The Effect of Metal-Ligand Affinity on Fe₃O₄-Supported Co–Rh Catalysts for Dicyclopentadiene Hydroformylation

YUBO MA,¹ SHAOJUN QING,³ NANA LI,¹,² LETAO ZHANG,¹ SHOUZHU LI,¹ ZHIXIAN GAO,¹,³ HONGYI LI,⁵ WUMANJIANG ELI,¹ TIANFU WANG¹,⁴
¹Xinjiang Technical Institute of Physics & Chemistry, Chinese Academy of Sciences, Urumqi, 830011, People’s Republic of China
²University of the Chinese Academy of Sciences, Beijing, 100049, People’s Republic of China
³Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, 030001, People’s Republic of China
⁴Department of Power Engineering, Xinjiang Institute of Engineering, Urumqi, 830011, People’s Republic of China
⁵Xinjiang Quality of Products Supervision & Inspection Institute of Technology, Urumqi, 830011, People’s Republic of China

Received 23 January 2015; revised 19 May 2015; accepted 21 May 2015
DOI 10.1002/kin.20933
Published online in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The catalytic performances of Co-Rh/Fe₃O₄ catalysts modified with phosphine ligands (PPh₃) and its analogues on dicyclopentadiene hydroformylation were evaluated. Among these catalysts, Co-Rh/Fe₃O₄ modified with tris(p-trifluoromethylphenyl)phosphine was determined to be effective for monoformyltricyclodecanes production, whereas Co-Rh/Fe₃O₄ modified with PPh₃ or tri-p-tolylphosphine was effective for the diformyltricyclodecanes production. To investigate the ligand effects, the complex catalyst system (Co-Rh/Fe₃O₄ and phosphine ligand) was subjected to pretreatment with syngas and then characterized by thermogravimetry and differential thermal analysis (TG-DTA). It was determined that the threshold decomposition temperature reflected the corresponding Rh-phosphine interaction strength, affecting the catalytic selectivity toward different products. A weak Rh-phosphine interaction was desirable to
produce monoformyltricyclodecanes with fast reaction kinetics, whereas a strong Rh-phosphine complex was required for the synthesis of diformyltricyclodecanes. In addition to the selectivity rule shown in the PPh₃ series, experiments with other ligands also demonstrated similar selectivity trends. © 2015 Wiley Periodicals, Inc. Int J Chem Kinet 1–8, 2015

INTRODUCTION

Hydroformylation of olefins represents an efficient and important route for the production of a multitude of chemicals used in plastic, pharmaceutical, and agricultural applications [1]. While most industrial applications focus on the hydroformylation of terminal linear olefins, cyclic olefins, due to their relative low reactivities, are generally underutilized. Efficient and economical utilization of dicyclopentadiene (DCPD), a high-volume by-product mostly produced from the light benzene fraction of coal coking and ethylene cracking processes, has attracted much attention recently [2,3]. A two-step hydroformylation followed by a hydrogenation process produces a series of value-added fine chemicals, such as monoformyltricyclodecanes (MFTD), diformyltricyclodecanes (DFTD), tricyclodecanedimethylol (TD-diol) [4–7]. DFTD and TD-diol could be used as the starting material for agricultural chemicals, lubricating oils, plasticizer, pharmaceuticals, and perfumes [8]. However, owing to steric constraints, as an internal olefin, high processing cost associated with homogeneous catalysts developed [3,9], the practical utilization of DCPD is yet to be realized [2,3,9].

It is well known that organic ligands added to catalytic systems can potentially have a great influence on catalytic activity and selectivity, mainly due to their electronic or steric effects [10–17]. For example, phosphine ligands were found to be particularly effective in promoting the hydroformylation reaction of olefins when added to a rhodium-based catalyst system [3,9]. In one recent study, an overall aldehyde (MFTD and DFTD) yield of up to ca. 98 mol% at nearly complete DCPD conversion was reported by Chen et al. The catalyst system, composed of a homogeneous Rh-based catalyst and various phosphine ligands, proceeded under moderate reaction conditions (5 MPa and 373 K) [2]. In our previous work, Co-Rh/Fe₃O₄ modified with PPh₃ was also found to be an effective catalyst for DCPD hydroformylation [18]. In addition, Longoni et al. found that a nearly stoichiometric yields of MFTD could be obtained over mixed cobalt–rhodium carbonyl system and PPh₃ as the ligand under the reaction conditions of 70–90°C and 20–40 atm reaction pressure [9]. Using the same catalyst system, a much higher reaction temperature and reaction pressure was needed to achieve DFTD yields of 94.5% with a 95% selectivity in an aqueous/organic biphasic system in the presence of a cationic surfactant [3]. However, despite the progress in catalyst development for the DCPD hydroformylation reaction, much more effort is required regarding (1) the heterogenization of the molecularly active species in the homogeneous system and (2) a more in-depth understanding on the correlation between catalytic performance and the catalyst–ligand interaction.

In general, the electron density on the aromatic ring in the phosphine ligand plays a key role in turning the catalytic activity/selectivity of olefin hydroformylation. For instance, Saidi et al. [19] found that the electron-withdrawing substituents on the aromatic ring lead to higher catalytic activities and faster reaction rates in comparison with electron-donating substituents. In another study, Leeuwen and Roobeek [20] found that ligands with strong electron-withdrawing groups readily catalyzed hydroformylation reactions even when less reactive internal olefins were used. The attached electron-withdrawing group used in the previous study can also improve the selectivity toward the linear aldehyde as well. Regarding the DCPD hydroformylation reaction, based on the dissociative mechanism of the hydroformylation proposed by Wilkinson et al. [21], an empirical rule might be suggested that the Rh-based catalyst modified with a weakly coordinated ligand favors the production of MFTD, whereas a strongly coordinated ligand promotes the selectivity toward DFTD. Scheme 1 illustrates two possible reaction pathways involved in DCPD conversion, producing MFTD and DFTD. To develop a more detailed understanding of DCPD hydroformylation, the
coordination strength of various phosphine-ligated metals needs to be obtained.

Herein, we examine how the coordination strength of phosphine ligands and Fe₃O₄-supported Co–Rh bimetallic catalysts (Co–Rh/Fe₃O₄) influences the activity and selectivity of DCPD hydroformylation utilizing TG-DTA. The metal-phosphine coordination strength was probed with TG-DTA. The results suggest that the strength of Rh-phosphine coordination affinity plays an important role in the catalytic activity and selectivity of the process.

**EXPERIMENTAL**

**Catalyst Preparation**

The Co–Rh/Fe₃O₄ catalyst was prepared by the coprecipitation method. Briefly, 104 mmol (42 g) Fe(NO₃)₃·9H₂O (Alfa Aesar), 2.08 mmol (0.5 g) RhCl₃ (Alfa Aesar), and 2.08 mmol (0.5 g) CoCl₂·6H₂O (Alfa Aesar) were dissolved in 150 mL distilled water and was added dropwise into a 600-mL Na₂CO₃ (Sinopharm, China) solution (0.47 M) under vigorous stirring for about 1 h. The reaction mixture was stirred continuously for additional 2 h. After filtration and washing with 150–200 mL of distilled water, and was added dropwise into a 600-mL Na₂CO₃ solution (Sinopharm, China) under vigorous stirring for about 1 h. The reaction mixture was stirred continuously for additional 2 h. After filtration and washing with 150–200 mL of distilled water, the resultant precipitate was dried at 120°C for 16 h and further calcined at 400°C in air for 4 h. The obtained solid was then reduced under H₂ flow at 400°C for 2 h, yielding a 2 wt%Co–2 wt%Rh/Fe₃O₄ catalyst.

Co–Rh/Fe₃O₄ modified with various ligands was prepared as follows: The Co–Rh/Fe₃O₄ catalyst was introduced into a tetrahydrofuran solution containing corresponding ligand, and this mixture was stirred for 0.5 h. The solvent was then removed under vacuum at room temperature, and the resulting ligated Co–Rh/Fe₃O₄ catalyst (the molar ratio of P:Rh of 10:1) was stored under argon atmosphere.

**Catalysts Characterization**

Thermal gravimetric analysis was used to determine the ligand degradation temperature (TA Instruments, model DTG-60). Fe₃O₄-modified with PPh₃, Co–Rh/Fe₃O₄ and Co/Fe₃O₄ modified with PPh₃, and Co–Rh/Fe₃O₄ modified with various ligands pretreated by syngas under the reaction were heated at 120°C for 16 h and further calcined at 400°C in air for 4 h. The obtained solid was then reduced under H₂ flow at 400°C for 2 h, yielding a 2 wt%Co–2 wt%Rh/Fe₃O₄ catalyst.

**Hydroformylation of DCPD**

Hydroformylation of DCPD to MFTD was carried out in an autoclave reactor. In a typical experiment, a 2 wt%Co–2 wt%Rh/Fe₃O₄ catalyst modified with PPh₃-type ligands (P1–P4 ligands in Group 1, Fig. 1) was used, and the reaction was run for 4 h. The results are summarized in Tables I and II, Fig. 2, and Fig. S1 in the Supporting Information. As shown in Table I, Co–Rh/Fe₃O₄ modified with different ligands all resulted in good selectivities (>95%) for the synthesis of MFTD by hydroformylation of DCPD.

**RESULTS AND DISCUSSION**

**Activity and Selectivity for MFTD Synthesis**

All the ligands used in this study are shown in Fig. 1 and classified into four different groups with similar structural features. A 2 wt%Co–2 wt%Rh/Fe₃O₄ catalyst modified with different ligands (Fig. 1) was tested for DCPD hydroformylation; plots of ln(1–X) (where X is the DCPD conversion) versus reaction time (t) were used to determine reaction rate constants assuming first-order kinetics on the substrate concentration. Table I summarizes rate constant values (k) over the catalyst modified with different ligands. In a typical experiment, a 2 wt%Co–2 wt%Rh/Fe₃O₄ catalyst modified with different ligands (Fig. 1) was tested for DCPD hydroformylation; plots of ln(1–X) (where X is the DCPD conversion) versus reaction time (t) were used to determine reaction rate constants assuming first-order kinetics on the substrate concentration.
Almost complete DCPD conversion was achieved for all catalyst systems except for Co–Rh/Fe$_3$O$_4$ modified with PPh$_3$–OMe. The kinetic results of DCPD conversion by Co–Rh/Fe$_3$O$_4$ modified with different ligands are presented in Table I, Fig. 2, and Fig. S1 in the Supporting Information. It is observed that the DCPD reaction rate is ligand dependent, and the order of the reaction rate constants was followed by P$_4$ > P$_3$ > P$_1$ > P$_2$ (entries 1–4 in Table I). For instance, over Co–Rh/Fe$_3$O$_4$ modified with tris(p-trifluoromethylphenyl)phosphine in which an electron-withdrawing substitute is attached to the aromatic ring, DCPD could be completely converted within 80 min, whereas at least 4 h is required for systems composed of Co–Rh/Fe$_3$O$_4$ in conjugation with other ligands (Fig. S1 in the Supporting Information). From the calculated initial rate, it can be summarized that the reaction rate decreases in following the order of P$_4$ > P$_3$ > P$_1$ > P$_2$.

Saidi et al. [19] found that the electron-withdrawing substituents lead to higher catalytic activities and a faster rate in comparison with electron-donating substituents. Leeuwen and Roobeek [20] also found that the ligand with a strong electron-withdrawing group can enhance the hydroformylation reaction rate greatly even with less active internal olefins. According to this empirical electronic hypothesis, the activity of Group 1 ligands can be ranked as follows: P$_4$ > P$_1$ > P$_3$ > P$_2$. However, the experimental results summarized in Fig. 2 showed a trend of P$_4$ > P$_3$ > P$_1$ > P$_2$. The experimental results and the predicted reaction rates indicated that the activity can be explained by the electronic effects. A dissociative mechanism of the hydroformylation by Wilkinson et al. was proposed and
Table I  Reaction Rate Constants ($k$) of DCPD Hydroformylation over Catalyst Modified with Different Phosphine Ligands

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ligand</th>
<th>$k$ (min$^{-1}$) $\times$ 10$^3$</th>
<th>Correlation Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>P1</td>
<td>9.5</td>
<td>0.996</td>
</tr>
<tr>
<td>2</td>
<td>P2</td>
<td>5.5</td>
<td>0.982</td>
</tr>
<tr>
<td>3</td>
<td>P3</td>
<td>17.2</td>
<td>0.976</td>
</tr>
<tr>
<td>4</td>
<td>P4</td>
<td>32.6</td>
<td>0.975</td>
</tr>
<tr>
<td>5</td>
<td>P5</td>
<td>10.6</td>
<td>0.959</td>
</tr>
<tr>
<td>6</td>
<td>P6</td>
<td>13.0</td>
<td>0.968</td>
</tr>
<tr>
<td>7</td>
<td>P7</td>
<td>9.1</td>
<td>0.990</td>
</tr>
<tr>
<td>8</td>
<td>P8</td>
<td>6.7</td>
<td>0.989</td>
</tr>
<tr>
<td>9</td>
<td>P9</td>
<td>12.2</td>
<td>0.989</td>
</tr>
<tr>
<td>10</td>
<td>P10</td>
<td>3.9</td>
<td>0.996</td>
</tr>
<tr>
<td>11</td>
<td>P11</td>
<td>0.7</td>
<td>0.979</td>
</tr>
<tr>
<td>12</td>
<td>P12</td>
<td>20.4</td>
<td>0.972</td>
</tr>
<tr>
<td>13</td>
<td>P13</td>
<td>9.0</td>
<td>0.962</td>
</tr>
</tbody>
</table>

Experimental conditions: reaction time: 4 h; reaction pressure: 40 atm; reaction temperature: 95°C.

Table II  Effect of Varied PPh$_3$ Derivatives on the MFTD Synthesis

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>Others (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>&gt; 99</td>
<td>97</td>
<td>3</td>
</tr>
<tr>
<td>P2</td>
<td>84</td>
<td>97</td>
<td>3</td>
</tr>
<tr>
<td>P3</td>
<td>&gt; 99</td>
<td>96</td>
<td>4</td>
</tr>
<tr>
<td>P4</td>
<td>&gt; 99</td>
<td>96</td>
<td>4</td>
</tr>
</tbody>
</table>

Experimental conditions: reaction time: 4 h; reaction pressure: 40 atm; reaction temperature: 95°C.

Combining of the reaction rate, DCPD conversion, and monoformyltricyclodecanes (MFTD) selectivity could lead to the conclusion that Co–Rh/Fe$_3$O$_4$ modified with tris(p-trifluoromethylphenyl)phosphine was determined to be an effective catalyst for MFTD production.

To test the above-mentioned empirical trend on the correlation between reactivity and substitute groups on the aromatic ring, catalyst systems composed of Co–Rh/Fe$_3$O$_4$ modified with other types of ligands (Groups 2–4 in Fig. 1) were also used for DCPD conversion. The corresponding DCPD conversion kinetic information is summarized in Table I, Figs. 3–5, and Figs. S2–4 in the Supporting Information. Shown in Fig. 3 is the reaction rate of the DCPD conversion reaction catalyzed by Co–Rh/Fe$_3$O$_4$ modified with Group 2 ligands in Fig. 1. After analyzing the reaction rate, it is found that the kinetics decreased in the order of P6 > P5 > P7, confirming that the reaction rate is correlated to the electron density on the aromatic ring linked to the P atom. In addition, similar to Group 1 ligands, systems containing an electron-deficient aromatic ring resulted

Figure 2  MFTD synthesis over Co–Rh/Fe$_3$O$_4$ modified with PPh$_3$ and its derivatives.

Figure 3  MFTD synthesis over Co–Rh/Fe$_3$O$_4$ modified with biphenvlphosphine and its derivatives.

Figure 4  MFTD synthesis over Co–Rh/Fe$_3$O$_4$ modified with diphosphines.
in faster reaction kinetics. Another set of experiments with Group 3 ligands in Fig. 1, containing two P atoms connected to an aromatic ring, was also studied, and the kinetic data are summarized in Fig. 4. The order of the reaction rates followed the order of P9 > P8 > P10 > P11. After 4 h, the catalyst system comprising of Co–Rh/Fe3O4 modified with P9 resulted in a DCPD conversion of 92% whereas only 11% DCPD conversion (Fig. S3 in the Supporting Information) was reached when ligand P11 was used. In addition to the above phosphine-type ligands, Co–Rh/Fe3O4 modified with phosphites (Group 4 ligands in Fig. 1) was also tested in the DCPD hydroformylation reaction (Fig. 5). A moderately high reaction rate was observed with P12 being faster than P13(Table I). To compare the effectiveness of ligands in different groups, P12 and P1 were experimented as the model phosphite and phosphine ligand, respectively, for DCPD conversion and their reaction rates are presented in Table I, Fig. 6, and Fig. S5 in the Supporting Information. Notably, a faster reaction rate was obtained with P12 as the modified ligand.

**Table III** Effect of PPh3 and Its Derivatives on the Hydroformylation of DCPD

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Conversion (%)</th>
<th>MFTD Selectivity (%)</th>
<th>DFTD Selectivity (%)</th>
<th>Other (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>&gt;99</td>
<td>15</td>
<td>81</td>
<td>4</td>
</tr>
<tr>
<td>P2</td>
<td>&gt;99</td>
<td>53</td>
<td>44</td>
<td>3</td>
</tr>
<tr>
<td>P3</td>
<td>&gt;99</td>
<td>14</td>
<td>83</td>
<td>3</td>
</tr>
<tr>
<td>P4</td>
<td>&gt;99</td>
<td>50</td>
<td>46</td>
<td>4</td>
</tr>
</tbody>
</table>

Experimental conditions: reaction temperature: 140°C; reaction pressure: 8 MPa; reaction time: 5 h.

**Activity and Selectivity for DFTD Synthesis**

Based on the results of Co–Rh/Fe3O4 modified with PPh3 and its derivatives in the synthesis of MFTD, the same catalyst system was further applied to the synthesis of DFTD from DCPD. DFTD is rather difficult to be produced due to the steric hindrance at the 3,4 double bond. Thus, higher temperatures (140°C), higher pressures (8 MPa), and longer reaction times (5 h) are needed for DFTD synthesis. The catalyst in this study was 2 wt%Co–2 wt%Rh/Fe3O4 modified with Group 1 ligands in Fig. 1. As shown in Table III, the conversion of DCPD was greater than 99% for Co–Rh/Fe3O4 modified with all phosphine ligands P1–P4; however, there is a big difference in the production distribution with selectivity of DFTD in the following order: P3 > P1 > P4 > P2. For instance, up to 80% DFTD selectivity were obtained over Co–Rh/Fe3O4 modified with P1 and P3 whereas only 46% and 44% DFTD selectivity were achieved over their counterparts P4 and P2, respectively. This indicates that high DFTD selectivity would be achieved over ligand systems with a medium Rh–P affinity, in contrast to low DFTD selectivity obtained from either strong Rh–P affinity present in P2 or weak Rh–P affinity present in P4. Combined with the activity rule observed for MFTD synthesis where a weak Rh–P affinity was required to promote the reaction kinetics, a medium Rh–P affinity was found to be the key in achieving higher DFTD product selectivity in addition to more severe reaction conditions. All these data suggested that Co–Rh/Fe3O4 modified with PPh3 or tri-p-tolylphosphine was effective for DFTD synthesis.

**Characterization of Rh–P Affinity Using the TG-DTA Method**

Co–Rh/Fe3O4 catalysts modified different ligands were firstly pretreated by syngas under the reaction conditions, recovered, and then subjected to TG-DTA
THE EFFECT OF METAL-LIGAND AFFINITY ON \( \text{Fe}_3\text{O}_4 \)-SUPPORTED Co-Rh CATALYSTS

As shown in Fig. 7, the temperature at which catalyst–ligand complexes start to decompose increases in the order of \( P_4 < P_3 < P_1 < P_2 \). Using \( P_1 \) as a model ligand, a slate of four different materials including \( \text{Co–Rh/Fe}_3\text{O}_4 \), \( \text{Co–Fe}_3\text{O}_4 \) with \( P_1 \), \( \text{Fe}_3\text{O}_4 \) with \( P_1 \), and \( \text{Co–Rh/Fe}_3\text{O}_4 \) with \( P_1 \) was pretreated by syngas under the reaction followed by TG-DTA analysis. The first three materials revealed approximately superimposable thermal decomposition behavior in contrast to the last one, \( \text{Co–Rh/Fe}_3\text{O}_4 \) with \( P_1 \) showed substantial weight loss with peak positions at about 240 and 340°C, respectively (Fig. 8). According to the previous literature [22], 240 and 340°C peaks could be assigned to the physically and chemically adsorbed PPh\(_3\), respectively. For materials without the presence of Rh, no appreciable difference was observed compared to \( \text{Co–Rh/Fe}_3\text{O}_4 \), indicating that Rh is required for the phosphine ligands to be adsorbed onto the catalyst surface. Based on previous studies, the starting temperature from which Co–Rh/phosphine complexes undergo decomposition can be inversely correlated to the strength of Rh–P affinity [22], and they followed the order of \( P_4 < P_3 < P_2 < P_1 \). By comparing the experimental reaction rate shown in Fig. 2 and strength of Rh–P reflected by the decomposition temperature in Fig. 7, it can be observed that these two sets of data are correlated very well. This suggested that Rh–P bond strength plays an important role in determining the rate of MFTD synthesis.

In addition, \( \text{Co–Rh/Fe}_3\text{O}_4 \) modified with biphenylphosphine and its derivatives, diphosphines and phosphites, were also pretreated by syngas and subsequently characterized with TG-DTA analysis, with the results provided in the supporting information, respectively. By examining the decomposition temperature of the phosphor-containing ligands adsorbed on \( \text{Co–Rh/Fe}_3\text{O}_4 \) catalysts, the Rh–P affinity can be ranked in the increasing order of \( P_6 < P_5 < P_7, P_9 < P_8 < P_{10} < P_{11}, P_{12} < P_{13} \) for Groups 2, 3, and 4 ligands, respectively. It is also observed that ligands containing two P atoms (Group 3) had a higher decomposition temperature than those having one P atom, indicating diphosphines can form more stable coordination complexes with a Rh metal core. Comparison of the decomposition temperature leads to the conclusion that the phosphine-type ligand is more strongly chemically adsorbed on the Rh-based catalyst surface. The reaction kinetic data of \( \text{Co–Rh/Fe}_3\text{O}_4 \) modified with biphenylphosphine and its derivatives, diphosphines and phosphites (Group 2–4 ligands, Fig. 5), validated the legitimacy of using the Rh–P affinity obtained from the TG-DTA method to predict hydroformylation reaction rates (data shown in Figs. S6–9 in the Supporting Information). This illustrates that the Rh–P affinity characterized by the TG-DTA method can be applicable to a variety of different ligand systems for the DCPD hydroformylation reaction.

CONCLUSIONS

Co–Rh/Fe\(_3\)O\(_4\) modified with a total of 13 phosphor-containing ligands were prepared; subsequently, these catalyst samples were pretreated with syngas under the DCPD hydroformylation reaction conditions and further characterized by the TG-DTA method. Rh–P ligand affinity correlated with the temperature at which the adsorbed ligands start to decompose. By comparing reaction kinetic profile of DCPD hydroformylation over these catalysts and the stability of catalyst–ligand complexes obtained by a means of using TG-DTA method, an empirical rule has been proposed that the Rh–P affinity greatly affects both

---

**Figure 7** DTA profiles of Co–Rh/Fe\(_3\)O\(_4\) modified with PPh\(_3\) and its derivatives.

**Figure 8** DTA profiles of PPh\(_3\)-Fe\(_3\)O\(_4\), Co–Rh/Fe\(_3\)O\(_4\), PPh\(_3\)-Co/Fe\(_3\)O\(_4\), and PPh\(_3\)-Co-Rh/Fe\(_3\)O\(_4\).
reaction kinetics and product selectivity during the course of the DCPD hydroformylation reaction. The fast reaction rate for MFTD synthesis could be obtained over Co–Rh/Fe₃O₄ modified a weakly chemisorbed phosphor-containing ligand, and a high DFTD selectivity could be obtained with medium strength Rh–P bond with Co–Rh /Fe₃O₄.

By systematically varying structural and electronic properties of different phosphine-type ligands, the general rule that a fast reaction rate to form MFTD could be obtained over Co–Rh/Fe₃O₄ modified with an easily dissociated ligand was established and further applied to explain the experimental results with other similar ligands such as biphenylphosphine and its derivatives, diphosphines, and triphenyl phosphate. The discrepancy of experimental results when solely explained by electronic or steric effects are successfully reconciled by a means of the TG-DTA method to characterize Rh–P affinity. Based on the information obtained in this study, it can be speculated that these principles can provide useful guidance in the future for designing ligands with appropriate electronic/steric properties to achieve specific activity/selectivity requirements for hydroformylation of DCPD or other olefins.

BIBLIOGRAPHY