Journal of Natural Gas Chemistry 论文中文摘要

甲烷在Mo/HZSM-5催化剂上的无氧转化 —在隔离活性位上的反应 (Methane Conversion over Mo/HZSM-5 Catalysts without Adding O_2 — A Reaction on Remotely Separated Active Sites) / 王志龙，刘 薇，舒玉瑛，王林胜，徐奕德 (中国科学院大连化学物理研究所催化重点实验室 辽宁 大连 116023) // *J.Nat.Gas Chem.*, **8**(1999)267

摘 要 报道了无氧条件下甲烷在Mo/HZSM-5催化剂上转化为高碳的碳氢化合物的新途径。主要产物苯是经由乙烯聚合而成。此反应可能在两个隔离活性位上进行。乙烯作为甲烷活化的初始产物主要在分子筛外表面Mo活性位上形成，芳烃在分子筛的孔道内B酸位上形成。因此，我们认为该过程是乙烯中间产物由外表面扩散到分子筛孔道内形成芳烃。

关键词 甲烷转化 Mo/HZSM-5 中间物扩散

直接合成二甲醚的新型双功能催化剂(New Bifunctional Catalyst for Direct Synthesis of Dimethyl Ether) / 葛庆杰，黄友梅，邱凤炎，张传卫(中国科学院兰州化学物理研究所 甘肃 兰州 730000) // *J.Nat.Gas Chem.*, **8**(1999)280

摘 要 采用共沉淀沉积法制备的Cu-ZnO-ZrO_2/HZSM-5系列双功能催化剂具有优异的从合成气直接制二甲醚的催化性能。其中Mg-(Cu-ZnO-ZrO_2)/V-HZSM-5表现出最佳的催化活性和选择性，CO转化率达91.4%，二甲醚选择性为84.6%。此外，Cu-ZnO-ZrO_2/HZSM-5催化剂也表现出优良的CO_2加氢性能，CO_2转化率可达35%，二甲醚选择性为60.1%。

关键词 二甲醚直接合成 合成气 二氧化碳加氢 双功能催化剂

铜基催化剂催化合成气一步合成甲醇和甲酸甲酯 III. 催化剂和助催化剂浓度的影响(Concurrent Synthesis of Methanol and Methyl Formate Catalyzed by Copper-Based Catalysts III. Influences of Concentrations of Catalysts and Promoters) / 刘兴泉，陈文凯，吴玉塘，贯朝霞，罗世忠，李顺芬，杨迎春，于作龙(中国科学院成都有机化学研究所 四川 成都 610041) // *J.Nat.Gas Chem.*, **8**(1999)286

摘 要 在低温低压条件下，采用铜基催化剂和浆态多相催化反应，考察了从合成气一步同时合成甲醇和甲酸甲酯的反应以及催化剂和助催化剂浓度对催化活性和甲酸甲酯选择性的影响。实验结果表明，在实验范围内，催化剂的催化活性随催化剂和助催化剂浓度的增加而有规律的增大，甲酸甲酯选择性随催化剂浓度的增加而降低，但随甲醇钠助催化剂浓度的增加而增高。

关键词 甲醇 甲酸甲酯 铜基催化剂 助催化剂 合成气 铬 锰

在Raney Fe催化剂上F-T合成产物的分布和选择性(Carbon Number Distribution and Selectivity of Slurry F-T Product over Raney Fe) / 吕毅军，张志新，周敬来(中国科学院山西煤炭化学研究所 山西 太原 030001) // *J.Nat.Gas Chem.*, **8**(1999)294

摘 要 在浆态相F-T合成的连续搅拌釜反应器中，研究了Raney Fe系列催化剂和其它工业铁基催化剂的性能。结果发现，Raney Fe的前驱体对其性能影响很大。由Al/Fe比为3的合金得到的Raney Fe表现出了良好的活性稳定性，常规条件下CO的转化接近完全，其较大的中孔分布可能对初级产物的扩散限制较小，因而生成的2-烯烃和异构烃就少。也比较分析了催化剂固载量和粒度对Raney Fe上的烷烃选择性的影响。此外，从产物分布的规律来看，在Raney Fe催化剂上以生成高碳数烷烃和低碳数烯烃为主。

关键词 Raney Fe 浆态相F-T合成 烯烷比 碳数分布 扩散限制

催化氢化硝基苯制备对氨基苯酚(Synthesis of *p*-Aminophenol via Hydrogneation of Nitrobenzene over Supported Platinum Catalysts) / 刘竹青，胡爱琳，王公应(中国科学院成都有机化学研究所 四川 成都 610041) // *J.Nat.Gas Chem.*, **8**(1999)305

摘 要 研究了硝基苯催化加氢制备对氨基苯酚的反应。通过实验发现，不同的反应介质、添加剂、载体和催化剂的制备方法对对氨基苯酚的收率有很大的影响。在硫酸介质中两次性加入硝基苯对反应最有利。$AlBr_3$作添加剂时，可以提高目标产物的收率。改性的γ-Al_2O_3作载体时，对氨基苯酚的收率可达74%。

关键词 硝基苯 催化氢化 对氨基苯酚 铂催化剂

CARBON NUMBER DISTRIBUTION AND SELECTIVITY OF SLURRY F-T PRODUCT OVER RANEY Fe

LÜ Yi-Jun ZHANG Zhi-Xin ZHOU Jing-Lai

Institute of Coal Chemistry, The Chinese Academy of Sciences
Taiyuan, Shanxi 030001

Abstract A series of Raney Fe and other common used iron-based catalysts were investigated for the slurry Fischer-Tropsch synthesis in a continuous stirred reactor. It was found that the precursor composition of Raney Fe influenced its performance greatly. Raney Fe prepared from alloy with Al/Fe ratio of 3 exhibited a higher F-T activity and a better stability with almost total conversion of CO under usual conditions. Its macro-pore structure was thought to be contributed to the less diffusion limitations of primary products and then yielded less 2-olefins and isomers. The effects of catalyst loading and particle size on the paraffin selectivity over Raney Fe were studied. From the carbon number distributions it is concluded that much more light hydrocarbons with high olefin content but less high molecular olefins are produced over Raney Fe .

Keywords Raney Fe, slurry F-T synthesis, olefin/paraffin ratio, carbon number distribution, diffusion limitation

Introduction

It is well known that amounts of literature[1~6,8,9] focus on the hydrocarbon product distribution and the selectivity to olefins in the whole products of Fischer-Tropsch synthesis. The apparent reason is that the light olefins are good feedstocks for chemical manufacture, *e.g.* the C_2 and C_3 olefins are the primary feedstocks for polymer and petrochemical products. An effectual improvement of the selectivity to light olefins is greatly dependent on the controlling of the molecular distribution and the secondary hydrogenation of the primary olefins. Thermodynamics analysis indicates that this

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Received June 10, 1998; *revised version received* February 8, 1999

selectivity is restricted by the high productivity of methane, and is also influenced by some by-product reactions such as Boudouard reaction, with temperature rising which is suitable to the high selectivity of light olefins. Since a few studies indicate that the iron-based catalyst is likely to produce more olefins, especially with the effectual promoters such as Mn, someone suggested to control the chain increase by controlling pore size or to decrease the activity of hydrogenation.

Raney Fe is a novel catalyst but is studied less than Raney Ni and other skeleton catalysts, the initial idea for developing this skeleton catalyst is to improve such a difficult condition of separating catalyst particles from the waxes in the slurry F-T synthesis. And its significant catalyst performance comparing with other commonly used catalysts is the higher selectivity to light olefins and lower molecular distribution in hydrocarbon products.

Experimental

Apparatus and procedure

All the tests were carried out in a 1 L continuous stirred tank reactor with the rotation rate above 750 rpm, the well-distributed gas flow equipment kept the process in the kinetic region completely. Syngas with the hydrogen to carbon monoxide ratio of 2.0 was fed to the bottom of the reactor through several nozzles and was allowed to react on the suspended catalyst. The reaction was carried out in the temperature range from 220°C to 280°C, pressure range from 1.2 MPa to 1.8 MPa, weight hollow space velocity range from 0.5 to 2.0 L/(g(Fe)·h), and H_2/CO ratio range from 1.3 to 2.4.

The liquid wax as the reaction slurry medium has an average b.p. of 340°C and a carbon number range of C_{17} to C_{30}. Among all the tested catalysts, the precipitated Fe was prereduced *in situ* while the Fused iron was reduced in the fixed bed reactor at a higher temperature with H_2 flow, but all the Raney Fe catalysts were not reduced before being transported into the slurry system.

Trapping and analysis

The complex product system was collected in two traps. The gasoline was condensed in a trap at room temperature, which has the carbon number from C_4 to C_{20}. The high molecular waxes were collected in a 100°C trap, and a lot of wax was accumulated in the liquid medium. All the high molecular products were analyzed by a capillary GC-9A(FID), the aqueous products were analyzed by GC-7A(FID). The volatile or light hydrocarbons in outlet gas were analyzed by SP-102(TCD) and SP-2305.

Catalyst preparation

The employed catalysts include precipitated Fe, Fused iron and a series of Raney Fe. The precipitated Fe is 506-II from the Institute of Coal Chemistry (ICC) prepared by co-precipitation method; Fused iron is F-007 from ICC prepared by melted magnetite and promoters. Raney Fe was prepared by leaching the Al from Fe-Al alloy. All the catalysts are similar in composition and were tested under the same catalyst loading (30g/0.5L), catalyst size(200~270 mesh) and similar conditions, except that mentioned elsewhere. XRD indicated that all the catalyst bulk phases before reaction are α-Fe. Table 1 lists the properties of the related catalysts.

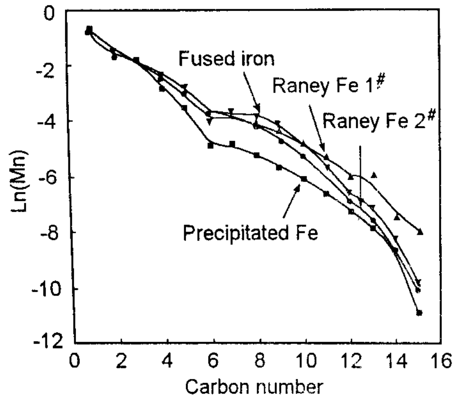
Table 1 Al/Fe ratio in the Fe-Al alloy and other properties of iron catalysts

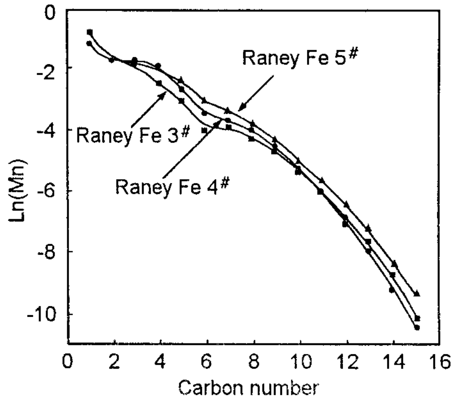
Raney Fe	Al : Fe ratio	BET surface area / $m^2 \cdot g^{-1}$	r_d (Å)	Promoter / %
Raney Fe $1^{\#}$	1.5	24.71	117	Cu 1.1
Raney Fe $2^{\#}$	1.5	22.6	108	Cu 2.2
Raney Fe $3^{\#}$	2.0	28.4	145	-
Raney Fe $4^{\#}$	6.0	~22	236	Cu 1.0
Raney Fe $5^{\#}$	3.0	25.2	244	Cu 1.0
Fused iron	-	12.0	350	-
Preci. Fe	-	130	79.5	Cu 0.5

Results and analysis

Carbon number distribution

The primary products of Fischer-Tropsch reaction over iron-based catalysts are 1-olefins, *n*-paraffins and some alcohols owing to further reaction of the initially formed 1-olefins[1]. However, larger amounts of paraffins and isomers produced in our tests indicated that secondary hydrogenation and isomerization were significant. The hydrocarbon distributions with carbon number over different catalysts have been found to follow the ASF law finely. Table 2 lists the values of α corresponding to various catalysts. The α value of Raney Fe (~0.58 to 0.68) is larger than that of precipitated Fe (~0.55) and approaches to that of Fused iron (~0.62). It was also found that there exist double α (~0.68 and ~0.4), *e.g.* for Raney Fe $4^{\#}$ and $5^{\#}$, while Raney Fe $3^{\#}$ is likely to have a single α. As shown in Figs.1 and 2, Raney Fe obviously produces more gasoline than precipitated Fe. And the apparent declination in carbon number distributions of ASF law can be referred to some literature (based on the tests both in the slurry reactor and the fixed reactor), the negative increase of the α is due to the hydrocracking and accumulating of the high molecular hydrocarbons (n>12) in the liquid film which are on the surface or in the interparticle pores[2].





T=543 K, P=1.5 MPa, SV=1.0 L/(g·h), H_2/CO=2.0

Fig.1 Comparison of the carbon number distributions over different Fe catalysts

Fig.2 Comparison of the carbon number distributions over different Raney Fe catalysts

Table 2 Variation of α of different catalysts

	Preci.	Fused	Raney	Raney	Raney Fe $3^{\#}$			Raney	Raney
Temp./ K	Fe	iron	Fe $1^{\#}$	Fe $2^{\#}$	H_2/CO=1.3	2.0	2.4	Fe $4^{\#}$	Fe $5^{\#}$
533	0.55	0.62	0.63	0.61	0.56	0.57	0.57	0.64	0.68
543	0.54	0.60	0.67	0.62	0.61	0.58	-	0.65	0.69
553	0.55	0.62	0.62	0.61	0.61	0.58	-	-	0.67

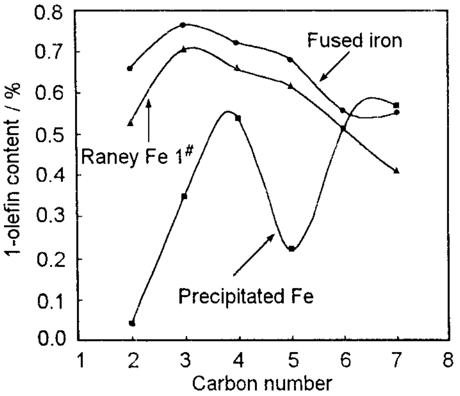
P=1.5 MPa, $WHSV$=1.0 L/(g·h), H_2/CO=2.0

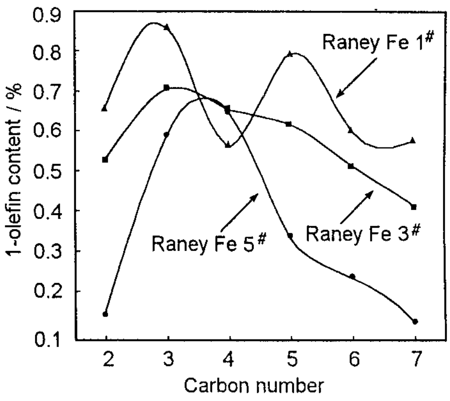
Olefin selectivity

1. Olefin selectivity in volatile hydrocarbons

The selectivities to olefins over three types of iron-based catalysts are compared as shown in Figs.3 and 4. Precipitated Fe shows lower selectivities to light olefins from C_2 to C_6, but Fused iron and Raney Fe yield more olefins of $C_{2\sim6}$. Another discrimination is in the maximum of olefin in volatile hydrocarbon, *i.e.* precipitated Fe produces much more C_4 olefins and Raney Fe gives rise to more C_3 and C_5 olefins.

Investigation on Raney Fe in a fixed bed reactor by K.R.Chen has resulted in following conclusions[3]. Of the total outlet gas products including CO_2, C_2~C_4 product keeps the unchanged percentage of 52% and CH_4 keeps a percentage of 20% with temperature increasing from 423 K to 473 K, which is lower than that obtained in a slurry reactor. The C_3 olefin content in $C_{2\sim4}$ is obviously high but is dependent on H_2/CO ratio and pressure.



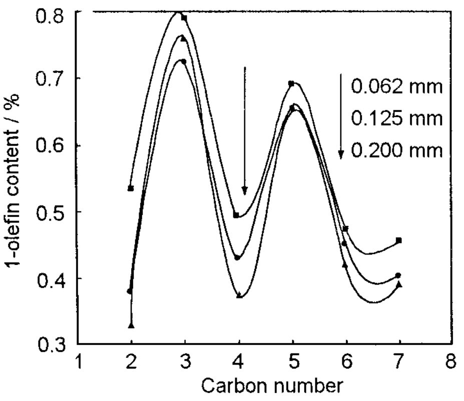


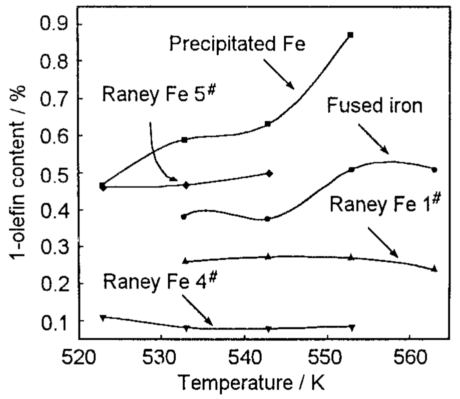
P=1.5 MPa, SV=1.0 L/(g·h), H_2/CO=2.0

Fig.3 1-olefin distribution of low molecular hydrocarbons on different catalysts at 533 K

Fig.4 1-olefin distribution of low molecular hydrocarbons on various Raney Fe at 533 K

The selectivity to olefins is also affected greatly by catalyst loading and catalyst particle size, which is thought to be due to the residence time and mass transfer limitation of reactants and the preliminary product. Fig.5 shows the variation trends of the 1-olefin content in light hydrocarbons over Raney Fe $5^\#$ at different particle sizes. The result of the effect by catalyst loading of Raney Fe $4^\#$ was not listed here, the major conclusion is that as the catalyst loading increases, $C_3^=$ and $C_5^=$ especially the later increase while $C_2^=$ goes contrary. Besides, $C_3^=$ over all Raney Fe increases more greatly than other olefins with temperature increasing, while the data of different particle sizes appear a slight increase with the catalyst size increases.





* T=543 K, P=1.5 MPa, SV=1.0 L/(g·h), H_2/CO=2.0

Fig.5 1-olefin content in light hydrocarbons over Raney Fe $5^\#$ with various pellet sizes

Fig.6 Comparison of 1-olefin content of high molecular HC over different iron catalysts

Temperature gives rise to different effects on the light olefin distributions with carbon number over different catalysts. Raney Fe causes the light olefin content of each carbon enhanced with temperature increasing, but precipitated Fe produces declined result.

2. Olefins in gasoline oil

The contents of olefins with carbon number from C_6 to C_{20} (C_{20}^+ is a negligible amount both in total hydrocarbons and olefins) over various catalysts are compared in Fig.6 and Table 3. It is obvious that the precipitated Fe produces more olefins in gasoline than the Fused iron and Raney Fe, which is averagely above 50% and increases up to 80% with temperature rising. While Fused iron is between Raney Fe and precipitated Fe, which gives an olefin content of 30% gasoline and attains to 65% as temperature increasing.

The olefin selectivities over Raney Fe catalysts are found to be affected seriously by the Al/Fe ratio of Raney Fe precursor. As shown in Table 3, Raney Fe 5# prepared from the alloy of Al/Fe=3 is likely to produce lower molecular olefin in high molecular products than other Raney Fe under the same conditions (catalyst size: ~0.062 mm).

Table 3 Ratio of 1-olefin to paraffin in high molecular hydrocarbons under different conditions

	Raney Fe 3#		Raney Fe 4#		Raney Fe 5#			
	H_2/CO		Stirred rate / rpm		Catalyst size / mm			
Temp. / K	1.3	2.0	600	>750	0.062	0.086	0.125	0.200
533	0.126	0.071	0.501	0.453	0.466	0.329	0.196	0.420
543	0.144	0.104	0.535	0.469	0.504	0.349	0.151	0.427

As well as we know, the selectivity to olefins increases with syngas ratio decreasing. Simultaneously, the effects of temperature, catalyst loading and catalyst size on the olefin content in gasoline are also analyzed, the former two factors have a positive effect on the olefin content, but the catalyst size has a negative effect in the range from 0.062 mm to 0.125 mm, except 0.2 mm, which probably due to that catalyst of larger pellet with macropores is similar in performance to that of small particle.

Secondary hydrogenation reaction

In order to demonstrate the occurrence of the secondary reaction over the Raney Fe, we compared the distributions of different olefins, including 1-olefins and 2-olefins, and the isomer of same carbon number over different Raney Fe catalysts. As shown in Fig.7, it is different from other reported results that Raney Fe gives various olefin selectivities in light hydrocarbons. Similar to Fused iron, Raney Fe shows a decreasing tendency in 1-olefin distribution with carbon number except ethylene. In accordance with the result mentioned above, Raney Fe 3# gives apparent lower contents of 1-olefins of each carbon number. And the amount of ethylene is lower than that of C_3 olefin, which accords with the conclusions of other reported results.

Ethylene is well known to be more reactive than other low carbon number 1-olefins. Davis has concluded that ethylene is likely to undergo carbonylation to produce propanol but not through ASF synthesis pathway[4]. Namely, the results of methane selectivity imply that it is easy for ethylene to be carbonylated to alcohol.

Fig.9 shows the variations of the isomer distribution with carbon number. Taking Figs.7 and 8 into account, the isomer distributions show a slight increase with carbon number increasing, and the significant low content of C_4 isomer over Raney Fe 5# is in accordance with that of C_4 1-olefin which is in lower content in Fig.7. As mentioned before, the 1#, 3#, 5# Raney Fe were all prepared under the same condition. Hence the difference was the alloy composition, which was characteristic of the Al/Fe ratio. And it was found the sequence of the pore radius of these Raney Fe was in accordance with th Al/Fe ratio.

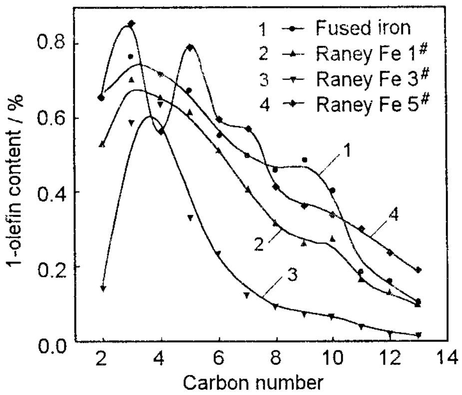


Fig.7 1-olefin content as a function of carbon number over various catalysts at 533 K

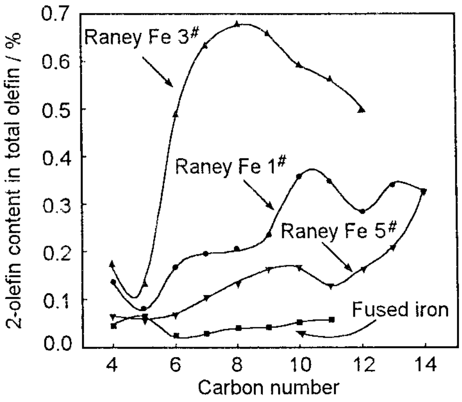


Fig.8 2-olefin content as a function of carbon number over various catalysts at 533 K

As shown in Figs.7, 8 and 9, the selectivities to 1-olefins decrease in an order of 5#>1#>3#, while that of the 2-olefin selectivity is in the opposite sequence. The isomer selectivity appears more complex but also indicates that Raney Fe 1# with the smallest pore radius yields much more isomers. The possible explanation is that the mediate pore distribution is suitable for the secondary hydrogenation from 1-olefin to 2-olefin, which is characteristic of product diffusion. It is concluded that the pore restriction to diffusion affects seriously the secondary hydrogenation reaction.

Selectivity of CH_4 and performance of WGS reaction

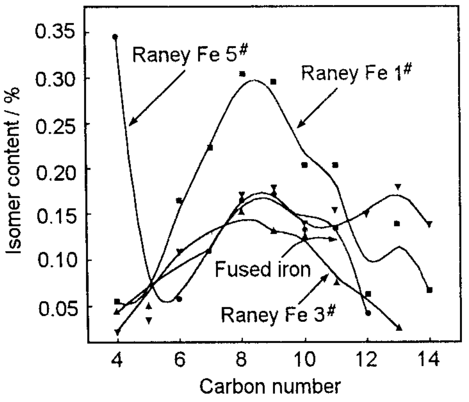


Fig.9 Isomer distribution with carbon number over different catalysts at 533 K

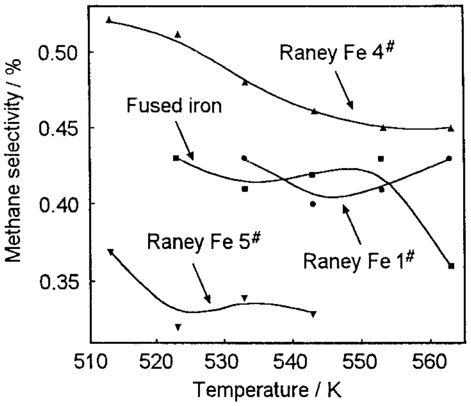


Fig.10 Methane selectivity with temperature over different catalysts

Methane selectivities in the hydrocarbons over different catalysts are shown in Fig.10. It was reported that larger pellets led to lower F-T synthesis rates and less light products[5,6] particularly methane. The higher methane content was assumed to be due to the presence of the hydrogenation sites that favor the production of methane. Raney Fe, especially Raney Fe 5#, produces less methane. And the higher alcohol selectivity is thought to be reasonable considering the lower ethylene selectivity and higher propanol content which may be carbonylated from ethylene.

Since the oxidation of the reduced catalyst is one of the main deactivation mechanism of the iron-based F-T catalysts, and the WGS reaction takes place on the magnetite[7], the performance of WGS surely affects the F-T rate and selectivity. Wainwright has reported that Raney catalyst is suitable to accelerate the reaction as $CO_2+H_2 \rightarrow H_2O+CO$, which is inverse to the WGS reaction[8].

Table 4 Performance of WGS reaction in the tests over different catalysts

	K_{app}= $[CO_2]$ $[H_2]$ / $[CO]$ $[H_2O]$							
Temp. /K	Preci. Fe	Fused iron	Raney Fe 1#	Raney Fe 2#	Raney Fe 3#	Raney Fe 4#	Raney Fe 5#	K_{eq}
523	26.65	15.14		8.52	17.18	30.96		78
533	43.41	20.39	8.52	15.5	27.39	42.64	67.85	71
543	40.46	29.03	21.13	16.47	34.58	45.91	66.11	64

Table 4 lists the evidence for the water-gas-shift reaction. It is clear that the equilibrium is not achieved for any cases, and the apparent equilibrium constant(K_{app}) increases with temperature and H_2 partial pressure increasing. This indicates that Raney Fe $5^{\#}$ exhibits lower WGS reaction activity but Raney Fe $1^{\#}$ and $3^{\#}$ possess a higher one.

Discussion

Usually, the 2-olefin selectivity which implies the secondary reaction increases with carbon number and gas space velocity increasing. It is due to that upon readsorption, 1-olefin becomes a reaction intermediate which can either continue to grow and terminate as a longer chain 1-olefin, *n*-paraffin or be terminated to *n*-paraffin or 2-olefin of the same carbon number. And lower ethylene content is due to its high activity[5,9].

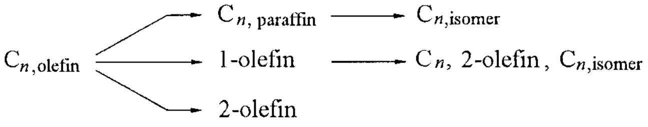
It was proposed by Madon that the decrease in 1-olefin content with molecular weight increasing was attributed to the decreasing diffusion rate of longer chain molecules and their longer residence times in the catalyst pores. Thus the longer residence time in catalyst pores or in the reactor itself increased the probability of the 1-olefin readsorption followed by termination as 2-olefin. The results of Raney Fe $3^{\#}$ and $5^{\#}$ with different pore radius indicated this point.

Davis reported that *cis-trans* isomerization of the added pentene did not occur during the synthesis reactions based on the investigation of labeled ethene addition, and the added pentene led to an increase of 40% of the C_6 and other higher molecular products by a mechanism that follows ASF selectivity[5,9]. But our results suggested that the micropores within precipitated Fe caused serious diffusion limitations of primary products, so the addition of pentene resulted in no distinct variation in C_5 hydrocarbons.

It was also reported that the significant fraction of light paraffins was because of the high rate of hydrogenation of these light olefins, and this indicated that significant secondary hydrogenation reaction occurred. However, the high content of lower olefins over Raney Fe catalysts indicated that the diffusion limitations affected olefin selectivity while high hydrogenation activity did not occur except for ethylene.

It is necessary here to recite the different conclusions from Schulz and Davis. One is that 2-olefin is one portion of the primary products, another is that between the hydrogenation and isomerization, which is the dominant secondary reaction.

The preliminary experiments over Raney Fe imply the following scheme related to the secondary reaction:



That is to say, the general definition of isomerization during secondary reaction includes the isomerization to *iso*-paraffins and 2-olefins (olefins). Raney Fe has higher selectivities to light 1-olefins and gives lower 1-olefin contents in high molecular hydrocarbons. On the other hand, the 2-olefin selectivities are lower than the selectivities of the isomers of the same carbon number. Except that Raney Fe with mediate pores exhibits a distinguished isomerization reaction from 1-olefins to 2-olefins. Compared with Fused iron (which also produces less secondary products), Raney Fe with larger pores has lower secondary reaction rate to form 1-olefins.

In a word, pore diffusion limitations increase probability of secondary readsorption of 1-olefins. It results in the formation of *n*-paraffins, 2-olefins and isomers. Raney Fe $3^{\#}$ showed significant pore limitations than Raney Fe $5^{\#}$ but Raney Fe $1^{\#}$ showed less limitations than Raney Fe $5^{\#}$. The similar 1-olefin and 2-olefin selectivities over Fused iron and Raney Fe $1^{\#}$ and $5^{\#}$ are due to that Raney Fe $5^{\#}$ has less pore diffusion limitations as Fused iron while Raney Fe $1^{\#}$ has higher isomerization reaction activity than Fused iron.

All these demonstrate that the optimum structure of Raney Fe catalyst can result in high activity in hydrogenation and desired selectivity. As some reports claimed[10], micropores contribute to the limitation and macropores decrease the pore volume and BET area. Raney Fe $5^{\#}$ somehow balanced this relation and showed high activity and low pore limitaion.

Conclusions

The dominant primary products over Raney Fe catalyst are 1-olefins and *n*-paraffins, isomers and 2-olefins are also found to be significant portions.

The secondary reaction over Raney Fe includes the isomerization from 1-olefins to 2-olefins and isomers of paraffins, and the hydrogenation from 1-olefins to *n*-paraffins. Raney Fe with larger pores has lower secondary reaction activity while smaller pores exhibit significant isomerization reaction activity. It is assumed that the optimum structure obtained by adjusting the preparation conditions can yield the desired products.

The selectivity and activity over Raney Fe $5^{\#}$ with macropores approach to that of precipitated Fe, and the differences are the lower methane selectivity and lower performance of WGS reaction.

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