

NEW DEVELOPMENTS IN RESEARCH BASED ON FT SYNTHESIS

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Abstract This paper introduces some recent results of "modified FT synthesis" over manipulating catalysts of traditional FT catalysts to produce some other valuable chemical feedstock like oxygenates, olefins, aromatic hydrocarbons, wax *etc.* instead of liquid fuel. Molecular sieves such as Al-MCM-41, ZSM-5 and aluminophosphate are playing a more and more important role in the reaction based on FT synthesis. Metal catalysts are still the focus of the research. Either molecular sieves or other carriers always serve the metallic active sites like Fe, Co, Pd, Rh, Ni and bimetallic such as Fe-Ir and Pt-Mo. Furthermore, some new methods were applied in the reaction, for example, supercritical FT synthesis, ultrafine particle catalyst *etc.*

Keywords modified FT synthesis, metal catalysts, molecular sieves

Introduction

Fischer-Tropsch (FT) synthesis, as conceived by Franz Fischer and Hans Tropsch (1923, 1926), has played an important role for the production of not only liquid fuel but also chemical feedstock from coal^[1]. Since the products of traditional Fischer-Tropsch synthesis have a wide spectrum from C₁ to C₂₃ according to Anderson-Schulz-Flory (ASF) model^[2], one of the most important tasks for catalyst researchers is to improve the catalysts to produce more profitable chemical feedstock. There has been renewed interest in recent years, especially for the selective production of oxygenates, olefins, aromatic hydrocarbons, wax *etc.* from synthesis gas directly. Even so, there are still a lot of researchers who have been focusing their attention on FT synthesis because 1) FT synthesis is considered as an economical proposition for a long term due to its economic

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and ecological meanings. 2) Many other subsequent reactions, such as preparation of oxygenates and lower molecular olefins, are based on FT synthesis. This paper has summarized some investigations on FT synthesis according to catalyst types, for example, molecular sieves, Fe-based catalysts, Co-based catalysts *etc.*

Modified FT synthesis

The FT synthesis concerns many kinds of products. Hydrocarbons up to C₂₃ are the most components among them. Oxygenates take a small part in the products. Through selective modification of catalyst composition, one can obtain certain products without consideration of any kinetic effects^[3]. For example, Rh/oxide leads to the production of alcohol; Cu/ZnO benefits methanol; Ni, Co and Fe are more selective for hydrocarbons. So, many reactions based on FT synthesis are developed in which different catalysts are applied for particular purpose. Oxygen-containing products such as methanol, ethanol and *iso*-butanol from syngas have been studied for a long time^[4-7]. Some processes have come into industrial uses. Catalysts C207 (a modified Cu-Zn/Al₂O₃ methanol synthesis catalyst) as well as NC208 modified from C207 were first developed by Xiamen University in China and both of them showed high CO conversion and yield of methanol^[6]. With the increase of the demand of gasoline additives (MTBE), people are managing to find another method to produce the stock of MTBE-isobutene through FT synthesis^[8]. Studies on aromatic hydrocarbon synthesis have been conducted for many years. Combined catalysts such as zirconia-based cobalt-nickel mixed with HZSM-5, Fe/MnO-GaZSM-5, Fe/MnO-ZnZSM-5 have been developed^[9]. Wax is widely used in many fields such as adhesives and cosmetics. Especially, wax produced by FT synthesis has been recognized for its high quality and stability because FT wax does not contain aromatics and it is also sulfur-free^[10].

Research progress in catalysts

1. Molecular sieve catalysts

Zeolite catalysts are extensively used in petroleum refining, petrochemical and chemical industries. In many industrial processes, zeolites are utilized as catalysts in their acid form. However, in recent years a number of new processes based on the metal loaded zeolite catalysts have been developed. In processes such as hydrocracking, selectofoming, dewaxing, hydroisomerization of C₆~C₅ alkanes, and hydroisomerization of C₈ aromatic hydrocarbons, zeolite loaded with metals are widely used as the catalysts.

The relative abundance of propane and butane and a great demand for aromatic hydrocarbons make it economically attractive to produce aromatic hydrocarbons by means of the aromatization of propane and butane^[11].

1.1. Micropore molecular sieve catalysts

On ZSM-5 type zeolite olefins and/or oxygenates can be catalytically converted to hydrocarbons and aromatics. The shape-selective acidic zeolite ZSM-5 has uniform pores of about 5.5 Å diameter governed by a 10-membered oxygen ring opening that results in a sharp cutoff in the aromatic product distribution at C₁₀. Most conventional Fischer-Tropsch (FT) catalysts give a wide spectrum of hydrocarbon products, however, if they are combined with a shape selective catalyst, a more selective hydrocarbon product can be produced. Thus, synthesis gas can be directly converted to gasoline range and other products by combining FT synthesis function with a shape-selective acid function of catalysts^[12]. Instead, if FT synthesis catalysts are combined with an aromatic-selective catalysts the synthesis gas could also be converted to aromatic hydrocarbons. The use of ZSM-5, ZrO₂-introduced β HY has got the results corresponding to expectations. There are little olefins in the products, but plenty of light paraffins^[13].

1.2. Mesoporous molecular sieves

In 1992, Mobil Company first synthesized a group of new molecular sieves using surface-active agent as the template. These new molecular sieves are attracting more and more researchers.

Mesoporous molecular sieve MCM-41 based catalysts were applied in FT synthesis (Table 1)^[13]. ZrO₂-introduced Al-MCM-41 was investigated in FT synthesis. The main products are light hydrocarbons. Researchers predict that mesoporous molecular sieves modified by Fe, Mn, K *etc.* would have high selectivity for C₂^o ~ C₄^o.

Table 1 Results of CO hydrogenation over ZrO₂ supported on mesoporous molecular sieves

Catalyst	CO		Product distribution / mol%									
	Conv./%	CH ₄	C ₂ ^o	C ₂ ^o	C ₃ ^o	C ₃ ^o	C ₄ ^o	C ₄ ^o	i-C ₄	i-C ₄ /C ₄	C ₂ ^o ~C ₄ ^o	
ZrO ₂ /HMS*	14.28	42.20	10.74	14.36	13.01	3.79	10.86	15.88	4.6	17.20	34.62	
ZrO ₂ /MCM*	5.31	31.58	7.88	12.95	13.70	7.18	17.61	26.68	6.0	13.54	39.21	
ZrO ₂ /AIMCM41	5.47	37.11	4.18	16.03	10.39	6.69	12.92	25.59	10.82	28.09	27.49	

Reaction condition: 673 K; 1.5 MPa; GHSV, 2 400h⁻¹ *: 723 K; 1.0 MPa

HMS was synthesized by applying DDA; MCM was synthesized by applying CTMAB.

1.3. Aluminophosphate molecular sieves

Luisa and Cubeiro first applied aluminophosphate molecular sieves in CO hydrogenation^[14]. The behavior in syngas conversion of Me/AlPO₄-5 and MeAPO-5 (Me=Fe, Co, ~4 wt%), as well as that of hybrid systems comprising an iron FT catalysts physically mixed with SAPO-5, FAPO-5, SAPO-11 and FAPO-11, were studied at 1.2 MPa, 573 K and H₂/CO=1. Conversion of CO was much lower for Fe/AlPO₄-5 and MeAPO-5 than that for Co/AlPO₄-5, which could be related to the presence of the metal in high-oxidation states in former case. Significant differences in selectivity were observed as a result of changes in the type of metal and the way that the metal is introduced into the catalyst (added to the synthesis gel or impregnated on the molecular sieve). These differences in selectivity were explained in terms of the facility of forming alkenes (related to metal sites) and the presence of acid sites^[14].

2. Metal catalysts

At present metal catalysts are the most studied catalysts used in FT synthesis. The most common catalysts for CO hydrogenation (FT synthesis) are group VIII elements such as cobalt, nickel, ruthenium and iron^[15]. Metal catalysts can be acquired through co-precipitating, melting and loading on certain supports such as SiO₂, TiO₂, ZrO₂ or Al₂O₃. Transition metals such as Ti, Mn and V have greater affinity to carbon monoxide than Fe. So Ti, Mn and V are widely used as the promoters for metal catalysts. Among these metals, manganese oxide catalyst is agreed to be the best promoter. The preparation method and the pretreatment conditions used for a catalyst have great influences on the surface states of metal and metal oxide species formed during the reaction, so they play important roles in determining the catalytic properties. Till now, the metals for obtaining higher hydrocarbons on an industrial scale are mainly restricted to iron and cobalt, to a less extent, also ruthenium and nickel^[16].

2.1. Fe/MnO based catalysts

Bulk iron catalysts promoted with manganese oxide have been verified to enhance the formation of low-molecular-weight olefins when used for carbon monoxide hydrogenation. The study on cobalt-manganese oxide come into the same conclusion^[17]. It is also found that high manganese content catalyst containing 10-20 wt% iron is more selective to olefins. In recent years, the production of aromatic hydrocarbons such as benzene, toluene and xylene from light alkane over Ga-, Zn- and Pt-modified ZSM-5 zeolite catalysts has been widely investigated. These catalysts have exhibited very high catalytic activities in the transformation of light hydrocarbons into aromatics because of their unique acidic property, shape selectivity, channel dimensions and low coke

formation. The mode of introduction of metal into zeolite is of crucial importance to many of these processes because of the dispersion of metals in zeolite and their interaction within the zeolite framework or on external surfaces. Metal modified zeolite catalysts are extremely useful for reactions such as aromatization, oxidation, dimerization, oligomerization and cyclization because of different states of metals, their mobilities and their high catalytic activities. Zeolite structure also affects the electronic properties of metals incorporated into them. Metals are generally incorporated into zeolites by methods such as ion exchange, impregnation and physical mixing. Taking into account of the efficiency of metal uptake and its uniform distribution in zeolites, these methods have both advantages and drawbacks^[11].

On the basis of the high aromatization activity of ZSM-5 zeolite promoted by Ga or Zn (GaZSM-5, ZnZSM-5)^[18], many subsequent studies have been conducted on combining iron manganese oxide with gallosilicate (GaZSM-5) in order to convert olefins to aromatic hydrocarbons. The synthesis is expected to produce aromatic hydrocarbons directly due to the bifunction of catalysts. The gallosilicate is also catalytically active in cracking the hydrocarbon, *e.g.* butane and the cracked product distribution are altered with olefins predominating. So this enhances the selectivity of olefins in the reaction. As a result the iron-manganese oxide combined with gallosilicate (Fe/MnO-GaZSM-5) has a high selectivity of about 40% to aromatic hydrocarbons. But the Fe/MnO-GaZSM-5 was deactivated in short time, which may result from the migration of Ga from bulk to surface^[9]. Similar to GaZSM-5 in catalytic activity, Fe/MnO-ZnZSM-5 is also expected to get good result, which needs further studies^[19].

2.2. Cobalt based catalysts

Cobalt is one of the most studied metals in Fischer-Tropsch synthesis. This metal is active and has good selectivity to alcohol or linear hydrocarbons, to short ($C_2\sim C_4$) or very long ($C_{20}\sim C_{60}$) chains, to paraffins or olefins, depending on the reaction conditions, on the metal promoter (Cu, Ru, Mn, *etc.*), on the oxide promoter (rare earth oxides, TiO_2 , *etc.*) or on the nature of support (SiO_2 , Al_2O_3 , *etc.*)^[19]. The cobalt-based catalysts showed high activity and wax selectivity even at lower reaction temperatures such as 210°C. And additions of lanthanum and nickel can promote the activity of Co-based catalyst^[10]. Cobalt-based catalysts exhibit characteristics which are superior to those of iron-based catalysts for the conversion of synthesis gas to hydrocarbons. These characteristics include the formation of smaller quantities of carbon and oxygenates, and a higher resistance to oxidation. These properties increase catalyst life and facilitate product processing, which makes the catalyst industrially attractive. Ground pelletized catalysts consisting of a co-precipitated mixture of cobalt and a partially reducible oxide, such as

manganese oxide, have given excellent yields of olefins from synthesis gas. The investigation on the performance of a cobalt-manganese oxide (Co/MnO) catalyst in a fixed bed reactor for the conversion of carbon monoxide with hydrogen showed a good result(Fig. 1)^[20].

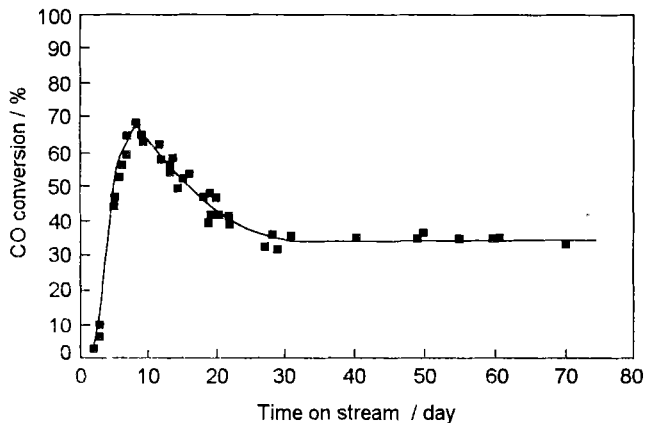


Fig.1 CO conversion versus time on stream
 Temperature=220°C; Pressure=2100 kPa; H₂:CO=2:1 (mol/mol);
 Co:Mn=1:3 (mol/mol); GHSV=75 h⁻¹ [20]

Comprehensive investigations on various Ru-promoted cobalt FT catalyst formulations have indicated the promoting effect of Ru on Co/Al₂O₃ as well as the optimal preparation technique for such catalysts. Ru, like other noble metal promoters, has been concluded to increase the reducibility of Co and possibly preserve its activity by preventing the build-up of carbonaceous deposits^[21].

The mechanism of deactivation of alumina supported cobalt catalysts due to water in Fischer-Tropsch synthesis has been studied using steady-state isotopic transient kinetic analysis (SSITKA) by Martin Rothaemel et al.^[22]. They reported that after treatment with water, both the Co/Al₂O₃ and the Co/Re/Al₂O₃ catalysts showed a reduced activity with respect to the conversion of syngas. Furthermore, an increase of the olefin selectivity after water treatment was observed. This result gave us another direction to proceed our study to suit the industrial production.

2.3. Palladium based catalysts

Supported palladium catalysts have been claimed to be good catalysts for the production of methanol from synthesis gas for many years. Recently, Gotti and Prins^[23] reported the results contrary to early claims for the supported Pd catalysts but in agreement with studies of unsupported Pd catalysts. Pd supported on impurity-free SiO₂

catalyst demonstrated that Pd is not a good methanol catalyst. Molecular adsorption of CO and the availability of activated hydrogen are not sufficient for the formation of methanol. Basic metal oxides are needed to make a Pd catalyst which has a high activity for methanol formation from CO and H₂. CO hydrogenation on supported Pd catalyst was investigated using steady-state isotopic kinetic analysis (SSITKA) in order to explore the differences in catalytic behavior which have been previously reported by others^[24]. The dispersion of the Pd particles on the prepared catalysts, as evaluated by CO chemisorption, was not affected by either the Pd precursor or the support used. In addition, for a given support the catalysts exhibited almost the same selectivity during CO hydrogenation toward methane, methanol (MeOH), and dimethyl ether (DME). However, catalysts prepared using PdCl₂ showed higher overall activities than those prepared using Pd(NO₃)₂ for a given support.

2.4. Rhodium based catalysts

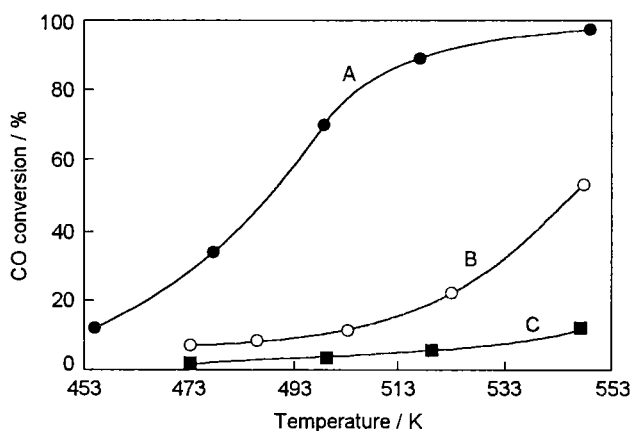


Fig.2 Activity of CO hydrogenation on RhVO₄/SiO₂, V₂O₅-Rh/SiO₂ and Rh/SiO₂ catalysts after H₂ reduction at 500 K
A: RhVO₄/SiO₂ B: V₂O₅-Rh/SiO₂ C: Rh/SiO₂

Vanadium-promoted Rh catalysts have been reported to have high activity and selectivity for syngas conversion to produce C₂ oxygenates such as ethanol and acetic acid^[25]. The hydrogenation of CO over a rhodium vanadate (RhVO₄) supported on SiO₂ (RhVO₄/SiO₂) catalyst has been investigated after H₂ reduction at 500°C. Fig.2 shows that the RhVO₄/SiO₂ catalyst exhibited higher activity and selectivity to C₂ oxygenates than the unpromoted Rh/SiO₂ catalyst after H₂ pretreatment. The CO conversion of the RhVO₄/SiO₂ catalyst was much higher than that of the V₂O₅-Rh/SiO₂ catalyst, and the

yield of C_2 oxygenates increased^[25]. The CO hydrogenation over Rh/SiO₂ catalysts promoted with oxides of VB transition metals was also studied^[26]. Promotion of Rh/SiO₂ with VB transition metal oxides leads to an increase in the overall CO hydrogenation activity. The promoting effect rises in the order of V<Nb<Ta.

2.5. Nickel based catalysts

Nickel has high catalytic activity for hydrogenation. Nickel-modified catalysts are widely used in CO hydrogenation^[27]. Titania(Ti)-supported nickel catalysts were reported to be more active in CO hydrogenation than silica- or alumina-supported catalysts^[28]. A series of nickel catalysts supported on pumice were prepared by precipitation and impregnation techniques^[27]. Changes of the ratio of C_2^+ yield to CH₄ yield versus nickel dispersion are attributed to the presence of the alkali ions in the structure of support.

2.6. Fe-Cu catalysts

In recent years several catalysts consisting of Fe-Cu were investigated, *e.g.* Fe-Cu-K and Fe-Cu-Mn^[29]. The Fe-Cu-K co-precipitated catalyst developed by Institute of Chemistry, The Chinese Academy of Sciences, has been used in industrial production^[2]. There is another different Cu-Fe catalysts got by mixing CuO and α -Fe₂O₃ mechanically or impregnating CuO with Fe(NO₃)₃ solution^[4]. From the results of XRD and CO-TPD, one concluded that the sample obtained by mechanically mixing formed CuFe₂O₄ solid solution after 850°C calcination. But the sample by impregnation stayed unchanged. There is a interreaction between Cu and Fe species, which resulted in the CO adsorption center homogeneous. Fe-Cu-Mn catalysts were also investigated. This catalyst was obtained by combination of a classical FT catalyst with an HZSM-5 aluminosilicate. As a result of the selection studies, a Mn and Cu-promoted iron oxide was used as the FT component and micromixed with the HZSM-5 zeolite^[29].

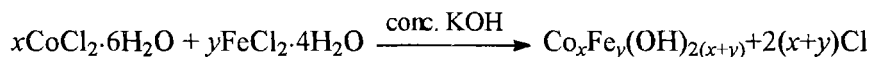
2.7. Bimetallic catalysts

Alloy catalysts exhibit different activity and selectivity from monometallic catalysts. This is because alloying changes the electronic properties and the surface state, and so changes the activity sites of the catalysts^[17]. As mentioned above iron is of high catalytic activity for FT synthesis. To enhance selectivity and CO-conversion of the iron catalyst, many kinds of promoters are introduced to the iron catalyst. A highly active fused iron catalyst for higher alcohol synthesis has been prepared by a simple fusion method in an electric furnace at about 1800 K^[30]. When preparing the catalyst, the purified Fe₃O₄, CuO, Co₃O₄, KNO₃ and other promoters were thoroughly mixed and fused in an electric furnace at about 1800 K, and then cooled, crushed and screened. The activity and selectivity of the catalyst have been measured at 503 K ~ 673 K, 6.0 MPa, 10,000 h⁻¹ and

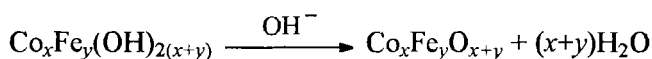
$V(\text{H}_2)/V(\text{CO})=2.3$. The space-time yield of alcohol can be up to 1.28 g/(mL·h) and the selectivity to C_2^+ oxygenates is about 60%.

An original synthesis of cobalt-iron alloy and cobalt doped magnetite catalysts (spinel structure) has been developed, in which metallic state cobalt and iron are obtained without any reducing treatment. The synthesis of these catalysts is believed to base upon several steps as follows^[16]:

— the coprecipitation of hydroxides of cobalt and iron in a boiling concentrated basic medium (from the corresponding chlorides):



— the dehydration of the hydroxide to an oxide in an alkaline medium:



But the catalyst activity was low and further studies are required.

Another bimetal Fe-Ir is used in CO hydrogenation. van Gruijthuijsen L.M.P. et al. conducted the study over the FeIr/SiO₂ catalysts of higher iron content (Fe/Ir ≤ 1). And it is reported that the methanol selectivity is as high as 80%~85%. However, the favorable steady state activity and selectivity are reached only after an activation period of 24 h to 48 h. A group of related bimetallic catalysts, consisting of a noble metal (Ru, Rh, Pd, Pt, Ir) and a less noble metal (Fe, Co, Ni) in a 1:1 atomic ratio show the same behavior^[31].

Bimetallic catalyst Pt-Mo has shown catalytic activity higher than monometallic catalyst of Mo or Pt in CO hydrogenation. Strong interaction between Mo atoms and the support was also identified with EXAFS and XANS for monometallic Mo catalysts and bimetallic catalysts. Regarding the activities of CO hydrogenation, it was concluded that the reduced Mo sites were responsible for the high activity and that Pt made Mo sites more reduced^[32].

3. Other methods

3.1. Supercritical FT synthesis

A frontier research area is supercritical FT synthesis. Institute of Coal Chemistry, The Chinese Academy of Sciences, has conducted some work to throw light on this area. Part of their work is FT synthesis over a Co/SiO₂ catalyst in a fixed-bed reactor system in the presence of supercritical fluid^[34]. They investigated the phase effect on the CO

conversion (Table 2) and hydrocarbon yield (Fig.3).

Table 2 Effect of reaction phase on CO conversion and hydrocarbons distribution

Reaction phase	CO conv. / %	C ₁ ~C ₄ yield / mol·g ⁻¹ ·h ⁻¹ (based on C)				C ₂₀ ⁺ sele./%
		C ₁	C ₂	C ₃	C ₄	
Gas phase	70	2.91	0.218	0.551	0.607	13.4*
SC phase	84	1.87	0.259	0.164	0.041	39.6

C₂₀⁺ selectivity is the fraction of C₂₀~C₆₀ in the total of C₁~C₆₀.

* Fraction of C₂₀~C₃₀ in the total of C₁~C₃₀ over Co/SiO₂ catalyst (20 wt%Co) [34]

The conclusion is that the supercritical fluid can move the reaction heat and heavy products from the bed in time and ameliorate heat transfer and mass transfer efficiency in the course of reaction. As a result, the conversion of CO and selectivity to hydrocarbons increase a lot^[34,5].

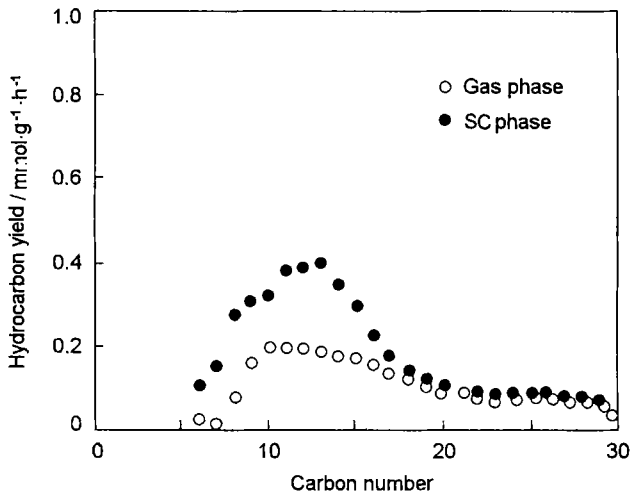


Fig.3 Phase effect on hydrocarbon yield
W/F=15, 483 K, without olefin addition

3.2. Ultrafine particle FT synthesis

Ultrafine particle catalysts are attractive because of their large surface area, high activity, high selectivity and long life^[35]. A preparation method of Fe₃C ultrafine particle (UFP) catalyst, from highly dispersed amorphous Fe powder and free carbon by laser pyrolysis technique, was investigated. The catalytic reactive species, α -Fe, and iron carbide catalyst for FT synthesis were obtained directly. The catalytic performance of the iron-carbonide UFP catalyst for FT synthesis has been evaluated using a continuous

flow fixed-bed microreactor^[36]. The results showed that both activity and selectivity became stable after 20 h reaction, and that the average CO conversion was 96.1% and the content of propylene in the gas product was 67.3% by mole. These were the average results within 20 h ~ 48 h of reaction under 1.5 MPa, 320°C and WHSV of 600 h⁻¹ without gas circulation.

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杂多化合物催化异丁烯氧化反应 (Oxidation of Isobutene Catalyzed by Heteropoly Compounds) / 何达云, 吴京琳, 钟邦克 (暨南大学化学系 广东 广州 510632) // *J.Nat.Gas Chem.*, 2000, 9: 217

摘要 用流动反应器、XRD、IR和DTA等方法对杂多化合物的组成和结构以及在异丁烯部分氧化中的催化行为进行了研究, 发现在 $\text{PMo}_{12}\text{As}_6\text{Cu}_0.1\text{O}_x$ 中加进适量的K和V得到的杂多化合物在异丁烯一步氧化为甲基丙烯酸的过程中显示出良好的催化性能。通过调变化化剂的组成和优化反应条件, 甲基丙烯酸和甲基丙烯醛总收率达67%。V和K加入到母体磷钼酸(PMo_{12})中增强了热稳定性, 和母体相比催化剂的分解温度提高了200°C。**关键词** 杂多化合物 氧化 异丁烯 甲基丙烯酸 甲基丙烯醛

无机膜反应器用于正丁烷氧化制顺丁烯二酐的研究 (Oxidation of *n*-Butane to Maleic Anhydride over an Inorganic Membrane Reactor) / 黄仲涛, 纪红兵, 姜红霞, 王乐夫 (华南理工大学化工学院 广东 广州 510641) // *J.Nat.Gas Chem.*, 2000, 9: 223

摘要 通过浸渍法在中孔 $\gamma\text{-Al}_2\text{O}_3$ 膜上制备出V-P-Co-Ce-O多组分金属氧化物催化膜, 将之应用于非燃料电池型催化膜反应器并研究其可行性及正丁烷制顺丁烯二酐的反应特性。考察了反应温度、空速和吹扫气流速对催化活性的影响, 对膜反应器的稳定性也进行了简单的测试。实验证明, 与固定床相比, 膜反应器具有更高的反应转化率和选择性。

关键词 V-P-Co-Ce-O多组分金属氧化物催化膜 正丁烷 顺丁烯二酐

不同制备方法对Ba/MgO催化剂催化甲烷氧化偶联反应性能的影响 (Effects of Preparation Methods on the Catalytic Properties of Ba/MgO Catalysts in Oxidative Coupling of Methane) / 达建文 (齐鲁石化公司研究院 山东 淄博 255400) 沈师礼 (石油大学(北京)化学学部 北京 102200) // *J.Nat.Gas Chem.*, 2000, 9: 231

摘要 采用BET、XRD、SEM和XPS等方法对Ba/MgO催化剂进行了分析, 并且对该催化剂对甲烷氧化偶联反应的性能进行了测试。结果表明, 制备方法对Ba/MgO催化剂的催化性能有很大影响。采用淤浆法制备的Ba/MgO催化剂具有合适的比表面积和表面物种分布, 因此对甲烷转化显示出良好的催化活性。而采用机械混合或浸渍等方法制备的催化剂由于表面不均匀以及表面烧结等原因其活性较差。

关键词 Ba/MgO 制备方法 催化性能

中孔硅酸盐材料MCM-41的合成与表征研究 (Synthesis and Characterization of Mesoporous Aluminosilicate MCM-41) / 宋春敏, 阎子峰 王怀平 (石油大学重质油加工国家重点实验室 山东 东营 257062) Lu Max (The University of Queensland, Australia) // *J.Nat.Gas Chem.*, 2000, 9: 237

摘要 以十六烷基三甲溴化铵为模板剂, 硅酸钠为硅源, 铝酸钠为铝源, 在水热条件下成功地合成出了MCM-41中孔硅酸盐材料。采用XRD、低温 N_2 吸附脱附等测试手段对合成的MCM-41样品进行了表征。通过优化合成条件, 合成出孔径3.2 nm、比表面 $904\text{ m}^2/\text{g}$ 和孔壁厚约1.46 nm的MCM-41分子筛。催化活性测定采用微反应活性实验来评价其活性和选择性。

关键词 分子筛 合成 表征 MCM-41

苯胺氧化羰基化研究 (A Study on the Oxidative Carbonylation of Aniline) / 王文峰¹, 张藩贤², 许翩翩² (福州大学化学系 福建 福州 350002; ²厦门大学化学系 福建 厦门 361005) // *J.Nat.Gas Chem.*, 2000, 9: 243

摘要 以Pd/C为催化剂, 以NaI为助催化剂, 以无水乙醇为溶剂, 进行了苯胺氧化羰基化反应。研究了苯胺氧化羰基化的最佳工艺条件, 解释了碘化钠在本反应中所起的助催化作用。在170°C, 反应两小时后, Pd/C显示了高活性(97.49%)和高选择性(85.26%)。最后, 提出了苯胺氧化羰基化反应的机理。

关键词 苯胺 氨基甲酸酯 羰基化 机理

费托(FT)合成及相关反应的研究进展 (New Developments in Research Based on FT Synthesis) / 王德生, 关乃佳 (南开大学化学系新催化材料研究室 天津 300071) // *J.Nat.Gas Chem.*, 2000, 9: 249

摘要 按催化剂分类介绍了改性FT合成及与其相关反应的近期研究成果。即通过调制催化剂组成和反应条件, 由合成气直接合成其他有价值的化工原料如醇、烯烃、芳香烃和石蜡等。分子筛, 如Al-MCM-41和ZSM-5/磷铝分子筛等在FT及其相关反应中扮演着越来越重要的角色, 但由于金属作为反应活性中心, 所以金属催化剂如Fe、Co、Pd、Rh和Ni, 双金属如Fe-Ir和Pt-Mo仍然是人们研究的重点。另外, 一些新的反应方法和新的材料也被采用, 如超临界方法及超微粒催化剂等。

关键词 改性FT合成 金属催化剂 分子筛