}}H$ values, which indicates yielding isomers approximately releases the same heats.
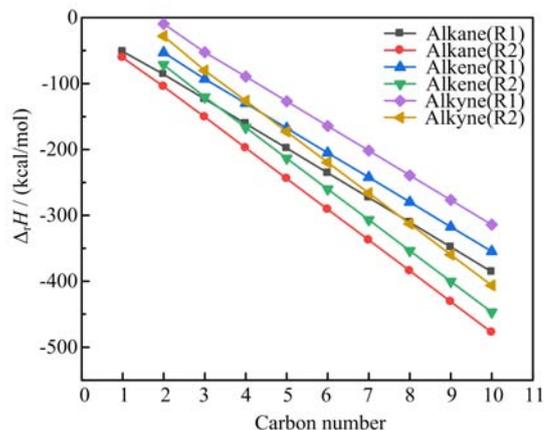
Because $\Delta_{\mathrm{r}}H$ does not change much with temperature, we chose 600 K, a typical temperature for FTS, to study the trends in $\Delta_{\mathrm{r}}H$s in detail. In FIG. 2, the variation of $\Delta_{\mathrm{r}}H$ with respect to the carbon number of normal alkanes, alkenes and alkynes are plotted. FIG. 2 shows that $\Delta_{\mathrm{r}}H$ becomes more negative when carbon number increases, indicating that yielding heavier molecule releases more heats. For the same product, $\Delta_{\mathrm{r}}H$(R2) is more negative than $\Delta_{\mathrm{r}}H$(R1) because WGS is a heat releasing process. For both reactions, the amount of released heat has a decreasing order of alkane>alkene>alkyne, implying that producing more saturated products releases more heats.

2. Oxygen containing compounds

In FIG. 3, the dependence of $\Delta_{\mathrm{r}}H$ of some oxygen containing compounds on carbon number is plotted. Compared to hydrocarbons, yielding an oxygenated product releases less heats than yielding a hydrocarbon with the same carbon number. FIG. 3 shows that $\Delta_{\mathrm{r}}H$ also becomes more negative when the carbon number

TABLE I $\Delta_r H$(R1) and $\Delta_r H$(R2) (in kcal/mol) of some aromatic hydrocarbons (C_6-C_{10}) at 600 K.

Molecular	Name	$\Delta_r H$(R1)	$\Delta_r H$(R2)
C_6H_6	benzene	−173.32	−228.56
C_7H_8	toluene	−213.56	−278.02
C_8H_{10}	ethylbenzene	−251.21	−324.87
	o-xylene	−253.92	−327.58
	m-xylene	−253.73	−327.40
	p-xylene	−253.54	−327.20
C_9H_{12}	propylbenzene	−288.96	−371.83
	isopropylbenzene	−290.13	−373.00
	1,2,3-trimethylbenzene	−292.94	−375.81
	1,2,4-trimethylbenzene	−294.00	−376.87
	1,3,5-trimethylbenzene	−293.95	−376.82
$C_{10}H_{14}$	butylbenzene	−326.49	−418.57
	isobutylbenzene	−328.01	−420.09
	sec-butylbenzene	−327.25	−419.33
	$tert$-butylbenzene	−328.98	−421.06
	1,2,3,4-tetramethylbenzene	−331.51	−423.59
	1,2,3,5-tetramethylbenzene	−332.96	−425.04
	1,2,4,5-tetramethylbenzene	−326.79	−418.87

increases. For the same product, $\Delta_r H$(R2) is also more negative than $\Delta_r H$(R1). Yielding alcohol is the most exothermic and yielding ester is the least exothermic.

3. Aromatics

$\Delta_r H$ values of some important aromatic hydrocarbons are listed in Table 1. Similar trends as those for alkanes, alkenes, alkynes, and oxygenated products can be observed except that aromatics have much more negative $\Delta_r H$s because they have more carbon atoms.

B. Gibbs free-energy change ($\Delta_r G$)

The variations of $\Delta_r G$ for reaction R1 ($\Delta_r G$(R1)) and R2 ($\Delta_r G$(R2)) with respect to temperature and pressure for different types of products are plotted in FIG. 4, FIG. 5, and FIG. S1−S7 in supplementary materials. All the plots show that $\Delta_r G$ has a linear relationship with temperature (T) and the natural logarithm of pressure (ln$P$). Generally, heavier products have more negative $\Delta_r G$s than lighter products. Lowering temperature and pressure lead to more negative $\Delta_r G$. This is easy to understand because both reactions are entropy decreasing reactions. However, kinetically, lowering temperature lowers the reaction rate constant. Therefore, what reaction conditions are the most suitable for FTS should take both thermodynamics and kinetics into consideration. In the following, we will not discuss the trends in the $\Delta_r G$s of every types of products in detail. We will mainly focus on the differences.
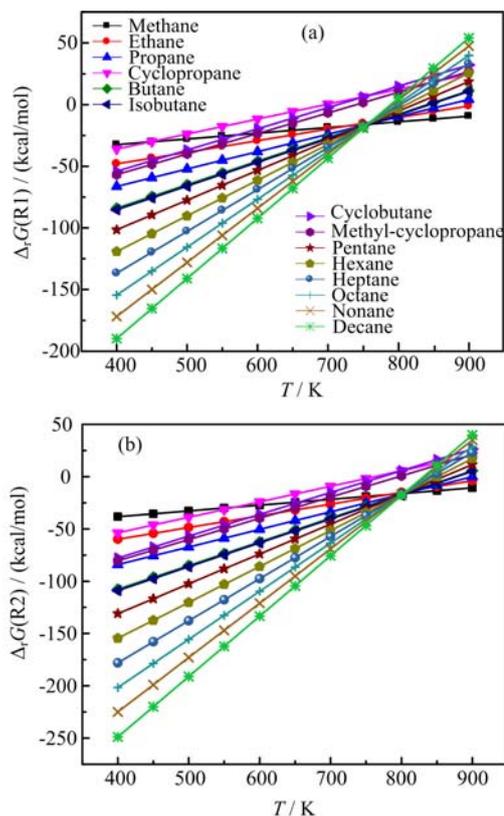
FIG. 4 Temperature dependence of (a) $\Delta_r G$(R1) and (b) $\Delta_r G$(R2) of alkanes and cycloalkanes at 15 atm.

1. Normal alkanes and cycloalkanes

In FIG. 4, the variation of $\Delta_r G$ for reaction R1 ($\Delta_r G$(R1)) and R2 ($\Delta_r G$(R2)) with respect to temperature is plotted for 14 selected alkanes and cycloalkanes, including 10 normal, *i.e.* unbranched alkanes (C_1-C_{10}), a branched alkane (isobutane), and three cycloalkanes (cyclopropane, cyclobutane and methyl-cyclopropane). For the two kinds of plots, the pressure was fixed to 15 atm.

FIG. 4 shows that $\Delta_r G$(R1) and $\Delta_r G$(R2) are negative below 700 K and 750 K, respectively, at 15 atm. This indicates that yielding these products are thermodynamically favorable below these two temperatures. Above 900 K, only some alkanes of low carbon number, such as methane, ethane and propane, are thermodynamically favorable. The plots also show that $\Delta_r G$ has a linear relationship with temperature. For normal alkanes the linear lines crossed at 750 K and 800 K for the R1 and R2 reactions, respectively. This is a very interesting phenomenon and a detailed explanation can be found in the supplementary materials. In short, this trend is because that $\Delta_r H$ has a linear relationship with the carbon numbers (indicating the contribution of a -CH$_2$- group is roughly the same for different normal alkanes), and the major contribution to the entropy change ($\Delta_r S$) of R1 and R2 comes from the entropies
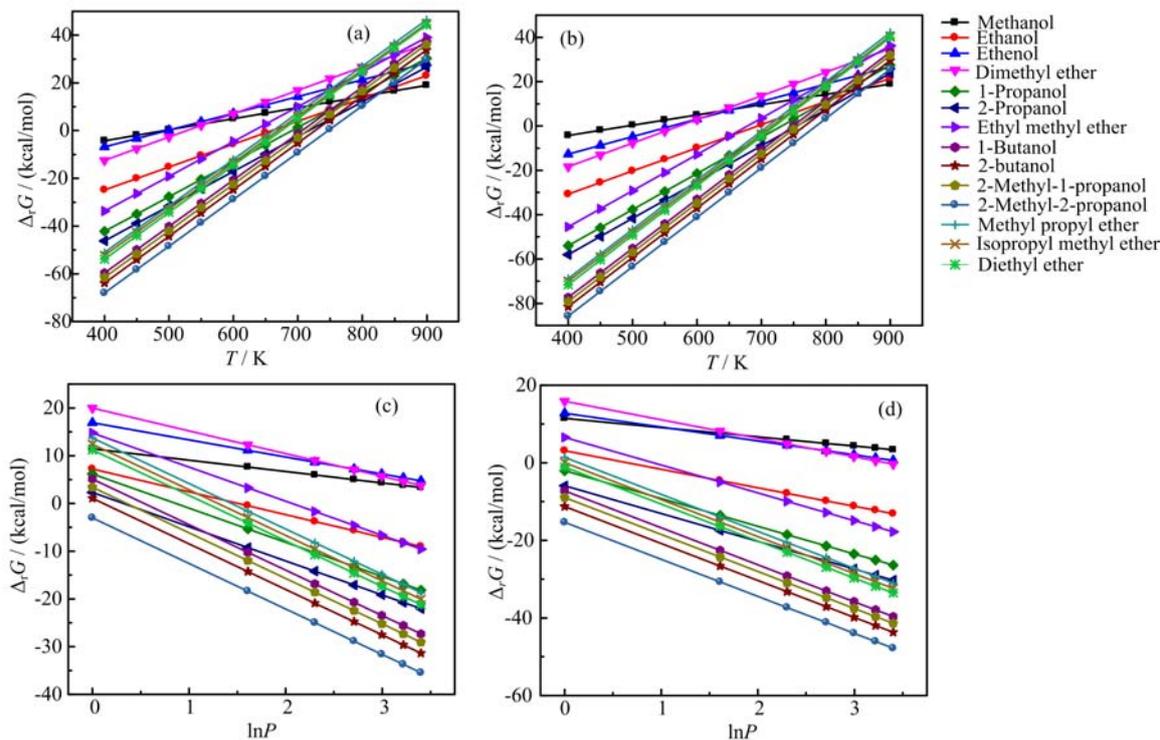
FIG. 5 Temperature ((a, b), at 15 atm) and pressure ((c, d), at 600 K) dependence of $\Delta_{\mathrm{r}}G(\mathrm{R1})$ and $\Delta_{\mathrm{r}}G(\mathrm{R2})$ of alcohols and ethers.

of the CO, H_2, and CO_2/H_2O molecules which also has a linear relationship with respect to the carbon numbers. Below the crossing temperatures, heavier alkanes are thermodynamically more favorable than lighter alkanes. Above the crossing temperatures, lighter alkanes are thermodynamically more favorable than heavier alkanes. The results indicate that product distribution can be adjusted by temperature. For cycloalkanes, their $\Delta_{\mathrm{r}}G$s are generally higher than those of normal alkanes and are thus thermodynamically less favorable. The agreement with experiment that cycloalkanes are seldom observed in FTS indicates that thermodynamics does play an important role in the product distribution.

We can also discuss the trends in $\Delta_{\mathrm{r}}G$s per carbon atom ($\Delta_{\mathrm{r}}G(\mathrm{per\ C})$). The plots (FIG. S2, supplementary materials) show that the $\Delta_{\mathrm{r}}G(\mathrm{per\ C})$ *vs.* T lines do not cross. On the other hand, they parallel to each other. The trends are still similar that $\Delta_{\mathrm{r}}G(\mathrm{per\ C})$ decreases when temperature decreases and pressure increases. However, on a per carbon atom basis lighter alkanes have more negative $\Delta_{\mathrm{r}}G(\mathrm{per\ C})$s than heavier alkanes for normal alkanes.

2. Alkenes and alkandienes

Generally, less saturated products are thermodynamically less favorable: alkenes have higher $\Delta_{\mathrm{r}}G$s than alkanes and cycloalkanes, and alkandienes have higher $\Delta_{\mathrm{r}}G$s than alkenes. Like alkanes, for normal alkenes the linear $\Delta_{\mathrm{r}}G$ *vs.* T lines have crosses at 750 K and 800 K,

for the R1 and R2 reactions, respectively (FIG. S3 in supplementary materials). Heavier products are thermodynamically more favorable than lighter ones below the crossing temperature and *vice versa* above the crossing temperature. The reason for the crossing is similar to that of the normal alkanes (see supplementary materials for details).

The trends in $\Delta_{\mathrm{r}}G(\mathrm{per\ C})$ are similar to those of alkanes (FIG. S4 in supplementary materials) that the $\Delta_{\mathrm{r}}G(\mathrm{per\ C})$ *vs.* T lines are almost parallel to each other and do not cross at a certain temperature. The difference is that for normal alkenes, $\Delta_{\mathrm{r}}G(\mathrm{per\ C})$ of the lighter alkene is more positive than that of the heavier one.

3. Alcohols and ethers

In FIG. 5, the variations of $\Delta_{\mathrm{r}}G(\mathrm{R1})$ and $\Delta_{\mathrm{r}}G(\mathrm{R2})$ with respect to temperature and pressure are plotted for 14 selected alcohols and ethers. FIG. 5 (a) and (b) show that at 15 atm, methanol, ethenol and dimethyl ether can only be thermodynamically favorable at low temperatures. FIG. 5 (c) and (d) show that at 600 K, a typical FTS temperature, all the $\Delta_{\mathrm{r}}G$ values for the three products are positive from 1 atm to 30 atm. These results indicate that in the FTS process, it is thermodynamically difficult to obtain high yields for the three products at 600 K. FIG. 5 shows that $\Delta_{\mathrm{r}}G$s of ethers are less negative than those of alcohols with the same

number of carbon atoms, indicating that alcohols are thermodynamically more favorable than ethers.

4. Aldehydes and ketones

The plots of $\Delta_r G$ *vs.* T and $\ln P$ (FIG. S5 in supplementary materials) show that formaldehyde and ketene are thermodynamically difficult to produce in the FTS process because at 15 atm most $\Delta_r G$ values are positive from 400 K to 900 K and at 600 K all the $\Delta_r G$ values are positive from 1 atm to 30 atm. In addition, ketones are thermodynamically less favorable than aldehydes with the same number of carbon atoms.

5. Carboxylic acids and esters

The plots of $\Delta_r G$ *vs.* T and $\ln P$ (FIG. S6 in supplementary materials) show that formic acid and methyl formate are thermodynamically difficult to produce because of the positive $\Delta_r G$ values. Esters are thermodynamically less favorable than carboxylic acids with the same carbon number.

6. Aromatic hydrocarbons

All $\Delta_r G$ values for aromatic hydrocarbons are negative below 800 K at 15 atm or with pressure higher than 1 atm at 600 K (FIG. S7 in supplementary materials). Benzene, with the least carbon atoms, is always thermodynamically more difficult to produce than other aromatic hydrocarbons below 800 K.

7. Fitting of $\Delta_r H$ and $\Delta_r G$

The plots of $\Delta_r H$ and $\Delta_r G$ *vs.* T or $\ln P$ show that $\Delta_r H$ and $\Delta_r G$ have a liner relationship with T and $\Delta_r G$ has a linear relationship with $\ln P$. $\Delta_r H$ and $\Delta_r G$ can be well fitted by Eq.(3) and Eq.(4), respectively.

$$\Delta_r H = aT + b \tag{3}$$
$$\Delta_r G = cT\ln P + d\ln P + eT + f \tag{4}$$

The fitting parameters a, b, c, d, e, and f were fitted for reaction R1 and R2 respectively for each product. These fitting parameters are available in Table S3 and Table S4 for 241 stable products in the FTS process. Designing proper thermodynamic cycle, $\Delta_r H$ and $\Delta_r G$ values for the other products can be obtained as well. These data can be used to estimate the reaction thermodynamic quantities under any reaction condition.

C. Equilibrium product yields in FTS

1. General analysis

From the $\Delta_r G$ values equilibrium product yields can be calculated (see supplementary materials for details).

In general, the yields are functions of temperature, pressure, and H_2/CO ratio. These data can be used to identify possible products in the FTS process because if the yield of a product is very low, it may not be a possible product. These data can also be used to help the experiment to design possible reaction mechanism for the highly selective production of lower olefins or aromatics from syngas in one-step using bi-functional composite catalysts [20−22, 32]. In these reaction processes, the metal oxides and zeolites were physically mixed. Transient intermediates produced from the hydrogenation of CO on the metal oxides entered the zeolite channels and from there lower olefins or aromatics were produced. These transient intermediates should not be too stable. Because if they are too stable, it is thermodynamically unfavorable for them to transfer into target products. On the other hand, they should not be too unstable because of two reasons. First, the metal oxides and zeolites are separated in space and before entering the zeolite channels they must diffuse for some distances. If they are too unstable, they may have transformed to other more stable intermediates before entering the zeolite channels. Second, if they are too unstable, their yields would be very low and therefore their concentration in the zeolite channels would be very low. This would lead to low yields of target products. Experimental evidences indicate that the carbon atoms in these transient intermediates may not be more than four. This can be understood from thermodynamic considerations because our thermodynamic results show that products with higher carbon number will generally be more stable. Therefore, intermediates with more than four carbon atoms may be too stable to serve as a possible transient intermediate. Therefore, we focus our discussion on the yields of those C_1-C_4 products. We somewhat set three arbitrary boundaries for product yields: 1%, 10%, and 99%. If the yield of a product is higher than 10%, this product is deemed as a main product in FTS. If the yield is between 1% and 99%, this product is deemed as a possible transient intermediate in the highly selective production of aromatics or lower hydrocarbons from syngas catalyzed by bi-functional composite catalysts. Because in these processes a high yield of CO_2 (usually higher than 40%) is obtained, in Table II only the number of possible intermediates out of 1229 C_1-C_4 products of reaction R2 is listed under various reaction conditions. The number of main products is listed in Table S5 in supplementary materials.

Results in Table II show that because $\Delta_r G$ becomes more positive when raising temperature and lowering pressure, the number of possible intermediates decreases when raising temperature and lowering pressure. With the same temperature and pressure, the number of possible intermediates decreases when raising H_2/CO ratio. The same trends can be observed for the number of main products (Table S5 in supplementary materials). When the temperature is as high as 800 K, the

TABLE II The number of possible intermediates of reaction R2 in FTS at different temperature, pressure, and H_2/CO ratio.

H_2/CO	T/K	Intermediates number		
		P=1 atm	P=2 atm	P=3 atm
1:1	400	365	515	596
	600	103	389	530
	800	11	114	281
2:1	400	308	438	561
	600	112	401	523
	800	11	121	305
3:1	400	278	396	499
	600	103	364	472
	800	11	117	312

pressure is as low as 1 atm, and the H_2/CO ratio is 1:1, only 11 possible intermediates and 17 main products are thermodynamically allowed. Therefore, in thermodynamics raising temperature and lowering pressure will raise the product selectivity. According to our analysis on $\Delta_r G$s, this leads to higher selectivity to lighter products such as methane. Thermodynamically, lowering temperature and raising pressure lead to heavier products. However, the product range becomes wider. These results can also help us to exclude some reaction paths or intermediates. We need to design only reaction paths containing those intermediates with a non-negligible yield.

2. Normal C_1−C_5 hydrocarbons

C_1−C_5 alkanes and alkenes are the most desirable products in FTS, especially C_2−C_4 alkenes. Therefore, in the following we discuss the trends in the yields of C_1−C_5 normal alkanes and alkenes. In FIG. 6, the temperature, pressure, and H_2/CO ratio dependences of the yields of C_1−C_5 hydrocarbons are plotted. Comparing FIGs. 6 (a) with (b), (c) with (d), and (e) with (f), we can see that the product yield of R2 is often higher than that of R1 for the same product. In addition, all normal C_1−C_5 hydrocarbons can achieve their maximum yield, *i.e.* 100% under proper conditions: low temperature, high pressure, and high H_2/CO ratio.

FIG. 6 (a) and (b) show that the product yields all decrease when raising temperature because $\Delta_r G$ rises. Except for ethene, for both reactions the less carbon atoms a product has, the slower the yield decreases. For example, the decrease in the yield of CH_4 does not exceed 2% from 400 K to 900 K for both R1 and R2 reactions. On the other hand, for pentane and 1-pentene, the yields decrease by more than 25% and 10% for R1 and R2, respectively, from 400 K to 900 K. This is because the heavier a hydrocarbon is, the higher the entropy loss for the FTS process is. As a result, for both

normal alkanes (FIG. 4) and alkenes (FIG. S3 in supplementary materials) the $\Delta_r G$ value for a product with more carbon atoms rises faster than that for a product with less carbon atoms when raising temperature. For the R1 reaction (FIG. 6(a)) below 800 K, the more carbon atoms a product has, the lower the product yield. On the other hand, at 900 K, pentane even has lower yield than ethane. For R2, except for ethene that has the lowest yield over the whole temperature range, the less carbon atoms a product has, the higher the product yield is for the other products.

FIG. 6(a) shows that below 700 K alkenes always have higher yields than alkanes. However, the yields of alkenes decrease faster than those of alkanes. Above 700 K, the yields of some alkenes are even lower than those of alkanes. At 900 K, the yield of ethene is even lower than those of all the alkanes. This implies that thermodynamically if more alkenes are wanted through the R1 reaction, the reaction temperature should be low. On the other hand, if more alkanes are wanted, the reaction temperature should be high. FIG. 6(b) shows that the yields of alkenes and alkanes are all close to 100% below 600 K for the R2 reaction. This implies that thermodynamically a mixture of all alkanes and alkenes can be obtained below 600 K. Therefore, controlling product selectivity can only be realized through controlling kinetic factors below 600 K. On the other hand, product yields separate wider above 600 K, implying that the products are thermodynamically more selective above 600 K, with alkanes always having higher yields than alkenes. Recently, Bao and coworkers achieved a selectivity higher than 80% for C_2−C_4 olefins at 673 K [20]. Our results show that it must be a kinetic factor that governs there.

FIG. 6 (c) and (d) show that for both reactions product yields increase with increasing pressure. The less carbon atoms a product has, the faster its yield increases. This is because that heavier product has higher entropy loss for the FTS process. Therefore, if heavier products are wanted, the reaction pressure should be high. For R1 at low pressures such as 1 atm, an alkene product has lower yield than an alkane with the same carbon atoms. On the other hand, at high pressures the trend reverses and alkenes always have higher yields than alkanes above 5 atm. For R2 below 5 atm, alkanes always have higher yields than alkenes. Above 5 atm, the yields of all alkanes and alkenes are close to 100%. This implies that thermodynamically a mixture of all kinds of alkanes and alkenes can be obtained above 5 atm. High selectivity of target product can only be realized through adjusting kinetic factors through the R2 reaction.

FIG. 6 (e) and (f) show that all the product yields increase when raising the H_2/CO ratio. At high H_2/CO ratio, ≥3 for R1 or ≥1 for R2, the product yields are all close to 100% (at 600 K and 15 atm). This implies that thermodynamically a mixture of all kinds of alkanes and alkenes can be obtained under such reaction conditions.
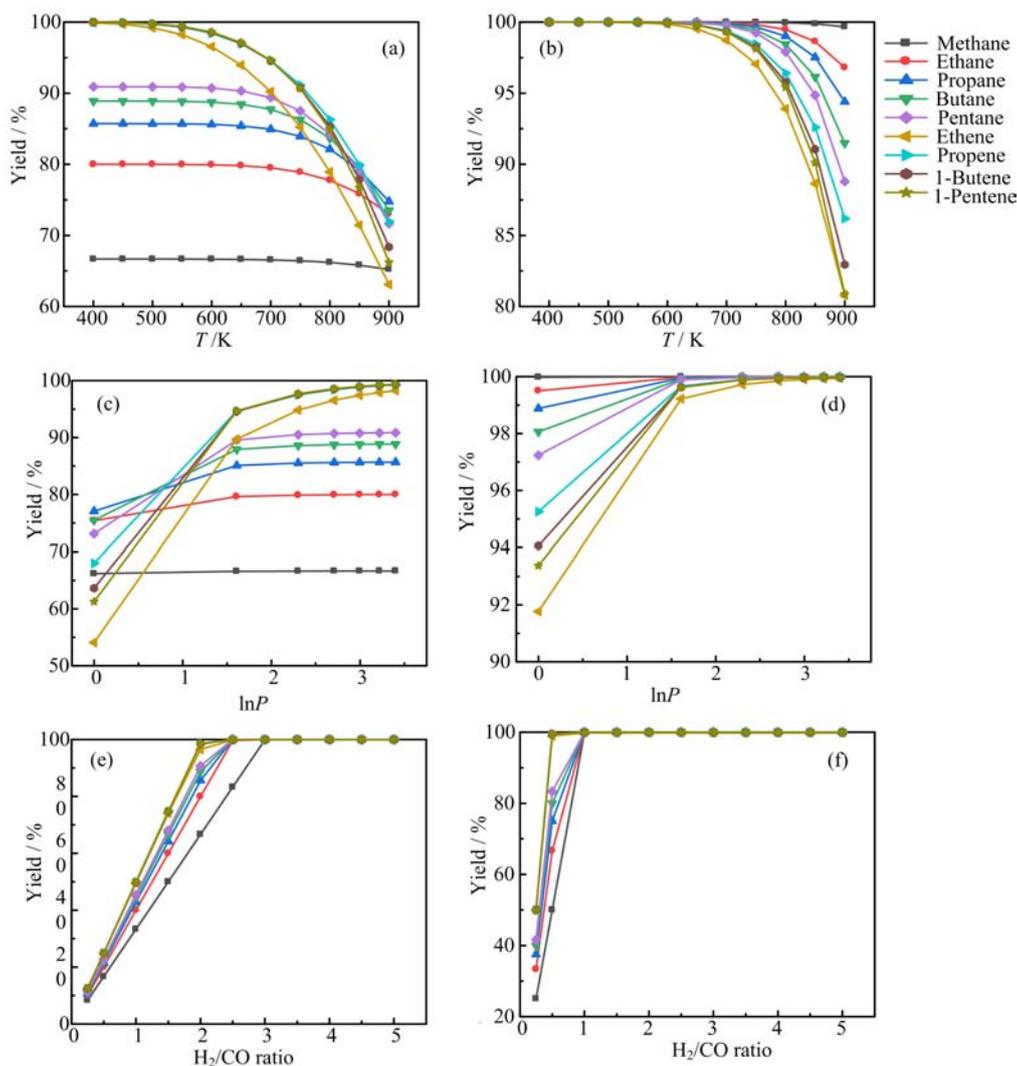
FIG. 6 Temperature ((a) for R1 and (b) for R2, with pressure fixed to 15 atm and H_2/CO ratio fixed to 2:1), pressure ((c) for R1 and (d) for R2, with temperature fixed to 600 K and H_2/CO ratio fixed to 2:1), and H_2/CO ratio ((e) for R1 and (d) for R2, with temperature fixed to 600 K and pressure fixed to 15 atm) dependence of the yields of normal C_1-C_5 hydrocarbons.

Therefore, if we want the reaction to be more selective, we can decrease the H_2/CO ratio.

In experiment, it is desired to obtain high olefin yield. Lu *et al.* [32] studied the olefin/paraffin ratios for short-chain hydrocarbons (C_2-C_5) on the metal catalysts and they found that the olefin/paraffin ratios became less than 1 when the reaction was steady at 483 K. According to our results, at such low reaction temperature, the equilibrium olefin/paraffin ratio should be greater than 1. This indicates that in their experiment it is a kinetic factor that governs the olefin/paraffin ratio. This is because that their experiment was performed at 483 K, and our results show that at such low reaction temperature most thermodynamically alkanes and alkenes can reach their maximum equilibrium yields. Therefore, it is the kinetic factors that affect the product distribution. In fact, to gain high selectivity of olefin, the FTS

process was always performed at a temperature range of 650−700 K and a pressure range of 10−25 atm in experiments [20−22]. This is in accordance with our finding that for R1 below 700 K and above 5 atm, alkenes have higher yields than alkenes. Besides, the H_2/CO ratio is also an important reaction condition and researchers always used a ratio of 2.0−2.5 [20−22]. This is in accordance with our results because the product yields would become lower if the H_2/CO ratio is below 2.

3. Oxygen containing compounds

Oxygenated products are suggested as possible intermediates in the highly selective production of lower olefins or aromatics from syngas in one-step using bifunctional composite catalysts [20−22, 24]. In FIG. 7,
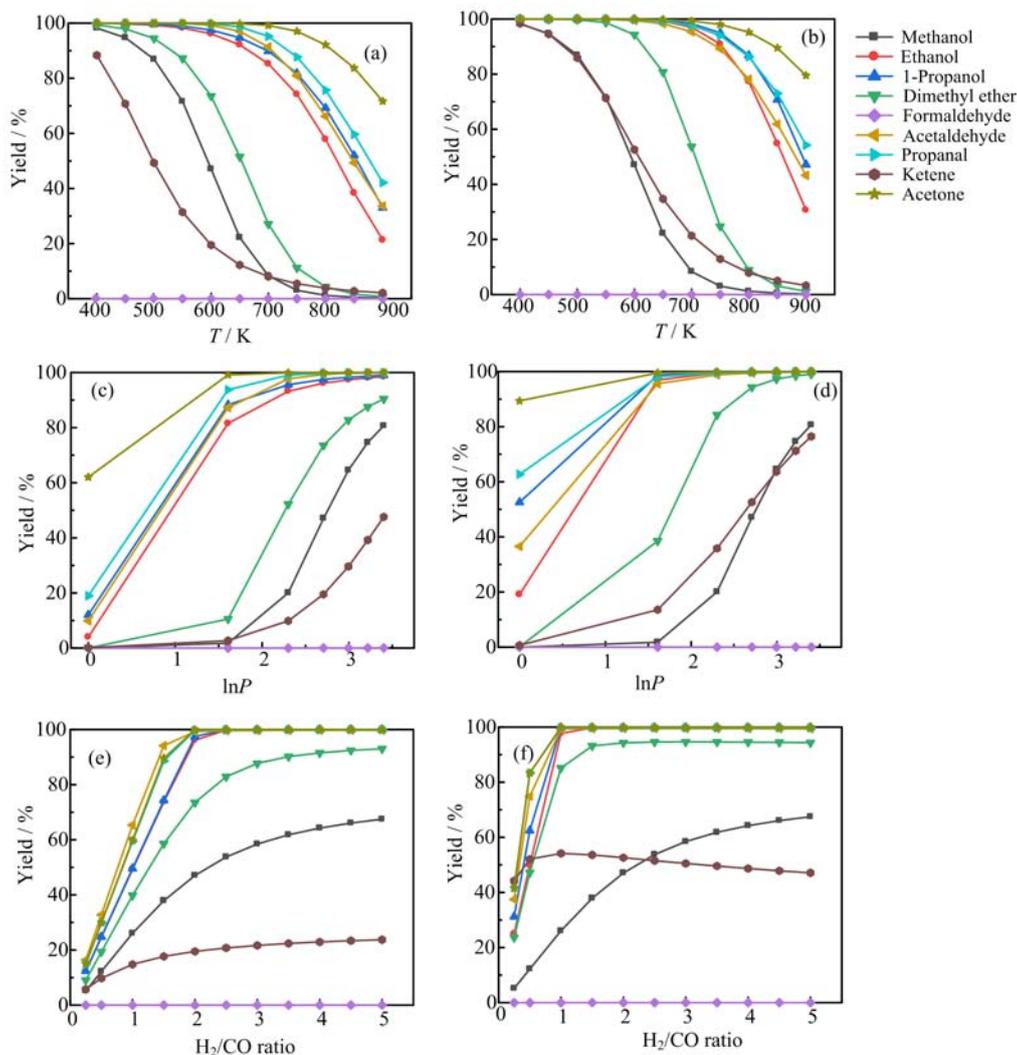
FIG. 7 Temperature ((a) for R1 and (b) for R2, with pressure fixed to 15 atm and H_2/CO ratio fixed to 2:1), pressure ((c) for R1 and (d) for R2, with temperature fixed to 600 K and H_2/CO ratio fixed to 2:1), and H_2/CO ratio ((e) for R1 and (d) for R2, with temperature fixed to 600 K and pressure fixed to 15 atm) dependence of the yields of oxygen containing compounds.

the temperature, pressure, and H_2/CO ratio dependence of the yields of nine oxygen containing compounds are plotted. The plots show that the product yields all decrease when raising temperature (FIG. 7 (a) and (b)) and increase when raising pressure (FIG. 7 (c) and (d)) and H_2/CO ratio increases (FIG. 7 (e) and (f)). Under all reaction conditions, formaldehyde has the lowest yield and its yield is always close to zero. On the other hand, acetone has the highest yield and its yield is close to 100% over a wide range of reaction conditions. FIG. 7 shows that except formaldehyde, the yields of other oxygen containing compounds are higher than zero unless the temperature is very high, or the pressure is very low. This implies that formaldehyde is neither a possible product in the FTS process nor a possible intermediate in the highly selective production of lower olefins or aromatics from syngas using

bi-functional composite catalysts. In the reaction mechanism study of the FTS process, reaction paths through formaldehyde should be avoided.

In the highly selective production of lower olefins from syngas, ketene was suggested as the possible intermediate produced on the metal oxide surface that entered the zeolite channel to produce C_2-C_4 hydrocarbons [20]. From our thermodynamic results, this is possible because under the best experimental reaction conditions (673 K, 25 atm, and $H_2/CO=2.5$), ketene has an equilibrium yield of 16%. In the one-step production of aromatic hydrocarbons using bi-functional composite catalysts, there are several guesses for the possible intermediates, such as methanol and dimethyl ether [22−24, 31]. From thermodynamic results, this is also possible unless the reaction temperature is very high (FIG. 7(b)), or the pressure is very low (FIG. 7(d)).

In experiment, Zhou *et al.* prepared methyl acetate, ethanol and ethylene by FTS under reaction conditions of 643 K, 30 atm, and H_2/CO ratio of 1 [31]. As shown in FIG. 7 (a) and (b), to prepare oxygen containing compounds, reaction temperature should not be too high. 650 K is perhaps a compromise between yield and reaction rate. As shown in FIG. 7 (c) and (d), high yields of oxygen containing compounds can only be obtained under high pressure. This is in accordance with the high pressure of 30 atm in the experiment of Zhou *et al.* However, our results show that there is still room to improve the yields of oxygen containing compounds because higher yields can be obtained with H_2/CO ratio higher than 1.

4. Aromatic hydrocarbons

Aromatic hydrocarbons are important chemical raw materials, especially BTX. Similar trends in the product yields (FIG. S8 in supplementary materials) to those for the normal C_1-C_5 hydrocarbons and oxygen containing compounds can also be found, *i.e.* the product yields all decrease when raising temperature and lowering pressure and H_2/CO ratio. Except at high temperature (>700 K), low pressure, or low H_2/CO ratio, their equilibrium yields are always close to 100% due to the very negative $\Delta_r G$ values (FIG. S7 in supplementary materials). Therefore, thermodynamically if we want the reaction to be more selective instead of obtaining a mixture of all kinds of aromatic hydrocarbons, we can raise the reaction temperature, lower the pressure, and use a low H_2/CO ratio.

IV. CONCLUSION

In this work, the thermodynamic properties of 1287 possible reaction products in the Fischer-Tropsch synthesis (FTS) process have been systematically investigated. From these results, enthalpy changes ($\Delta_r H$s) and Gibbs free-energy changes ($\Delta_r G$s) of the reactions to produce these products were computed. From $\Delta_r G$s their equilibrium yields were calculated. The results show that over the temperature range of $400-900$ K, almost all the FTS reactions are exothermic and $\Delta_r H$ has a linear relationship with temperature T (Eq.(3)). Producing oxygen containing compounds releases less heats than producing compounds without oxygen. Reactions producing more saturated products are more exothermic: $\Delta_r H$s have an ascending order of alkanes, alkenes, and alkynes.

Over the temperature range of $400-900$ K and the pressure (P) range of $1-30$ atm, which are possible reaction conditions for FTS, $\Delta_r G$ has a linear relationship with T and $\ln P$ and can be fitted with Eq.(4). When lowering temperature and raising pressure, $\Delta_r G$ becomes more negative. $\Delta_r G$ becomes more negative if

the product is heavier, or has lower degree of unsaturation, or contains less oxygen atoms.

The analysis on the equilibrium yields can help the experiment to optimize reaction conditions. The results show that the equilibrium yields reach maximum and remain unchanged when lowering temperature, raising pressure, and raising H_2/CO ratio to some limits, implying that optimizing reaction conditions have no effect on equilibrium product yields beyond these limits. The results also show that reaction conditions have a huge impact on product distribution. The number of the thermodynamically allowed products decreases, *i.e.* product selectivity increases, when raising temperature, lowering pressure, and lowering H_2/CO ratio. At high temperature, low pressure, and low H_2/CO ratio, the FTS process yields more lighter products. At low temperature, high pressure, and high H_2/CO ratio, many thermodynamically possible products can be produced. To increase the selectivity of a desired product under these reaction conditions, kinetic factors must be considered. Our results agree with experimental results that the reaction temperature should generally be controlled in the range of $600-700$ K, a compromise of high product yield and high reaction rate. Pressure and H_2/CO ratio also have a huge impact on the product yield and distribution and should be carefully controlled.

The analysis on the equilibrium yields can also help the experiment to design more plausible reaction mechanisms. The analysis shows that ketene is a possible intermediate in the highly selective production of low olefins from syngas using bi-functional composite catalysts. The analysis also shows that methanol and dimethyl ether are possible intermediates in the direct production of aromatics from syngas in one step using bi-functional composite catalysis. When designing reaction mechanism for the FTS process, reaction paths through formaldehyde should be avoided.

Supplementary materials: Correction schemes for the energies of H_2, H_2O, CO and CO_2 at 0 K, equilibrium product yields, and a detailed explanation of the cross of $\Delta_r G$ *vs.* T lines are available.

V. ACKNOWLEDGMENTS

[1] S. Abelló and D. Montané, Chemsuschem **4**, 1538 (2011).
[2] J. Z. Lu, L. J. Yang, B. L. Xu, Q. Wu, D. Zhang, S. J. Yuan, Y. Zhai, X. Z. Wang, Y. N. Fan, and Z. Hu, ACS Catal. **4**, 613 (2014).

[3] V. U. S. Rao, G. J. Stiegel, G. J. Cinquegrane, and R. D. Srivastava, Fuel Process. Technol. **30**, 83 (1992).

[4] H. Schulz, Appl. Catal. A **186**, 3 (1999).

[5] Y. Sun, J. Chen, J. Wang, L. Jia, B. Hou, D. Li, and J. Zhang, Chin. J. Catal. **31**,919 (2010).

[6] N. E. Tsakoumis, M. Rønning, Ø. Borg, E. Rytter, and A. Holmen, Catal. **31**, Today **154**, 162 (2010).

[7] B. Buragohain, P. Mahanta, and V. S. Moholkar, Energy **35**, 2557 (2010).

[8] Ø. Borg, N. Hammer, B. C. Enger, R. Myrstad, O. A. Lindvåg, S. Eri, T. H. Skagseth, and E. Rytter, J. Catal. **279**, 163 (2011).

[9] K. Jothimurugesan, J. G. Goodwin Jr., S. K. Gangwal, and J. J. Spivey, Catal. Today **58**, 335 (2000).

[10] N. Lohitharn, J. G. Goodwin Jr., and E. Lotero, J. Catal. **255**, 104 (2008).

[11] X. Q. Gong, R. Raval, and P. Hu, J. Chem. Phys. **122**, 024711 (2005).

[12] J. M. Wu, Q. W. Sun, T. F. Gao, J. P. Yue, and L. F. Pang, Chem. Eng. **40**, 30 (2012).

[13] I. Y. Zhang and X. Xu, Chemphyschem **13**, 1486 (2012).

[14] R. B. Anderson, C. B. Lee, and J. C. Machiels, Can. J. Chem. Eng. **54**, 590 (1976).

[15] D. F. Smith, Ind. Eng. Chem. **19**, 801 (1927).

[16] G. W. Norval, Can. J. Chem. Eng. **86**, 1062 (2008).

[17] G. W. Norval and M. J. Phillips, J. Catal. **126**, 87 (1990).

[18] K. Rajagopal, V. R. Ahón, and E. Moreno, Catal. Today **109**, 195 (2005).

[19] H. Lubarsky, I. Polishuk, and D. NguyenHuynh, J. Supercrit. Fluids **110**, 11 (2016).

[20] F. Jiao, J. J. Li, X. L. Pan, J. P. Xiao, H. B. Li, H. Ma, M. M. Wei, Y. Pan, Z. Y. Zhou, M. R. Li, S. Miao, J. Li, Y. F. Zhu, D. Xiao, T. He, J. H. Yang, F. Qi, Q. Fu, and X. H. Bao, Science **351**, 1065 (2016).

[21] Y. F. Zhu, X. L. Pan, F. Jiao, J. Li, J. H. Yang, M. Z. Ding, Y. Han, Z. Liu, and X. H. Bao, ACS Catal. **7**, 2800 (2017).

[22] K. Cheng, B. Gu, X. L. Liu, J. C. Kang, Q. H. Zhang, and Y. Wang, Angew. Chem. Int. Ed. **128**, 4803 (2016).

[23] K. Cheng, W. Zhou, J. C. Kang, S. He, S. L. Shi, Q. H. Zhang, Y. Pan, W. Wen, and Y. Wang, Chem **3**, 334

[24] Z. Huang, S. Wang, F. Qin, L. Huang, Y. H. Yue, W. M. Hua, M. H. Qiao, H. Y. He, W. Shen, and H. L. Xu, ChemCatChem **10**, 4519 (2018).

[25] L. A. Curtiss, P. C. Redfern, and K. Raghavachari, WIREs Comput. Mol. Sci. **1**, 810 (2011).

[26] M. M. Ghahremanpour, P. J. van Maaren, J. C. Ditz, R. Lindh, and D. van der Spoel, J. Chem. Phys. **145**, 114305 (2016).

[27] A. Karton, E. Rabinovich, J. M. L. Martin, and B. Ruscic, J. Chem. Phys. **125**, 144108 (2006).

[28] A. Karton, N. Sylvetsky, and J. M. L. Martin, J. Comput. Chem. **38**, 2063 (2017).

[29] X. M. Duan, G. L. Song, Z. H. Li, X. J. Wang, G. H. Chen, and K. N. Fan, J. Chem. Phys. **121**, 7086 (2004).

[30] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, J. M. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian 09, Revision A.02*, Wallingford CT: Gaussian, Inc., (2009).

[31] W. Zhou, J. C. Kang, K. Cheng, S. He, J. Q. Shi, C. Zhou, Q. H. Zhang, J. C. Chen, L. M. Peng, M. S. Chen, and Y. Wang, Angew. Chem. Int. Ed. **57**, 12012 (2018).

[32] X. J. Lu, D. Hildebrandt, X. Y. Liu, and D. Glasser, Ind. Eng. Chem. Res. **51**, 16544 (2012).