催 化 学 报

2011 Chinese Journal of Catalysis Vol. 32 No. 12

文章编号: 0253-9837(2011)12-1790-13 国际版 DOI: 10.1016/S1872-2067(10)60285-9 研究论文/封面文章: 1790~1802

极性溶剂相费托合成的产物分布特征

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摘要: 在间歇反应釜中研究了极性溶剂中工业铁基催化剂上费托合成的产物分布特点, 考察了不同极性溶剂 (聚乙二醇 400 和 600, 1,4-丁二醇, 乙二醇) 和非极性溶剂正辛烷, 反应条件 (温度, 进料 H_2/CO 比, 反应时间) 和操作模式 (间歇, 半连续) 对产物选择性和链增长因子 α 的影响. 结果表明, 在所考察的条件下, 产物中 α-烯烃 (除了乙烯) 的选择性几乎不随碳数变化, 这完全不同于采用非极性介质的传统费托合成, 对于高选择性地生产线性 α-烯烃具有重要的意义. 通过优化操作条件, 产物中 α-烯烃的平均含量可超过 70%. 产物分布大多偏离理想的 ASF 分布, 无法用烯烃再吸附理论来解释. 链增长因子 α 均大于 0.85, 表明极性介质有利于长链烃的生成.

关键词: 费托合成; α-烯烃选择性; 极性溶剂; 聚乙二醇; 反应介质; 二次反应; 产物分布

中图分类号: O643 **文献标识码**: A

收稿日期: 2011-07-22. 接受日期: 2011-08-12.
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基金来源: 国家杰出青年科学基金 (20625620); 中国科学院知识创新工程项目 (KJCX2-YW-N41).
本文的英文电子版(国际版)由Elsevier出版社在ScienceDirect上出版(http://www.sciencedirect.com/science/journal/18722067).

Product Distribution of Fischer-Tropsch Synthesis in Polar Liquids

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Abstract: The effect of using polar liquid as the reaction medium for Fischer-Tropsch synthesis on the product distribution was studied. The experiments were performed with an industrial iron-based catalyst in a batch autoclave reactor with different liquid phases (polyethylene glycol 400, polyethylene glycol 600, 1,4-butanediol, and glycol). The reaction conditions were temperature of 200–240 °C, initial H_2/CO molar ratios of 1.00–2.03, catalyst particle sizes of 20–40 mesh and > 150 mesh, and reaction time of 24–144 h. The α-olefin selectivity was significantly increased to more than 70% and was almost independent of carbon number with all the polar liquids. Most of the hydrocarbon distribution were not of the ideal Anderson-Schulz-Flory pattern and could not be explained by the mechanism of olefin readsorption and secondary reactions. The chain growth probability α was larger than 0.85 for all conditions, and it was slightly influenced by changes of reaction conditions, liquid, and reaction time. There was product separation during reaction in this catalytic system, which meant that it did not have the problem of separating the catalyst from the wax product that traditional slurry reactors have. The result suggested new opportunities for the selective production of linear α-olefins and for mechanistic investigations of Fischer-Tropsch synthesis.

Key words: Fischer-Tropsch synthesis; α-olefin selectivity; reaction medium; polar liquid; polyethylene glycol; product distribution; secondary reaction

Received 22 July 2011. Accepted 12 August 2011.
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This work was supported by the National Outstanding Young Scientists Foundation of China (20625620) and the Chinese Academy of Sciences Knowledge Innovation Project (KJCX2-YW-N41).
English edition available online at Elsevier ScienceDirect (http://www.sciencedirect.com/science/journal/18722067).

费托合成 (FTS) 是将煤、天然气和生物质等经合成气催化转化为烷烃、烯烃和含氧化合物等液体燃料及化学品的过程, 被认为是未来替代石油衍生品的重要途径之一[1~3].

通常认为[3], 费托合成是个连续反应过程, 初级产物主要是直链的 α-烯烃及少量的正构烷烃. 这些 α-烯烃可以进一步发生二次加氢或异构化反应, 生成对应的烷烃或异构烃; 也可发生链引发或加氢裂解反应, 生成长链烃或短链烃. 烯烃二次反应受催化剂所处反应环境 (反应介质) 的影响较大, 可以显著地改变最终产物的选择性[4~7]. 例如, 催化剂孔道常常被生成的产物蜡所填充, 由于烯烃在蜡中溶解度较高且扩散速率较慢, 导致烯烃在催化剂孔道中停留时间增加, 二次反应的概率显著增加, 因而最终产物中烯烃含量降低. 同时, 由于烯烃的溶解度和扩散速率与其自身链长有关, 因此,非极性介质中费托合成产物中烯烃与烷烃之比总是随碳数的增加而呈指数下降. 通过调变催化剂组成、制备方法和预处理条件等, 通常无法有效地控制费托合成的烯烃二次反应[8], 因而很难得到理想的目标产物. 由此可见, 控制费托合成产物选择性应同时考虑初级反应和二次反应, 即需要对催化剂颗粒本身及其所处的反应环境同时进行优化设计, 如图 1 所示.

要同时控制费托合成的初级反应和二次反应, 根据目标产物的不同, 一般通过促进或抑制二次反应来实现. 对于液体燃料 (如汽油) 的生产, 为了增加油品的辛烷值, 常常需要促进烯烃二次反应 (加氢或异构化) 来提高产物中异构烃的含量; 而对于化学品 (如高附加值的 α-烯烃) 的生产, 则需要抑制烯烃的二次反应.

为了促进烯烃二次反应, Bao 等[9]设计了一种核壳催化剂, 即用分子筛催化剂包裹传统钴基费托合成催化剂. 在这种情况下, 费托合成的初级产物必须强行通过分子筛膜的孔道才能离开反应体系, 有效地促进了烯烃的二次反应, 使得产物中异构烃选择性显著增加.

线性 α-烯烃是一种重要的化工原料和中间体. 乙烯和丙烯可作为合成塑料的聚合单体; 碳数为偶数的 α-烯烃 (C_4, C_6 和 C_8) 可作为烯烃聚合的共聚单体; 更高碳数的 α-烯烃可用于生产可塑剂、洗涤剂、消毒杀菌剂以及高品质的合成润滑油[10~12]. 为了获得高附加值的线性 α-烯烃, Gao 等[10]提出了一种有效抑制烯烃二次反应的方法. 在固定床反应器中, 通过加入一种高沸点极性溶剂, 使催化剂颗粒完全被溶剂所包裹. 反应生成的 α-烯烃由于在极性溶剂中的溶解度非常低, 可以快速离开催化剂孔道, 从而降低其发生二次反应的可能性. 结果表明, 这种调变反应介质的方案使产物中 α-烯烃含量几乎不随其碳数的增加而减少, 为高选择性地生产线性 α-烯烃提供了一条新途径.

烯烃二次反应的控制也可以通过在反应体系中引入超临界流体来实现[11,13~15]. 采用非极性的正辛烷、正己烷或丙烷作为溶剂, 超临界费托合成可以明显地增加 α-烯烃的选择性. 图 2 对超临界费托合成和 Gao 等[10]提出的极性溶剂相费托合成进行了定性的比较. 对于超临界费托合成, 由于超临界溶剂同时具有液体的密度和气体的扩散能力, 可以提高烯烃在催化剂孔道中的脱附速率和扩散转移能力, 但因为这些非极性溶剂与烯烃溶为一相, 如果不能将溶剂连同烯烃快速移出反应器, 烯烃还会发生再

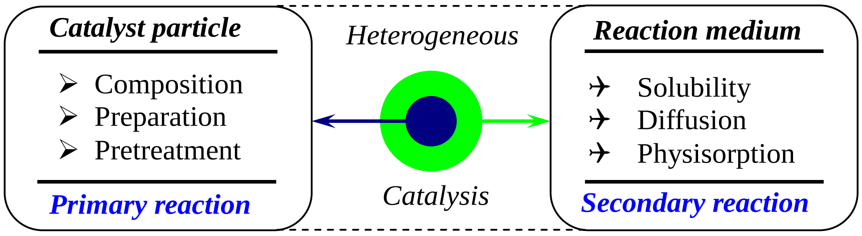


图 1　费托合成产物选择性控制方案

Fig. 1.　Scheme for product selectivity control in FTS.

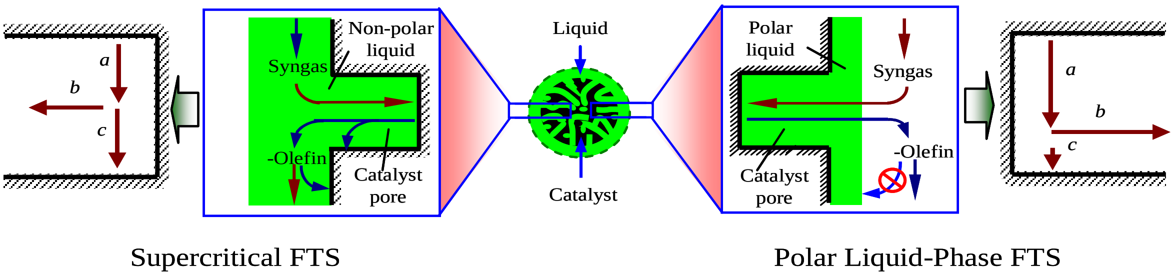


图 2 极性溶剂相费托合成与超临界费托合成 (非极性溶剂相) 的比较

Fig. 2. Comparison of polar liquid-FTS with supercritical FTS (non-polar liquid). *a*: desorption; *b*: diffusion; *c*: readsorption.

吸附和二次反应. 因此, 要获得高的烯烃选择性, 通常需要很高的溶剂进料流率, 这不但增加了溶剂循环的成本, 而且溶剂与产物分离困难. 同时, 高的系统压力也会增加过程功耗, 从而降低整个工艺的经济性. 对于极性溶剂相费托合成, 生成的烯烃由于在极性溶剂中的溶解度低, 因而可以快速地被排斥到液膜之外 (增加了脱附速率); 另一方面, 由于催化剂被极性液膜包裹, 烯烃很难再扩散回催化剂表面 (降低了再吸附速率), 导致烯烃发生二次反应的概率大大降低. 因此, 溶剂流率 (0.05 ml/min) 远低于超临界费托合成 (1 ml/min), 且产物和溶剂的分离也很容易 (相互不溶).

本课题组[10]曾重点考察了这种新颖的极性溶剂相费托合成方案在固定床反应器上的可行性. 如果在浆态床反应器中采用该溶剂相费托合成方案, 可以避免溶剂的循环, 也具有一定工业应用前景. 本文在实验室间歇反应釜中对这一方案的可行性进行了深入的研究. 聚乙二醇 (PEG) 是一种廉价易得、安全无毒、不易挥发、化学和热稳定性好的聚合物, 作为一种绿色溶剂而备受关注, 已经广泛应用于很多有机反应中[16], 包括纳米粒子催化的费托合成反应[17~20]. 本文对比了 PEG400 (平均分子量为 400) 和 PEG600、1,4-丁二醇、乙二醇等极性溶剂作为反应介质时的费托合成反应特性, 并考察了反应条件对产物选择性的影响.

1 实验部分

1.1 催化剂的还原

实验采用的催化剂为中科合成油技术有限公司自行研发的工业 Fe 基催化剂, 其制备方法和催化性能参见文献[21~23]. 新鲜制备的催化剂粒径小于 100 μm, 先在离线的石英管反应器中还原后, 再转移至高压釜中进行费托反应. 还原条件为 $n(H_2)/n(CO) = 2.05$, 压力 1×10^5 Pa, 250 °C, 空速 1000 h^{-1} 和还原 24 h. 实验中采用的溶剂 PEG、1,4 丁二醇、乙二醇和正辛烷均购自上海国药化学集团, 使用前未经处理.

1.2 实验过程与产物分析

用 50 g 溶剂将新鲜还原的催化剂转移至 100 ml 不锈钢高压釜中 (反应装置图参见文献[10]). 合成气 (由 99.95% 的 H_2 和 99.99% 的 CO 混合得到) 分别经脱硫、脱氧、脱羰和脱水后引入反应釜中, 并在常压下连续通气 3~5 min 以置换反应器中的空气, 之后关闭反应器出口阀门, 将其压力升至 3.0 MPa. 对于间歇反应, 关闭进气阀门并升至反应温度, 在搅拌速率为 800 r/min 的条件下反应 24 h (可调变量). 对于半连续反应, 首先按间歇反应的步骤进行, 每当反应压力低于 1.0 MPa 时, 打开进气阀补充合成气至压力为 3.0 MPa, 重复这一操作直至反应结束.

间歇釜中费托合成产物主要分为气相和液相. 间歇反应结束后, 先将反应器冷却至室温, 再取上层气相产物进行离线色谱分析. 再向反应器中加入含有内标 (十氢萘) 的萃取剂环己烷 20 ml, 升温至 60 °C 萃取 1 h, 取上层油样进行色谱分析. 气相产物采用 Agilent 6890N (C^0_{22}/C_{22} 玻璃柱, FID 检测器) 和 Agilent 4890N (13X 分子筛, TCD 检测器) 色谱分析 C_1~C_9 的烃、H_2、CO 和 CO_2, 液相产物采用 Agilent 6890N (DB-1 石英毛细管柱, FID 检测器) 分析.

1.3 物理量的定义

CO 转化率 (X_{CO}) 根据反应前后室温下反应器的压降估算. 考虑到测定间歇反应器的 CO 转化率不够精确, 本文只对其定性讨论, 不考察其对产物选

择性的影响. 产物总烃分布是指相同碳数烃 (包括正构和异构的烷烃与烯烃) 的总摩尔数随碳数的变化规律, 通常以 ASF 分布[3]描述. α-烯烃选择性或含量是指每个碳数的烃类产物中, α-烯烃所占的摩尔百分比. 链增长因子 α 是预测产物链增长能力的重要指标, 对于间歇式反应, 它比文献中通常采用 C_{5+}或 C_{21+}烃选择性来表示重质烃含量更准确, 这是由于间歇反应的产物量很少, 重质烃含量很难准确测量, 采用 C_{5+}等形式分析会使测量的重质烃选择性偏低. 文中 α 值的计算以 C_{10}~C_{30} 范围的总烃分布为基准, 采用最小二乘法拟合.

2 结果与讨论

2.1 典型产物分布

图 3 为极性溶剂相费托合成油相产物的典型色谱图. 可以看出, 随着产物碳数的增加, 每个碳数的 α-烯烃峰和正构烷烃峰总是成对出现, 且烯烃峰高、烷烃峰低, 直至两个峰完全重合, 这预示着产物中烯烷比基本不变, 这与传统费托合成产物差别非常大. 在后者色谱峰的低碳数区烯烃峰比烷烃的大[24], 但随着碳数增加, 烯烃峰面积逐渐下降, 而烷烃的逐渐增加, 预示着产物中烯烷比逐渐变小. 还可以看出, 异构烃和氧化物的色谱峰 (每两组正构烃色谱峰之间的小峰) 远远小于正构烃的峰, 基本可以忽略.

极性溶剂相费托合成的典型产物分布如图 4 所示. 可以看出, 在整个碳数范围内, 每个碳数的产物中 α-烯烃选择性均最大, 是正构烷烃的 3 倍多. 总烃分布出现先下降, 后升高再下降的特点. 从烃选择性的分段分布图 (图 4 中小图) 上可以看出, 甲烷含量非常低, 只占总产物的 6%; C_{10}~C_{20} 区间的烃含量最高, 约占总产物的 30%, 其中 α-烯烃的选择性也很高, 而这个碳数区间的 α-烯烃是高附加值的化工原料.

2.2 反应条件对产物选择性的影响

2.2.1 溶剂对产物选择性的影响

首先对比了极性溶剂和非极性溶剂 (代表传统浆态床反应器) 中费托合成产物分布的区别, 接着考察了不同极性溶剂中反应产物分布的差异.

传统浆态床费托合成实验通常采用液体石蜡作

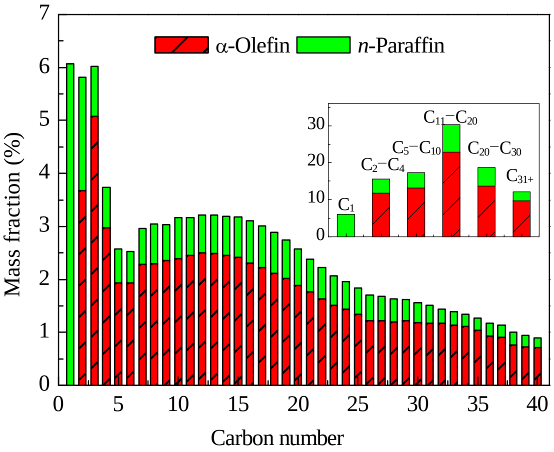


图 4 极性溶剂相费托合成的典型产物分布

Fig. 4. Typical product distribution of polar liquid-FTS.

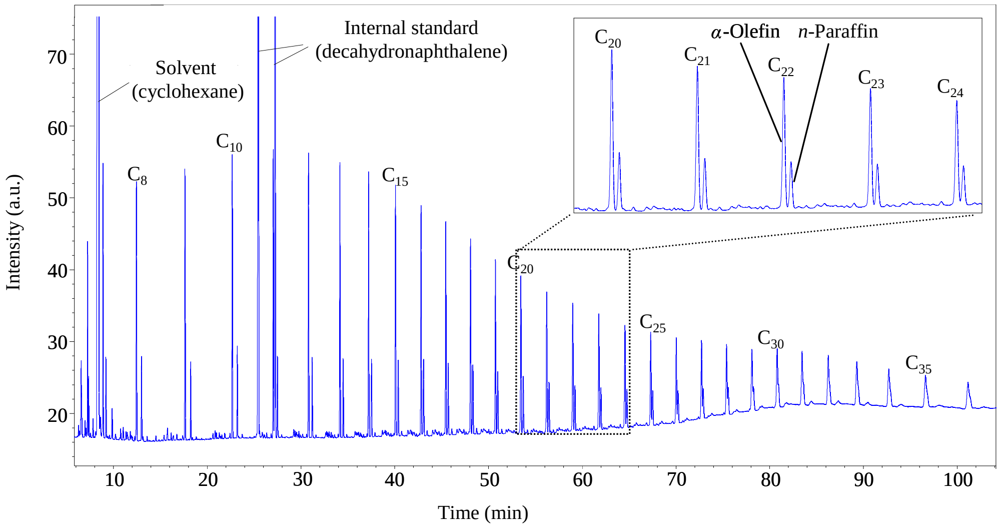


图 3 极性溶剂相费托合成液相产物的典型气相色谱

Fig. 3. Typical gas chromatogram of the liquid product from polar liquid-FTS.

为初始反应介质[25]. 这种非极性的液体混合物会干扰实际费托合成产物的准确分析. 由于间歇反应生成的产物量非常小, 加上实验操作和产物分析方面的考虑, 这里选择正辛烷作为非极性反应介质, 代表传统的浆态床费托合成.

图 5 是分别以 PEG400 和正辛烷为反应介质时间歇反应釜中费托合成反应后的产物分布和 α-烯烃选择性变化曲线. 可以看出, 当反应介质由正辛烷改为 PEG400 时, 尽管 C_2~C_4 烯烃选择性基本不变, 但 C_{5+} 的 α-烯烃选择性显著增加, 且基本不随碳数的变化而变化. 反应介质主要影响 α-烯烃二次反应的停留时间, 对反应速率的影响较小[10]. 由于低碳数区 α-烯烃在两种反应介质中的溶解度均较小, 扩散速率也非常快, 因此基本不受反应介质的影响. 但对于高碳数区, 当反应介质由正辛烷改为 PEG400 时, 烯烃在溶剂中的溶解度和扩散速率均发生明显变化, 造成烯烃在溶剂中停留时间大大缩短, 因而 α-烯烃选择性显著提高[10]. 对于 PEG400 体系, 由于不同碳数 (C_4 以上) α-烯烃在溶剂中溶解扩散等物性参数差别较小, 因而停留时间均非常短, 导致其含量几乎不随碳数的增加而减小. 但对于正辛烷体系, 随着 α-烯烃链长的增加, 它们在溶剂中的溶解度呈指数增加[4~5], 扩散速率也显著下降[6~7], 从而导致 α-烯烃二次反应的概率明显增加, 因此其含量随碳数增加而快速下降. 还可以看出, 溶剂对产物分布有一定的影响: PEG400 体系的产物 ASF 分布线性度更高, 更接近理想分布.

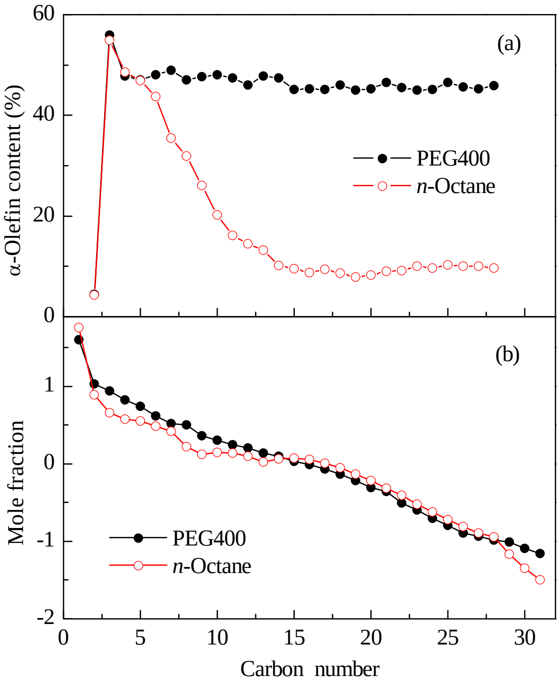


图 5 反应介质对费托合成产物分布及 α-烯烃选择性的影响

Fig. 5. Effect of reaction medium on α-olefin selectivity (a) and hydrocarbon distribution (b) for Fischer-Tropsch synthesis in a batch reactor. Reaction conditions: batch operation, 240 °C, initial pressure = 3.00 MPa (at room temperature), initial $n(H_2)/n(CO)$ = 2.03, 24 h.

图 6(a)~(d) 分别是 PEG400、PEG600、1,4-丁二醇和乙二醇中费托合成的产物选择性. 可以看出, 溶剂对 α-烯烃选择性、总烃分布、CO 转化率 (X_{CO}) 和链增长因子 α 均有所影响, 与文献[18]报道中溶剂对纳米粒子催化剂上费托反应速率有显著影响的结论相一致. 以 α-烯烃选择性为指标, 以 PEG400 作溶剂效果最好 (C_{3+}烯烃含量基本不随碳数变化), PEG600 和 1,4-丁二醇略差, 乙二醇最差. 从产物分布上看, 1,4-丁二醇作溶剂时 α 值 (0.90) 最大, 说明最有利于重质烃的生成; PEG400 ($\alpha = 0.87$) 和 PEG600 ($\alpha = 0.87$) 的次之, 乙二醇较差 ($\alpha = 0.83$). 对于反应活性 (CO 转化率), 1,4-丁二醇为溶剂时 X_{CO} 最高 (80%), 其次是 PEG400 (X_{CO} = 67%) 和乙二醇 (X_{CO} = 50%), PEG600 的最差 (X_{CO} = 16%). 综合考虑, PEG400 是调变 α-烯烃选择性较为理想的极性溶剂. 乙二醇的效果最差, 不但 α-烯烃选择性随碳数下降明显, 而且自身不稳定, 可能发生了脱水反应并参与链增长 (图 6(d)) 中甲烷偏低, C_2 总烃偏高, 与传统费托合成产物分布明显不符). 溶剂沸点差异是导致 α-烯烃选择性不同的一个重要原因. 例如, 乙二醇沸点 (常压下 197 °C) 最低, 1,4-丁二醇 (224 °C) 略高, PEG600 最高. 另外, 溶剂的密度和粘度等其它性质也可能对费托反应性能产生很大的影响, 需要进一步的研究.

2.2.2 反应温度和 CO 分压对产物选择性的影响

反应条件对费托合成二次反应速率影响较大[3]. 例如, 高的 CO 分压会抑制烯烃的再吸附及其二次反应, 高温可以同时提高费托合成初级反应和二次反应的反应速率. 因此, 通过优化反应条件, 可以进一步提高 α-烯烃选择性. 同时, 在极性溶剂相中考察反应条件对费托合成反应性能的影响, 可以排除非本征因素 (溶解、扩散等) 对产物选择性的影响, 即可以在烯烃含量基本不随碳数变化的情况下考察产物分布的规律性, 这是传统费托合成很难做到的.

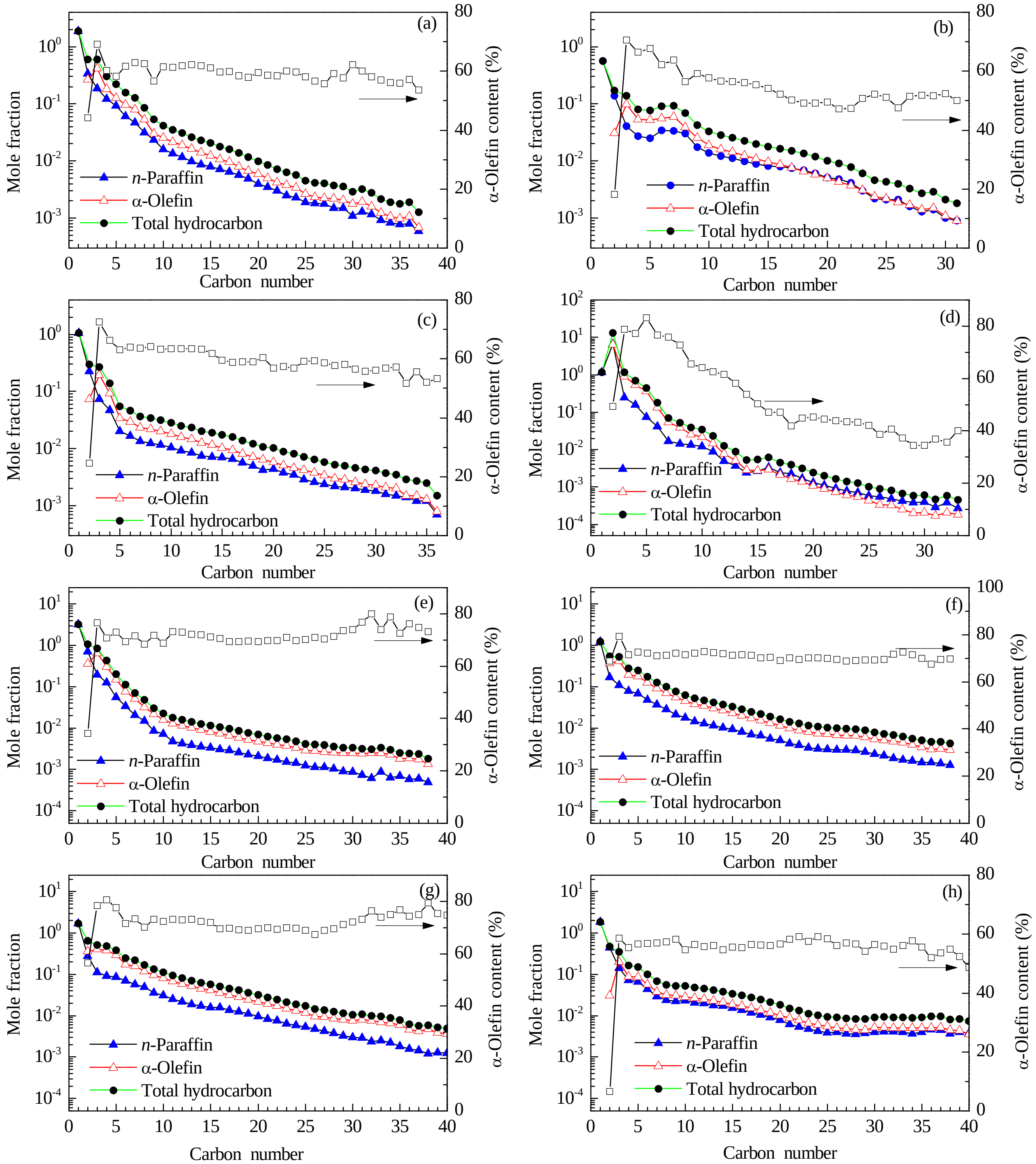


图 6 费托合成 α-烯烃选择性与烃类产物分布

Fig. 6. α-Olefin selectivity and hydrocarbon distribution of Fischer-Tropsch synthesis. Reaction conditions: (a) PEG400 liquid, batch operation, 200 °C, initial pressure 3.00 MPa (at room temperature), initial $n(H_2)/n(CO)$ = 2.03, 24 h; (b) PEG600 liquid, batch operation, 200 °C, initial pressure 3.00 MPa (at room temperature), initial $n(H_2)/n(CO)$ = 2.03, 24 h; (c) 1,4-butanediol liquid, batch operation, 200 °C, initial pressure 3.00 MPa (at room temperature), initial $n(H_2)/n(CO)$ = 2.03, 24 h; (d) glycol liquid, batch operation, 200 °C, initial pressure 3.00 MPa (at room temperature), initial $n(H_2)/n(CO)$ = 2.03, 24 h; (e) PEG400 liquid, batch operation, 240 °C, initial pressure 3.00 MPa (at room temperature), initial $n(H_2)/n(CO)$ = 1.00, 24 h; (f) PEG600 liquid, batch operation, 220 °C, initial pressure 3.00 MPa (at room temperature), initial $n(H_2)/n(CO)$ = 1.00, 24 h; (g) catalyst particle size 20–40 mesh, PEG400 liquid, batch operation, 240 °C, initial pressure 3.00 MPa (at room temperature), initial $n(H_2)/n(CO)$ = 1.00, 24 h; (h) PEG400 liquid, 220 °C, initial pressure 3.00 MPa (at room temperature), initial $n(H_2)/n(CO)$ = 2.01, semi-continuous operation, 144 h.

比较图 5 (PEG400 为溶剂) 和图 6(a) 可以看出，

当反应温度从 200 °C 升至 240 °C 时, α-烯烃的平均

含量从约 60% 降至约 50%, 而 CO 转化率从 67% 升至 93%. 这是由于尽管温度升高使烯烃在溶剂中的扩散增强, 溶解度下降, 烯烃停留时间减少, 但同时使烯烃二次反应的速率显著增加, 因而总的效果是 α-烯烃含量随温度升高略有下降. 较高的温度可以增加费托合成的 CO 转化率.

对比图 6(e) 和图 5 (PEG400 为溶剂) 可以看出, 当初始 $n(H_2)/n(CO)$ 从 2.03 下降至 1.00 时, CO 转化率从 93% 下降至 45%, α-烯烃平均含量从约 50% 上升至约 70%. 这是由于提高 CO 分压, 使得 CO 和 α-烯烃在催化剂表面发生竞争吸附[7], 降低了烯烃发生二次反应的本征速率, 因而 α-烯烃含量显著提高. 通常, CO 转化率与 H_2 分压成正比[3], 因此 H_2/CO 比下降会导致 CO 转化率降低.

比较图 6(b) 和 (f) 可以发现, 尽管在低温、高 H_2/CO 比时, 以 PEG600 为溶剂的反应活性较低 (X_{CO} = 16%), 产物中 α-烯烃含量随碳数增加而略有下降, 但当采用较高温度和较低 H_2/CO 比时, CO 转化率有所提高 (X_{CO} = 26%), 同时, α-烯烃平均含量超过了 70%. 这说明通过优化反应条件, 可使原本反应效果较差的反应体系获得更好的反应结果.

2.2.3 催化剂粒径大小对产物选择性的影响

对于传统的费托合成, Iglesia 等[7]认为, 反应物和产物在催化剂孔道中的扩散对烯烃二次反应的影响较大, 粒径越大, 烯烃二次反应越快, 产物中烯烃含量越少. 本文在 PEG400 溶剂中比较了大颗粒 (粒径范围 350~830 μm 或 20~40 ASTM 目) 与小颗粒 (新鲜催化剂, 粒径小于 100 μm) 催化剂的反应行为, 结果见图 6(e) 和 (g). 可以看出, 对于极性溶剂相费托合成, 催化剂粒径对产物 α-烯烃选择性的影响非常小. 采用大颗粒催化剂得到的 α-烯烃选择性依然不随碳数变化而变化, 这说明在极性溶剂相中, 产物在催化剂孔道中的扩散速率非常大, 因而产物扩散不是反应的速控步骤. 采用大颗粒时 CO 转化率有所下降 (小颗粒 X_{CO} = 45%, 大颗粒 X_{CO} = 25%), 这是由于当两个实验所采用的催化剂质量相同时, 较大颗粒的催化剂比表面积较小, 因而活性位减少, CO 转化率下降.

2.2.4 反应时间对产物选择性的影响

对于传统费托合成, α-烯烃在反应器中停留时间越长, 发生二次反应的概率就越大, 最终产物中 α-烯烃含量就越低. 对于极性溶剂相费托合成反应体系, 为了考察烯烃在反应器中的停留时间对其选择性是否存在影响, 设计了以下半连续实验: 在间歇反应器中, 每当反应器的系统压力低于 1.00 MPa 时, 打开进气阀向反应器中补充新鲜合成气至压力升到 3.00 MPa, 不断重复此操作直至累计反应时间达到 144 h. 这种操作模式不但可以增加反应器中 α-烯烃的停留时间, 而且使其生成量大大增加. 图 6(h) 表明, α-烯烃含量依然不随碳数的增加而下降, 与传统费托合成的结果差别很大. 这表明对于极性溶剂相费托合成, 生成的烃类产物可以快速离开催化剂表面和溶剂相, 因而 α-烯烃二次反应的概率不因反应时间和生成 α-烯烃实际量的增加而增加, 这与文献[10]结果一致.

2.3 产物烃分布比较

对于极性溶剂相费托合成, 由图 5 和图 6 可以看出, 尽管 α-烯烃的选择性在 C_{4+} 范围内基本不随碳数而变化, 但总烃分布有的接近理想 ASF 分布, 有的则呈现明显的正偏离, 必须用两个或多个链增长因子 α 才能较好地描述这一现象, 且不能用传统的烯烃再吸附及二次反应理论来解释.

$$\alpha = \frac{k_g}{k_g + k_{t,p} + k_{t,o}} \tag{1}$$

式 (1) 为费托合成链增长因子 α 的计算公式, 其中 k_g 为链增长速率常数, $k_{t,p}$ 为烷烃的链终止速率常数, $k_{t,o}$ 为烯烃链终止速率常数. 烯烃再吸附理论认为, 由于烯烃会发生再吸附及二次反应, 导致 $k_{t,o}$ 减小, 从而使 α 值增加, 产物分布出现正偏离. 然而, 由上式可见, $k_{t,o}$ 的减小必然会导致 $k_{t,o}/k_{t,p}$, 即烯烷比或烯烃含量的变化. 既然极性溶剂相费托合成产物中烯烃含量基本不随碳数变化, 说明式 (1) 中 $k_{t,o}/k_{t,p}$ 为常数, 不随碳数变化. 那么, 如果产物分布出现正偏离, 即 α 值随碳数的增加而增加, 就可能是由于链增长速率常数 k_g 增大或总的链终止速率常数 $k_{t,o} + k_{t,p}$ 减小所致. 文献[10]报道, 在完全相同的 CO 转化率条件下, 极性溶剂的添加使产物分布的 α 值有所增加, 表明这种极性溶剂体系可能会促进链增长反应, 使 k_g 增大. 这一问题还需要在连续实验装置中稳态反应条件下作进一步的研究, 以排除间歇反应器中产物累积等效应对产物分布的影响.

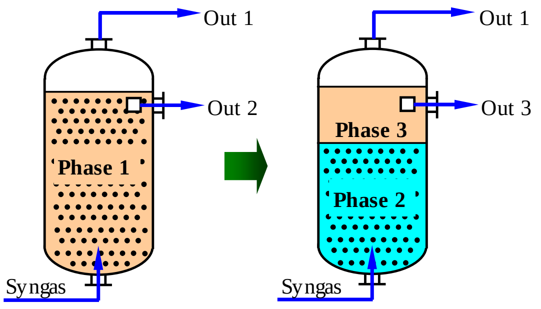
以上所有极性溶剂相费托合成实验中总烃分布

的 α 值均大于 0.85, 表明该体系有利于生成长链烃. 在该极性溶剂相反应体系中, 链长较长的烃可用于生产优质蜡或被裂解成柴油, 链长较短的烃可以分离得到高纯度的线性 α-烯烃, 两者耦合生产将有利于提高费托合成过程的经济性.

2.4　工业应用前景

以上研究表明, 极性溶剂相费托合成最显著的特点是产物中 α-烯烃的含量几乎不随碳数而变化, 这对于高选择性地生产各种链长的直链 α-烯烃非常重要. 如果能将催化剂自身的组成结构优化与反应介质的合理选择有机结合, α-烯烃的含量还可进一步提高.

对于传统的浆态床鼓泡塔反应器, 为了使催化剂很好地分散在反应介质 (反应生成的蜡) 中, 通常需要采用粒径较小的催化剂颗粒, 但会造成催化剂与蜡的分离困难. 如图 7(a) 所示, 当从反应器中排放蜡时, 总是不可避免地夹带大量的催化剂颗粒. 这些细小的颗粒需要非常复杂的工艺才能从蜡中分离出来. 但是, 对于本文提出的极性溶剂相费托合成, 如图 7(b) 所示, 催化剂分散在溶剂相中, 生成的烃类产物在溶剂中溶解度较小, 因此可以快速离开溶剂相, 在上部形成新的产物相, 避免了产物与催化剂的分离问题. 这一方案得到了上述半连续实验结果的验证: 当反应结束后打开反应釜, 大量烃类产物浮于溶剂相之上, 催化剂全部悬浮在溶剂相中. 这是由于所采用的极性溶剂 PEG 400 的密度、粘度和在催化剂表面的吸附能力均大于烃类产物, 因此可以更好地悬浮催化剂颗粒.



(a)　　(b)

图 7　传统浆态床鼓泡塔反应器和极性溶剂相费托浆态床鼓泡塔反应器示意图

Fig. 7.　Traditional (a) and polar liquid (b) FTS slurry bubble column reactor. Phase 1: catalyst and wax; Phase 2: catalyst and liquid; Phase 3: wax; Out 1: gaseous product; Out 2: catalyst and wax; Out 3: wax.

如果采用极性溶剂作为浆态床反应器的反应介质, 由于溶剂组成单一, 其溶解扩散性能将更容易测定, 这可大大简化费托合成的动力学和流体力学研究, 加快费托合成的工业化进程.

3　结论

通过将费托合成的反应介质由传统的长链烃改变为极性溶剂, 在间歇反应釜中实现了产物选择性的有效控制, 使 α-烯烃选择性显著提高, 且基本不随碳数而变化. 这一特性可用于高选择性地生产各种链长的线性 α-烯烃. 同时, 费托反应的链增长概率因子均大于 0.85, 说明该体系有利于长链烃的生成, 可在一个反应器中实现 α-烯烃和液体燃料的多联产. 结果表明, 新生成的烃类产物可以快速离开溶剂和催化剂相, 即可以实现在反应的同时分离产物, 这一特性可用于优化费托合成浆态床反应器, 避免传统工艺存在的催化剂与蜡分离困难的问题. 该体系还演示了反应环境在非均相催化反应过程中控制产物选择性的重要意义.

致谢　本研究得到了中科合成油技术有限公司在设备和资金上的大力支持, 特此鸣谢.

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英译文

English Text

Fischer-Tropsch synthesis (FTS) converts coal, natural gas, and biomass into liquid fuels or chemicals via syngas and will be an important route for the production of petroleum-based products in the future [1–3]. Generally, FTS is a consecutive reaction and linear α-olefins are its main intermediates [3]. These α-olefins can undergo secondary hydrogenation and isomerization reactions to the corresponding paraffins and isomers. They can also undergo secondary chain initiation or hydrogenolysis to heavier and lighter hydrocarbons. The olefin secondary reactions are markedly influenced by the catalyst environment (that is, the reaction medium) [4–7]. The catalyst pores are frequently filled with the wax formed during reaction, which reduces the transport rate of α-olefins in the catalyst pore and enhances α-olefin solubility in the liquid phase. This leads to a higher probability for olefin secondary reactions and thus a lower olefin content in the final product. Moreover, this physical effect is dependent on the chain length of the α-olefin. Therefore, the olefin/paraffin ratio in a conventional FTS product decreases exponentially with chain length. Accordingly, to effectively limit olefin secondary reactions and to get an ideal FTS product, the type of reaction medium and catalyst particle used [8] should be considered together, as shown in Fig. 1.

The olefin secondary reactions can be enhanced or inhibited to give a desired product. For the production of liquid fuels, e.g. gasoline, olefin secondary reactions should be enhanced to increase the isomeric hydrocarbon content to improve the gasoline octane value. On the other hand, for α-olefin synthesis, the olefin secondary reactions should be totally suppressed.

To enhance olefin secondary reactions, Bao et al. [9] designed a core-shell catalyst by wrapping a traditional cobalt-based catalyst with a zeolite catalyst. This required the primary products of FTS to diffuse through the zeolite membrane to leave the catalyst particle. As a result, secondary reactions were promoted, and the product was mainly isomeric hydrocarbons.

Linear α-olefins are highly valuable chemicals and intermediates for the production of many industrial and consumer products [10–12]. Even numbered carbon α-olefins (C_4, C_6, and C_8) are used as co-monomers for ethylene and propylene polymerization. Higher molecular weight olefins are used in plasticizers, household detergents, and sanitizers. Linear C_{10} olefins are used in premium value synthetic lubricants. In order to increase α-olefin selectivity, Gao et al. [10] have proposed an effective method for suppressing olefin secondary reactions, which was achieved by surrounding the traditional FTS catalyst particle with a polar liquid by co-feeding this liquid in a fixed bed reactor. α-Olefins, once produced, can leave the catalyst pores rapidly due to their negligible solubility in the polar liquid, which prevents their secondary reactions. The results showed that the α-olefin content was almost independent of the carbon number, and it was suitable for the highly selective synthesis of linear α-olefins with long molecular chains.

Olefin secondary reactions can also be inhibited with a supercritical FTS system that uses a non-polar liquid, e.g., *n*-octane, *n*-hexane or propane, as the reaction medium [11,13–15]. Figure 2 illustrates a comparison between supercritical FTS and polar liquid-FTS proposed by Gao et al. [10]. In supercritical FTS, the desorption and transport of α-olefin in the catalyst pores were promoted because the supercritical liquid has a liquid-like density and allowed gas-like diffusion rates. However, because α-olefins can dissolve in the non-polar supercritical liquid, they can still return to the catalyst surface and undergo secondary reactions if they stay in the reactor for a long time. Therefore, to get high α-olefin selectivity, the liquid flow rate should be as high as possible. This would increase the cost of liquid separation and recycling. Also, the higher reactor pressure required for the supercritical state will increase energy consumption. In contrast, in the polar liquid-FTS, α-olefins can leave the catalyst pores and the liquid rapidly (desorption is promoted) due to its low solubility in the polar liquid. At the same time, they cannot diffuse back to the catalyst surface (readsorption is inhibited) through the polar liquid. Therefore, olefin secondary reactions are avoided. The liquid flow rate for polar liquid-FTS (0.05 ml/min [10]) can be much less than that for supercritical FTS (1 ml/min [13]). In addition, product separation from the polar liquid is much easier than that from a non-polar liquid.

Previously, we studied this novel polar liquid-FTS in a fixed bed reactor [10]. It would be significant to also apply this scheme in a slurry phase reactor because this can avoid liquid recycle. In this work, the product distribution of FTS in a polar liquid was studied in an autoclave reactor. The effects of liquid reaction conditions on FTS product selectivity were considered. Polyethylene glycol (PEG) is a cheap, readily available, safe, and stable polymer with a high boiling point. It has been used as a green liquid in many organic reactions [16] including FTS catalyzed by nanoparticles [17–20]. PEG was used as the main test liquid in this work.

1 Experimental

1.1 Catalyst and liquid

A stable iron-based catalyst prepared by Synfuels China Co. Ltd. for an industrial slurry reactor was a used. The preparation and catalytic performance of this catalyst had been reported [21–23]. The fresh catalyst (particle size < 100 μm) was reduced in a fixed bed reactor (quartz tube, 10 mm i.d., 0.5 m in length) using syngas with $n(H_2)/n(CO)$ of 2.05, 1×10^5 Pa, 250 °C, and 1000 h^{-1} for 24 h. PEG, 1,4-butanediol, and glycol were purchased from Guoyao Group (Shanhai, China) and used without further purification.

1.2 Reactor operation and product analysis

Freshly reduced catalyst was transferred rapidly into a 100 ml autoclave reactor (see Gao et al. [10] for details) under the protection of 50 g liquid. Syngas was a blend of 99.95% H_2 and 99.99% CO. This was purified by passing through a series of traps for removing tiny amounts of oxygen, water, and other impurities. The reactor was purged continuously with syngas for 3–5 min, and the reactor pressure was then elevated to 3.00 MPa. For the batch operation, the autoclave was maintained at the reaction temperature with stirring at 800 r/min for about 24 h.

After reaction, the autoclave was cooled to room temperature and the gaseous product was analyzed by an offline GC (Agilent 6890N, C_{22}^{0}/C_{22} column, FID detector). The liquid product was extracted by cyclohexane at 60 °C with decahydronaphthalene as an internal standard, and was analyzed by an Agilent 6890N GC (DB-1 capillary column, FID detector). The details of the reactor configuration and product analysis can be found in Ref. [10].

1.3 Parameter definition

The CO conversion (X_{CO}) for the batch operation was determined by the pressure drop and composition changes of the gas phase before and after reaction. The effect of CO conversion on product selectivity is not discussed in this paper because accurate X_{CO} values were difficult to get. The total hydrocarbon (all hydrocarbon products with the same carbon number) distribution was defined as the distribution of the total hydrocarbon amount with carbon number, which is usually described by the ASF (Anderson-Schulz-Flory) probability pattern [3]. The α-olefin selectivity or content was defined as α-olefin/total hydrocarbon with the same carbon number × 100%. The chain growth probability α is an important parameter for predicting FTS product selectivity, and is more reliable than the generally used parameters such as C_{5+} or C_{21+} selectivity for a batch experiment. This is because the amount of product produced in the batch mode was so small that the heavy hydrocarbon amounts were hard to measure accurately. In this paper, the α value was estimated by the least square method using hydrocarbons in the carbon number range of C_{10}–C_{30}.

2 Results and discussion

2.1 Typical product distribution

Figure 3 shows a typical GC chromatogram of the oil sample from polar liquid-FTS. In the whole carbon number range, the α-olefin and *n*-paraffin peaks appeared in pairs and the peak areas of the former were all larger. This result was an obvious difference from the GC spectrum for the products of traditional FTS [10,24], in which the peak area of the α-olefin decreased rapidly with increasing carbon number. Also, the peak areas of isomeric hydrocarbons and oxygenates (between every two sets of high peaks in Fig. 3) were much less than those of the normal hydrocarbons and can be neglected.

The typical product distribution of polar liquid-FTS is illustrated in Fig. 4. For each carbon number in the C_{2+} range, the selectivity for α-olefin was more than three times larger than that for *n*-paraffin. The total hydrocarbon selectivity in the C_{5+} range increased at first and then decreased with carbon number. The inset in Fig. 4 shows that the methane content was very low, while the hydrocarbon content in the C_{11}–C_{20} range was the highest and accounted for about 30 wt%. The α-olefins in this carbon number range are a high value-added industrial feedstock.

2.2 Effect of reaction conditions on product selectivity

2.2.1 Effect of liquid on product selectivity

In this section, first, the product distribution of FTS in a polar liquid is compared with that of FTS in a non-polar liquid (representing traditional slurry phase FTS). Then, the effect of the different polar liquids on FTS product selectivity is discussed.

Liquid paraffin (a mixture of saturated hydrocarbons) is frequently used as the liquid of slurry-phase FTS experiments [25]. Unfortunately, this mixture can make the analysis of the FTS product very difficult, especially for a batch experiment where the product amount is much less than the liquid amount. Therefore, in this study, *n*-octane was used as the non-polar liquid of the slurry-phase FTS that was used for comparison.

Figure 5 shows that when the reaction medium was changed from *n*-octane (non-polar) to PEG400 (polar), the α-olefin selectivity in the C_{5+} range increased markedly and became almost independent of the carbon number, while the selectivity in the C_2–C_4 range remained unchanged. Gao et al. [10] proposed that the reaction medium has a larger influence on the residence time of the olefin in the catalyst pore than on the reaction rate of the olefin secondary reactions. For the olefins in the C_2–C_4 range, because their residence times were very short for both the polar and non-polars, their selectivities were insensitive to the liquid. For the olefins in the C_{5+} range, however, the solubilities and diffusivities differ significantly in *n*-octane and PEG400. This had a marked influence on the residence time of the olefins in catalyst pores. Therefore, the selectivities for olefins increased prominently. In contrast, the solubilities of olefins with different chain lengths in the C_{5+} range in the polar liquid were all negligible and were thus nearly equal. As a result, the olefin selectivity became less dependent of the carbon number. In the *n*-octane system, the olefin solubility increased exponentially with carbon number [4,5]. This was because its diffusivity decreased with an increase of chain length [6,7], resulting in a higher secondary reaction probability for heavier olefins. Figure 5 also illustrates that the product distribution from the polar liquid-FTS almost followed the ideal ASF pattern, possibly because of less olefin secondary reactions.

The α-olefin selectivity and product distribution of FTS in the different polar liquids, PEG400, PEG600, 1,4-butanediol, and glycol, are compared in Figs. 6(a)–(d). The PEG400 system showed the highest α-olefin selectivity (independent of carbon number in the C_{3+} range), followed by PEG600 and 1,4-butanediol, and the glycol system gave the lowest selectivity (which depended on carbon number). The chain growth factor α is an important parameter reflecting the product selectivity of FTS. A larger α value gives a higher selectivity to heavy hydrocarbons. The α values were calculated from the ASF plots shown in Figs. 6(a)–(d). The order of α values was 1,4-butanediol (0.90) > PEG400 (0.87) > PEG600 (0.87) > glycol (0.83). Fan et al. [18] have studied the effect of the liquid on reaction activity (CO conversion) in a nanoparticle catalyst in a catalyzed and low temperature FTS reaction system. They found that the reaction medium had a marked influence on the CO conversion, which is consistent with the results in this study. The order of decreasing CO conversion in the different liquids was 1,4-butanediol (80%) > PEG400 (67%) > glycol (50%) > PEG600 (16%).

From the above comparison of α-olefin selectivity, chain growth factor, and CO conversion, we found that PEG400 was the best liquid for tuning the α-olefin selectivity and glycol was the worst. In the glycol system, the α-olefin content decreased with carbon number, while the liquid itself was unstable in the reaction. Figure 6(d) shows that there were some irregularities in the product distribution: C_1 was lower and C_2 was higher than the typical FTS product distributions in the other figures. This phenomenon indicated that glycol may undergo dehydration and chain initiation reactions. The boiling point of the liquid is an important parameter for the effect of the liquid on α-olefin selectivity. For example, the order of the liquid boiling point was glycol (197 °C under atmosphere pressure) < 1,4-butanediol (224 °C) < PEG400 < PEG600, which is the order of the α-olefin selectivity. Moreover, the density, viscosity, and other physical properties of the liquid may also influence the FTS reaction performance, which needs further investigation.

2.2.2 Effects of reaction temperature and CO partial pressure on product selectivity

The reaction condition has a large influence on olefin secondary reactions [3]. For instance, a high CO partial pressure inhibits the readsorption of olefins on the catalyst surface while a high reaction temperature promotes the reaction rate of both primary reactions and olefin secondary reactions. Therefore, the α-olefin selectivity can be further improved by choosing proper reaction conditions. In addition, because the α-olefin selectivity in a polar liquid was nearly independent of carbon number, this provides a new route to study the effect of reaction conditions on FTS product distribution.

From Figs. 5 (PEG400 as the liquid) and 6(a) we can find that when reaction temperature increased from 200 to 240 °C, the α-olefin content decreased from 60% to 50%, while the CO conversion increased from 67% to 93%. At the higher reaction temperature, olefins have a faster diffusion rate in the catalyst pore and a lower solubility in the liquid, which leads to a reduction of residence time for the olefin secondary reactions. However, the olefin secondary reaction rates increased at the higher reaction temperature. Therefore, whether the α-olefin selectivity increased or decreased depends on which factor is dominant.

It can be seen from Figs. 5 and 6(e) (PEG400 as liquid) that as the initial H_2/CO ratio was reduced from 2.03 to 1.00, the α-olefin selectivity increased from 50% to 70% while the CO conversion dropped from 93% down to 45%. It was reported [3] that CO can compete with α-olefins for the active sites [7], and thus a lower H_2/CO ratio favors the formation of α-olefin. Because the FTS reaction rate generally has a first order dependence on H_2 partial pressure [3], the CO conversion decreased with the decrease of H_2/CO ratio.

Figures 6(b) and (f) show that the α-olefin selectivity and CO conversion can be improved significantly by tuning the reaction conditions. When using PEG600 as liquid, although the average α-olefin selectivity was less than 60% with the higher H_2/CO ratio and lower temperature, it increased to more than 70% with the lower initial H_2/CO ratio and higher temperature. The CO conversion increased from 16% to 26% due to the higher reaction temperature employed.

2.2.3 Effect of catalyst particle size on product selectivity

For conventional FTS, Iglesia et al. [7] pointed out that the diffusion of reactant and product in the catalyst pores has a significant influence on the olefin secondary reactions. A larger particle size allows more olefin secondary reactions and thus a lower olefin content in the final product. This was tested in the polar liquid-reaction system using two sizes of catalyst particles (large pellet: 350–830 μm or 20–40 ASTM mesh; small pellet: < 100 μm). Comparing Figs. 6(e) and (g), we can find that the α-olefin contents (C_{5+} range) in the two reaction systems were almost independent of carbon number. This result indicated that the diffusion rate of olefins in the polar liquid was so fast that diffusion was not the rate controlling step. The CO conversion decreased when the large catalyst particle was used (small pellet: X_{CO} = 45%; large pellet: X_{CO} = 25%), which was attributed to the lower specific surface area of the large catalyst particle because the catalyst amounts were the same for both reaction systems.

2.2.4 Effect of reaction time on product selectivity

For conventional FTS, a longer residence time of α-olefins in the reactor gives a higher probability of olefin secondary reactions, and thus a lower α-olefin content in the final product. A semi-continuous experiment was designed here to study whether the reaction time has an influence on α-olefin selectivity in this polar liquid reaction system. In this procedure, as the reaction pressure in the autoclave dropped to 1.00 MPa, the syngas inlet valve was opened and the reaction pressure was elevated to 3.00 MPa. This operation was repeated until the total reaction time exceeded 144 h. This semi-continuous experiment increased the residence time of the α-olefins in the reactor and also increased the product amount formed. Figure 6(h) shows that the α-olefin content was still independent of carbon number even after 144 h on stream. This result indicated that for the polar liquid-FTS, the hydrocarbon product can leave the catalyst surface and liquid phase quickly, thereby, the probability of α-olefin secondary reactions did not increase with the increase of reaction time and the product amount formed, which is consistent with the literature [10].

2.3 Comparison of product distribution

For the polar liquid-FTS, it can be seen from Figs. 5 and 6 that most of the product distributions deviate from the ideal ASF pattern and can only be well described by two or more chain growth factors although all the α-olefin selectivities were nearly independent of carbon number in the C_{4+} range. It is hard to explain this by the well-known olefin secondary reaction mechanism:

$$\alpha = \frac{k_g}{k_g + k_{t,p} + k_{t,o}} \tag{1}$$

Equation (1) is the expression for the chain growth factor α, where k_g, $k_{t,p}$, and $k_{t,o}$ are the rate constants of chain growth, chain termination for paraffin, and chain termination for olefin, respectively. According to the olefin readsorption mechanism, the olefin selectivity decreases exponentially with carbon number due to the consumption of olefins by secondary chain initiation, which leads to a decrease of $k_{t,o}$ and thus an increase of the α value. Moreover, $k_{t,o}/k_{t,p}$, which reflects the olefin/paraffin ratio, will decrease with carbon number. However, for the polar liquid-FTS, the olefin content was independent of carbon number in the C_{4+} range, which means that $k_{t,o}/k_{t,p}$ was constant for the carbon numbers in the C_{4+} range. As a result, the possible reasons for the change of α value (deviation of the product distribution) can only be due to an increase of k_g or a decrease of $k_{t,p} + k_{t,o}$. Gao et al. [10] reported that under the same CO conversion level, the addition of a polar liquid in a fixed bed reactor favored the chain growth reaction (k_g increases) and led to the increase of the α value. For the slurry reactor in this study, however, the reason of the non-ideal product distribution should be further studied in a continuous reactor under steady state conditions in order to exclude the possible effect of product accumulation on product distribution.

The chain growth factors were larger than 0.85 for almost all the reactions that used a polar liquid as the reaction medium. This implied that the polar liquid reaction system favored the production of heavy hydrocarbons. These heavy hydrocarbons can be upgraded to a high quality wax or be cracked into diesel while the lighter ones can be used to synthesize high purity linear α-olefins. The combined generation of diesel and linear α-olefins will improve the economics of the FTS process.

2.4 Industrial application

The most significant characteristic of polar liquid-FTS is the carbon number independence of the α-olefin selectivity. This is very important for the production of linear α-olefins with various chain lengths. If liquid selection and the catalyst itself can be further optimized, the α-olefin selectivity can be higher.

For a traditional slurry bubble column reactor, fine catalyst particles are usually chosen in order to disperse the catalyst well in the reaction medium. This brings the challenge of catalyst and wax separation. Figure 7(a) shows that when the wax is removed from reactor, the catalyst is always entrained with it. This would increase the complexity of product separation. In contrast, for the polar liquid-FTS, as shown in Fig. 7(b), the catalyst is only present in the liquid phase. The hydrocarbon products, once generated, leave the liquid phase immediately to form a new phase on the top of it. Therefore, the wax product can be separated easily from the catalyst. This was confirmed by the above semi-continuous experiment: when the reactor was observed after reaction, a large amount of hydrocarbon product was found floating on the top of the liquid phase while the catalyst particles were all suspended in the liquid phase. This can be attributed to the greater density, viscosity, and adsorption ability of the polar liquid used.

When a polar liquid is used as the reaction medium of a slurry reactor, FTS kinetics and hydrodynamics investigations will be easier because of the more convenient measurement of the physical property parameters in a polar liquid comprising a single component.

3 Conclusions

By changing the reaction medium of Fischer-Tropsch synthesis (FTS) from a conventional heavy hydrocarbon to a polar liquid, effective control of α-olefin selectivity was obtained in a batch autoclave reactor. The α-olefin selectivity increased markedly and was almost independent of chain length in the C_{4+} range, which would provide a novel route for the selective synthesis of linear α-olefins. The high chain growth factors (> 0.85) indicated that the chain growth reaction was favored in the polar liquid-FTS system and the combined production of α-olefins and liquid fuels can be achieved in a single reactor. A semi-continuous experiment revealed that the hydrocarbon products, once formed, leave the liquid-catalyst phase immediately, and this system has product separation during reaction, which avoids the difficulty of separating fine catalyst particles from wax product that exists in traditional slurry phase FTS. This study also demonstrated the importance of the reaction environment in the control of product selectivity in heterogeneous catalytic reactions.

Acknowledgments

The authors acknowledge the support received from the Synfuels China Co. Ltd.

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