P/Rh 比对 PPh₃-Rh/SiO₂ 催化剂上丙烯氢甲酰化反应的影响

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摘要: 研究了 P/Rh 比对 PPh₃-Rh/SiO₂ 催化剂上丙烯氢甲酰化反应性能的影响. 结果表明, 当 P/Rh 比为 15 时, 丙烯氢甲酰化反应性能最好, 丙烯转化率为 25.9%, 产物丁醛正异比为 14, 转换频率为 241 h⁻¹. PPh₃-Rh/SiO₂ 催化剂的固体 ³¹P 核磁共振结果表明, 在合成气气氛下, 物理吸附的 PPh₃ 能够溢流到 Rh/SiO₂ 表面形成化学吸附的 PPh₃, 从而促进了具有氢甲酰化活性的铑膦络合物的形成. Wilkinson 催化平衡理论也很好地解释了本实验结果.
关键词: 三苯基膦; 铑; 二氧化硅; 膦铑比; 丙烯; 氢甲酰化; 核磁共振
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Influence of Phosphine Concentration on Propylene Hydroformylation over the PPh₃-Rh/SiO₂ Catalyst

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Abstract: The effect of triphenyl phosphine concentration in the novel PPh₃-Rh/SiO₂ catalyst for propylene hydroformylation was studied and found an optimum P/Rh ratio of 15, a butyraldehyde n/i ratio of 14, a butyraldehyde TOF of 241 h⁻¹, and high catalytic stability for PPh₃-Rh/SiO₂. Solid-state ³¹P NMR shows that in an atmosphere of syngas the physically adsorbed PPh₃ migrates onto the surface of Rh/SiO₂ where it chemically adsorbs and then promotes the in situ formation of carbonyl phosphine complexes.
Key words: triphenyl phosphine; rhodium; silica; phosphine/rhodium ratio; propylene; hydroformylation; nuclear magnetic resonance

与多相催化反应相比, 均相催化反应能够在较温和的条件下具有较高的反应活性、选择性和可重复性, 但产物分离过程繁琐, 严重阻碍了其在工业中的应用. 而传统的多相催化反应具有产物易分离的优点. 几十年来, 人们对均相催化剂固载化进行了广泛研究, 所采用的载体包括有机多聚体、无机物和杂化材料, 以及树枝状嵌合体[1~7]. 但仍存在催化剂活性组分的流失以及催化剂易失活等问题, 且活性和选择性低, 至今仍没有固载化均相催化剂工业应用的实例[8]. 所以, 开发一种具有高活性、高选择性而且活性组分不流失的多相催化体系仍面临巨大的挑战.

近年来, 基于多年积累的多相催化方面的研究经验, 本课题组成功开发了一种有机膦配体修饰的 PPh₃-Rh/SiO₂ 催化剂, 它兼具均相催化剂反应活性高、选择性高、反应条件温和以及多相催化剂产物易分离的优点[9,10]. 鉴于均相氢甲酰化反应中, P/Rh 比对 HRhCO(PPh₃)₃ 催化剂性能影响很大[11~13], 本文系统研究了 P/Rh 比对 PPh₃-Rh/SiO₂ 催化剂上丙烯氢甲酰化反应性能的影响.

PPh$_3$-Rh/SiO$_2$ 催化剂制备、评价过程以及表征结果参考文献[9]. ^{31}P 固体核磁实验在 VARIAN Infinityplus 型核磁共振波谱仪上进行. 振动频率 161.8 MHz, 脉宽 0.7 μs, 弛豫延迟时间 3 s, 使用 Chemagnetics Wideline NMR 探头和 2.5 mm ZrO$_2$ 转子, 转动频率 12.0 kHz, 采样次数 500 次.

图 1 为 P/Rh 比对 PPh$_3$-Rh/SiO$_2$ 催化剂上丙烯氢甲酰化反应产物丁醛正异比的影响. 可以看出, 当 P/Rh 比为 6, 反应 8 h 左右, 正异比达最大 (为 12.02), 继续延长反应时间, 正异比开始降低, 至 75 h 时降到 7.14. 还可以看出, 随着 P/Rh 比的增加, 丁醛正异比逐渐增加, 且随反应时间的延长而降低的趋势变缓. 当 P/Rh 比为 20, 反应 8 h 左右, 正异比达最大 (16.54), 随着反应时间的延长, 正异比缓慢降低, 至 120 h 后仍可保持在 13.31.
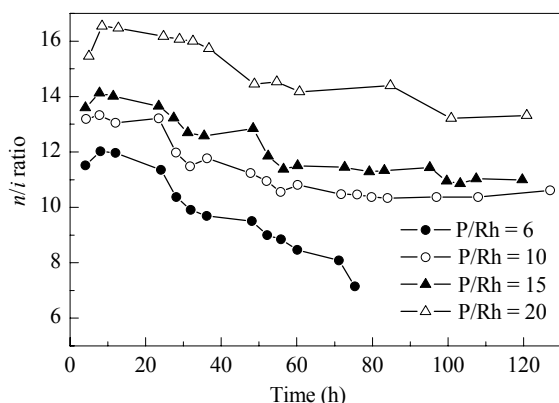

图 1 P/Rh 比对 PPh$_3$-Rh/SiO$_2$ 催化剂上丙烯氢甲酰化反应产物丁醛正异比的影响

Fig. 1. Influence of P/Rh ratio on the *n/i* ratio of butyraldehyde over PPh$_3$-Rh/SiO$_2$ catalyst. Reaction conditions: *T* = 393 K, *p* = 1.0 MPa, SV = 2000 h^{-1}.

图 2 为 P/Rh 比对 PPh$_3$-Rh/SiO$_2$ 催化剂上丙烯氢甲酰化反应产物丁醛转换频率 (TOF) 的影响. 由图可见, 当 P/Rh 比为 6, 反应至 28 h 时, 丁醛 TOF 可达到 241 h^{-1}, 然后迅速下降, 至 75 h 时降到 99 h^{-1}. 还可以看出, 丁醛 TOF 的最大值随 P/Rh 比增至 15 后变化不大, 但随着反应时间的延长, 其波动明显变小. 当 P/Rh 比为 20 时, 丁醛 TOF 值受反应时间的影响变小, 但其最大值急剧降至 64 h^{-1}. 综合考虑, 适宜 P/Rh 比为 15 左右.
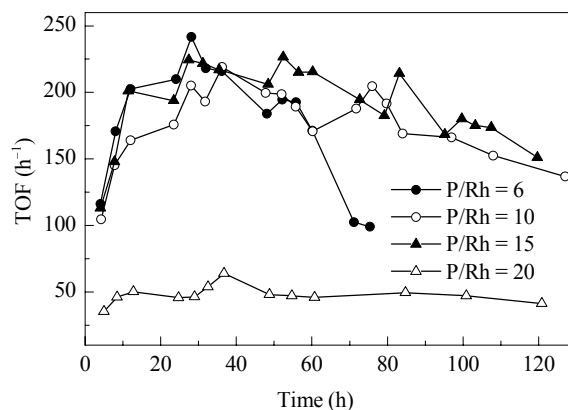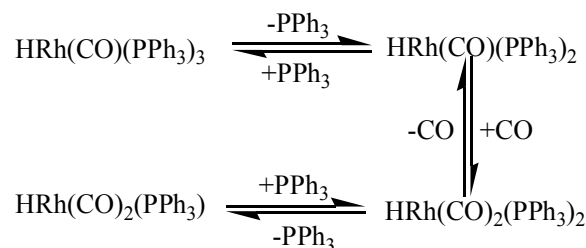
Evans 等[14,15]对均相催化体系氢甲酰化反应机理的研究表明, 在氢甲酰化反应条件下,

图 2 P/Rh 比对 PPh$_3$-Rh/SiO$_2$ 催化剂上丙烯氢甲酰化转换频率的影响

Fig. 2. Influence of P/Rh ratio on the TOF of butyraldehyde over PPh$_3$-Rh/SiO$_2$ catalyst. Reaction conditions: *T* = 393 K; *p* = 1.0 MPa; SV = 2000 h^{-1}.

HRh(CO)$_m$(PPh$_3$)$_n$ 型络合物有多种存在形式, 每种络合物的活性和选择性都不同, 如下面方程式中所示的平衡:

$$HRh(CO)(PPh_3)_3 \underset{+PPh_3}{\overset{-PPh_3}{\rightleftharpoons}} HRh(CO)(PPh_3)_2$$

$$-CO \uparrow\downarrow +CO$$

$$HRh(CO)_2(PPh_3) \underset{-PPh_3}{\overset{+PPh_3}{\rightleftharpoons}} HRh(CO)_2(PPh_3)_2$$

络合物的主要形式取决于 CO 和 PPh$_3$ 的浓度. 我们前期工作证实 PPh$_3$-Rh/SiO$_2$ 催化剂上原位生成了 HRh(CO)(PPh$_3$)$_3$ 和 HRh(CO)$_2$(PPh$_3$)$_2$ 物种. 因此, PPh$_3$-Rh/SiO$_2$ 催化剂上羰基铑膦配合物物种与均相催化剂在溶液里的情况类似, 当 P/Rh 比很低时, 羰基铑膦配合物主要以 HRh(CO)$_2$(PPh$_3$) 形式存在, 它若再失去一个 PPh$_3$ 就会导致催化剂失活. 如果提高 P/Rh 比, 平衡就会向左移动, 羰基铑膦配合物从 HRh(CO)$_2$(PPh$_3$) 转换成以 HRh(CO)$_2$(PPh$_3$)$_2$ 为主, 而后者氢甲酰化活性较低, 选择性较高. 因此, 丁醛正异比随着 P/Rh 比的增加而不断提高, 但是丙烯转化率和产物丁醛 TOF 值增至一个最大值后就变化很小. 当 P/Rh 比高于 15, 铑膦配合物主要以 HRh(CO)(PPh$_3$)$_3$ 形式存在, 这个配合物最稳定, 活性最差, 导致丙烯氢甲酰化活性很低. 膦配体浓度对 PPh$_3$-Rh/SiO$_2$ 催化剂性能的影响与对 HRh(CO)(PPh$_3$)$_3$ 的影响类似, 这进一步证明

Rh/SiO₂ 催化剂在氢甲酰化反应过程中原位生成了类似的均相催化活性物种. 由于铑膦配合物化学平衡比较复杂, 还很难依据现有的实验结果确定具体的单一活性物种.

由于考察 P/Rh 比对 PPh₃-Rh/SiO₂ 催化剂性能影响的过程中, 采用的是同一个催化剂前驱体 Rh/SiO₂, 发生变化的主要是 PPh₃ 浓度, 因此本文采用 ^{31}P MAS NMR 表征了合成气处理前后不同 P/Rh 比的 PPh₃-Rh/SiO₂ 催化剂, 结果示于图 3. 由图可见, 位于 $\delta = -5.8$ 处的峰应归属于物理吸附在 SiO₂ 上的 PPh₃, 而 $\delta = +38.4$ 的峰应归属为化学吸附在 SiO₂ 上的 PPh₃ 或者是与 Rh 粒子化学配位的 PPh₃[11~13]. 将 PPh₃-Rh/SiO₂ 催化剂经一定量的合成气处理后, 所有 P/Rh 比的催化剂 ^{31}P MAS NMR 谱中都仍然仅有两个吸收峰, 而且吸收峰位置也没有变化.

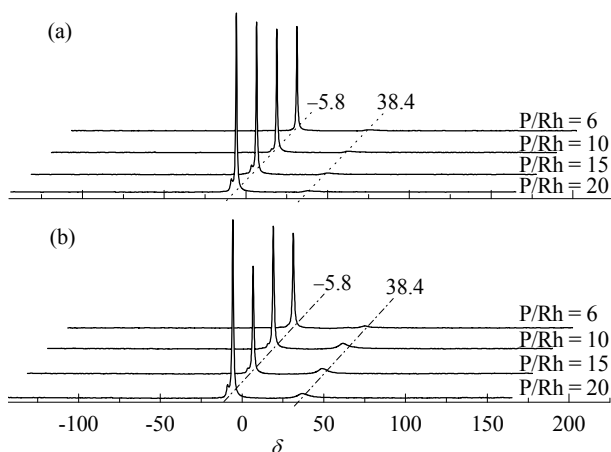**图 3** 合成气处理前后不同 **P/Rh** 比的 **PPh₃-Rh/SiO₂** 催化剂的固体 ^{31}P **MAS NMR** 谱

Fig. 3. Solid-state ^{31}P MAS NMR spectra of PPh₃-Rh/SiO₂ catalysts with different P/Rh ratios before (a) and after (b) treated with syngas.

我们将合成气处理前后不同 P/Rh 比的 PPh₃-Rh/SiO₂ 催化剂的 ^{31}P MAS NMR 谱峰面积进行积分, 并将各谱中的化学吸附和物理吸附的 PPh₃ 的峰面积比示于图 4. 可以看出, 合成气处理前, PPh₃-Rh/SiO₂ 催化剂随着 P/Rh 比从 6 增加到 20, 化学吸附和物理吸附 PPh₃ 的比值从 0.11 急剧下降到 0.01. 而经过合成气处理的各 PPh₃-Rh/SiO₂ 催化剂上该比值要高很多, 在 P/Rh 比为 15 时, 达到最大, 为 0.33, 然后随着 P/Rh 比的增加而减小. 化学吸附 PPh₃ 增加的原因可能是 SiO₂ 载体表面的一部分物

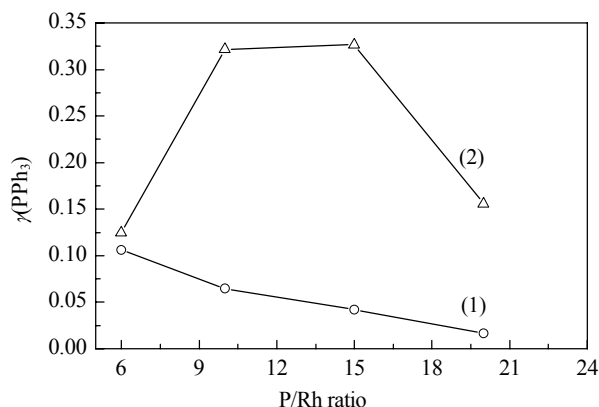**图 4** 合成气处理前后不同 **P/Rh** 比的 **PPh₃-Rh/SiO₂** 催化剂的固体 ^{31}P **MAS NMR** 谱图中化学吸附与物理吸附的 **PPh₃** 的比值

Fig. 4. The ratio of chemically adsorbed PPh₃ and physically adsorbed PPh₃ (γ(PPh₃)) in solid-state ^{31}P MAS NMR spectra of PPh₃-Rh/SiO₂ catalysts with different P/Rh ratio. (1) Before treatment with syngas; (2) After treatment with syngas.

理吸附的 PPh₃ 发生了迁移.

比较图 1 和图 4 可以发现, 丁醛正异比随着 P/Rh 比的增加而不断提高, 说明 Rh 表面化学吸附的 PPh₃ 越多, Rh 周围的配体数目越多, 空间位阻越大, Rh 上电子云密度增加, 使反应物烯烃更易按反马氏规则以 –CH₂–CH₂–R 形式插入 Rh–H 键形成直链产物. 同时依据叔膦修饰的烯烃氢甲酰化反应机理, 配体浓度的增加有利于反应按催化缔合机理进行, 提高了反应对直链醛的选择性, 从而使产物正异比升高. 当 P/Rh = 20 时, 丁醛 TOF 值下降, 这可能是因为过量的配体将催化活性中心包埋, 造成活性中心中毒.

综上所述, P/Rh 比对 PPh₃-Rh/SiO₂ 催化剂上丙烯氢甲酰化反应影响很大, 当 P/Rh 比为 15 时反应活性最高. 而丁醛正异比随 P/Rh 比增加而线性增加, 即 P/Rh 越高, 丁醛的正异比越高. 综合考虑, 我们认为 PPh₃-Rh/SiO₂ 催化剂在 P/Rh 为 15 时达到最优的催化性能. 固体 ^{31}P MAS NMR 结果和 Wilkinson 平衡理论很好地解释了这一结果.

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英 译 文
English Text

Homogeneous catalysts often exhibit higher selectivity, better reproducibility and reactivity under mild conditions in contrast to heterogeneous catalysts. However, the disadvantages of homogeneous catalysts include difficulties in the separation of the catalysts from the products after a reaction and this is not a problem with typical heterogeneous catalysts. The immobilization of homogeneous catalysts onto organic, inorganic, or hybrid supports has attracted widespread interest [1–7]. The main problems found in many systems are catalyst stability and the leaching of expensive metal ions from the catalysts to the product phase [8]. Recently, we developed a novel ligand modified heterogeneous catalyst (PPh_3-Rh/SiO_2) for the hydroformylation of olefins with excellent activity, selectivity, and stability [9,10]. No deactivation was observed over more than 1000 h on condition that PPh_3 was supplemented at about 300–350 h in the PPh_3-Rh/SiO_2 catalyst. The reason for the decrease in activity and selectivity of PPh_3-Rh/SiO_2 from about 300 to 350 h is the leaching of PPh_3.

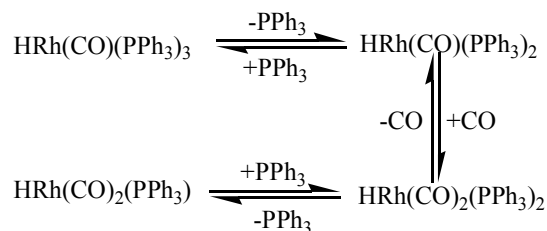The importance of having excess PPh_3 present in solution for the regioselectivity of homogeneous hydroformylation has been well documented [11–13]. In general, excess ligand favors the formation of linear aldehydes at the expense of conversion. However, it should be noted that under certain experimental conditions both high rate and high regioselectivity may be encountered simultaneously. Therefore, we systematically investigated the influence of phosphine concentration on the activity, selectivity (especially n/i ratio of butyraldehyde), and stability for propylene hydroformylation to determine the optimum P/Rh ratio for the PPh_3-Rh/SiO_2 catalyst in this work.

The synthesis and characterization of PPh_3-Rh/SiO_2 as well as its hydroformylation reaction have been discussed in reference [9] in detail. We carried out solid-state ^{31}P MAS NMR experiments using a VARIAN Infinityplus spectrometer with a Chemagnetics Wideline NMR probe. Data were obtained by measuring the samples using a frequency of 161.8 MHz, a pulse width of $\pi/4$, a delay of 3.0 s, and 500 scans. Solid-state ^{31}P NMR chemical shifts were reported relative to 85% H_3PO_4.

Influence of the P/Rh ratio on the n/i ratio of butyraldehyde in propylene hydroformylation is shown in Fig. 1. Generally, a short induction time of about 8 h was observed before the maximum n/i ratio was obtained. The reason for the induction time is that the homogeneous active species grows gradually in situ on the surface of the heterogeneous Rh/SiO_2 catalyst [9]. When the P/Rh ratio changes from 6 to 20 the n/i ratio increases from 12.02 to 16.54 and the stability of the n/i ratio increases.

Figure 2 shows the influence of the P/Rh ratio on the turnover frequency (TOF) of the formation of butyraldehyde. We found that the TOF initially increases slowly as the P/Rh ratio changes from 6 to 15 and then it decreases rapidly from 226 to $64 \cdot h^{-1}$ when the P/Rh ratio increases further. The stability of PPh_3-Rh/SiO_2 improves from 60 h to 120 h when the P/Rh ratio increases from 6 to 20.

Evans et al. [14,15] reported that in a solution of $HRh(CO)(PPh_3)_3$, different rhodium carbonyl phosphine complexes are presented under hydroformylation conditions and each complex has its own specific activity and selectivity. The equilibrium can be represented as follows:

$$HRh(CO)(PPh_3)_3 \underset{+PPh_3}{\overset{-PPh_3}{\rightleftharpoons}} HRh(CO)(PPh_3)_2$$

$$-CO \parallel +CO$$

$$HRh(CO)_2(PPh_3) \underset{-PPh_3}{\overset{+PPh_3}{\rightleftharpoons}} HRh(CO)_2(PPh_3)_2$$

The complex that dominates is determined partly by the carbon monoxide concentration and by the phosphine concentration. Our previous work confirmed that the homogeneous active species of $HRh(CO)(PPh_3)_3$ and

$HRh(CO)_2(PPh_3)_2$ can form in situ on the surface of the PPh_3-Rh/SiO_2 catalyst [9]. Therefore, the rhodium carbonyl phosphine complexes on the PPh_3-Rh/SiO_2 catalyst are comparable to those in a solution of $HRh(CO)(PPh_3)_3$. If the P/Rh ratio is too low, the major rhodium carbonyl phosphine complex will exist as $HRh(CO)_2(PPh_3)$ and it may lose its single PPh_3, which will lead to deactivation. By increasing the P/Rh ratio, the equilibrium is shifted to the left. The dominant carbonyl phosphine complex shifts towards the less active but more selective $HRh(CO)_2(PPh_3)_2$ complex from the $HRh(CO)_2(PPh_3)$ complex. Therefore, the n/i ratio increases with the P/Rh ratio while the propylene conversion and the TOF reach their maximum values. However, if the P/Rh ratio is higher than 15, the main carbonyl phosphine complex is the $HRh(CO)(PPh_3)_3$ complex, which is the most stable but the least active complex and results in very low activity during propylene hydroformylation. The similarity in the effect of phosphine concentration on propylene hydroformylation between the PPh_3-Rh/SiO_2 catalyst and $HRh(CO)(PPh_3)_3$ further confirms the in situ formation of the homogeneous active species on the surface of Rh/SiO_2 for the PPh_3-Rh/SiO_2 catalyst during the hydroformylation of olefins. Because of the complexity of the equilibria involved, it is impossible to reach a firm conclusion solely on the experiments reported here.

For the preparation of the PPh_3-Rh/SiO_2 catalysts with different P/Rh ratios, the Rh/SiO_2 catalyst remains essentially the same with the only difference being the amount of PPh_3. Therefore, solid-state ^{31}P MAS NMR is one of the best measurement tools to characterize the PPh_3-Rh/SiO_2 catalysts with different P/Rh ratios and the results are shown in Fig. 3 for the catalysts that were not treated and those that were treated with syngas, respectively. All the spectra in Fig. 3 imply that there are only two kinds of PPh_3 in the PPh_3-Rh/SiO_2 catalysts with different P/Rh ratios: one is physically adsorbed PPh_3 at $\delta = -5.8$ and the other is chemically adsorbed PPh_3 at $\delta = +38.4$.

However, the ratio of chemically adsorbed PPh_3 and physically adsorbed PPh_3 for each spectrum are very different and this is shown in Fig. 4. For the PPh_3-Rh/SiO_2 that was not treated, the ratio decreases from 0.11 to 0.01 and the P/Rh ratio increases from 6 to 20. After treatment with syngas, the ratio becomes larger and reaches the highest value 0.33 at a P/Rh ratio of 15. The increased chemically adsorbed PPh_3 may migrate from the physically adsorbed PPh_3 on the surface of the SiO_2 supports.

The increased n/i ratio that results from an increase in the P/Rh ratio can also be explained by a comparison of the results shown in Figs. 1 and 4. These figures show that when more chemisorbed PPh_3 is present on the Rh surface more steric hindrance will result and propylene will more likely insert into Rh–H in the form of $-CH_2-CH_2-CH_3$ to produce linear butyraldehyde. The decline in the TOF of butyraldehyde that was observed upon the further addition of PPh_3 (P/Rh = 20) is considered to be the result of the active species being embedded by an excess of PPh_3.

In summary, the use of excess PPh_3 (P/Rh = 15) in the PPh_3-Rh/SiO_2 catalyst ensures high activity, selectivity, and stability for the hydroformylation of propylene on a fixed-bed reactor. When the P/Rh ratio of the PPh_3-Rh/SiO_2 catalyst changes from 6 to 20, the n/i ratio of butyraldehyde increases as well. However, the TOF of butyraldehyde reaches its maximum at a P/Rh ratio of 15. Subsequently, the best P/Rh ratio for the PPh_3-Rh/SiO_2 catalyst is 15.

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