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Activities of Co(II) Schiff Base Complexes in the Redox Carbonylation of Aniline and Nitrobenzene to Methyl N-Phenyl Carbamate[1]

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Abstract—The series of cobalt(II) complexes with different Schiff base ligands was synthesized and used as catalyst for the redox carbonylation of aniline and nitrobenzene. Effects of reaction temperature, CO pressure, promoter, and catalyst additions on the conversion of substrate were studied. When Co[$(OH)_2$saloph] – *p*-toluenesulfonic acid system was used as catalyst, the reaction was carried out at the next conditions: both Co[$(OH)_2$saloph] and *p*-toluenesulfonic acid—0.2 mmol, aniline—20 mmol, nitrobenzene—10 mmol, methanol—30 ml, Co—5 MPa, temperature 170°C, reaction time 7 h. The highest conversion of nitrobenzene and selectivity of methyl N-phenyl carbamate were 54.5 and 92.2%, respectively.

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Isocyanates are of commercial importance in the manufacture of polyurethanes and herbicides. Conventional process for the production of isocyanates is carried out by the reaction of primary amines with phosgene. Despite the high yield of this method, the toxic phosgene and a large amount of corrosive HCl coproduct caused serious environmental problems. Many efforts have been made to develop the phosgene-free routes. Most proposed green processes are indirect ones, in which the isocyanates were synthesized through the carbamate intermediate, and the corresponding isocyanate was produced by the thermal dealcoholization of carbamate at high temperature. Methyl N-phenyl carbamate (MPC) is the important precursor for the production of methanediphenyl-4,4'-diisocyanate, an important monomer in polyurethanes manufacture. Presently, the mainly studied phosgene-free routes for the production of MPC are catalytic carbonylation, including oxidative carbonylation (I), reductive carbonylation (II) and the transesterification reaction of aniline and dimethyl carbonate (III):

$$PhNH_2 + CO + 1/2O_2 + MeOH \xrightarrow[T,\,P,\,Cat]{} PhNHCOOCH_3 + H_2O, \quad (I)$$

$$PhNO_2 + 3CO + MeOH \xrightarrow[T,\,P,\,Cat]{} PhNHCOOCH_3 + 2CO_2, \quad (II)$$

$$PhNH_2 + H_3CO{-}CO{-}OCH_3 \xrightarrow[Cat]{} PhNHCOOCH_3 + CH_3OH, \quad (III)$$

$$2PhNH_2 + RNO_2 + 3CO + 3MeOH \xrightarrow[T,\,P,\,Cat]{} 3PhNHCOOCH_3 + 2H_2O. \quad (IV)$$

Unlike catalytic carbonylation, the transesterification process has the limitation in the separation of methanol–dimethyl carbonate (DMC) azeotrope and the high cost associated with the use of the expensive raw DMC. Besides, catalytic carbonylation is preferable with regard to its higher efficiency and ease of handling. However, both reductive and oxidative carbonylations have some drawbacks. The CO utilization efficiency in reductive carbonylation is one-third, and it is difficult to separate CO from CO_2. In the case of oxidative carbonylation, the conversion of CO to carbonylation product is complete, but there is the safety problem because of in the start materials are used the explosive mixture of oxygen and CO. The improvement of carbonylation processes carried out by adding nitrobenzene in the reaction mixture without oxygen, as depicted in reaction (IV). Nitrobenzene in the reaction system acts as an oxidant, aniline reacts with CO to generate the products of carbonylation. The active catalysts for the carbonylation process are a group of transition metal compounds, sulfur, selenium and tellurium [1–3].

The metal Schiff base complexes have been successfully employed in a number of catalytic reactions, such as oxidation [4], carbonylation [5], epoxidation [6], ring opening [7], hydration [8], etc. Their partic-

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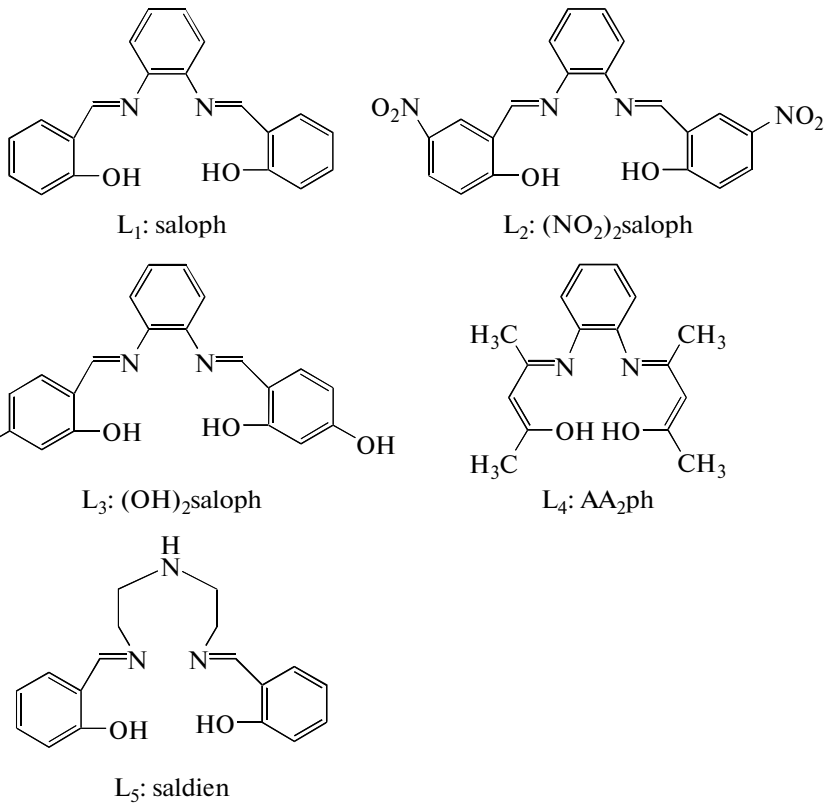

Scheme. Structures of Schiff base ligands L_1–L_5.

ular catalytic activities are attributed to the unsaturated coordinating state and variable valency of center ions. In our previous papers [9–11], cobalt complexes with substituted or non-substituted salen-type ligands were prepared and used as catalysts for the oxidative carbonylation. In another work [12], we studied the reaction of nitrobenzene, aniline and CO catalyzed by *N*,*N*'-bis(salicylidene)-*o*-phenyldiimine cobalt(II) in toluene solution. *N*,*N*'-diphenyl urea was produced in a good yield. In this paper, the catalytic activities of different cobalt(II) Schiff base complexes were investigated in the redox carbonylation (IV) in methanol. The ligand effect, substituent effect of ligand and the effect of other reaction parameters are discussed in detail.

EXPERIMENTAL

Materials

Nitrobenzene and aniline are commercial reagents and distilled under reduced pressure before using. Salicylaldehyde, 2,4-dihydroxybenzylaldehyde, 5-nitrosalicylaldehyde, *o*-phenylenediamine, diethylenetriamine, and acetylacetone are of analytical quality and distilled under inert atmosphere prior to use. All the solvents used were analytical reagents and dried by standard method. Cobalt acetate tetrahydrate was used as received. Carbon monoxide with a purity of 99.99% was purchased from the local manufacturer.

Synthesis of Cobalt(II) Schiff Base Complexes

Five Schiff base ligands L_1–L_5, as depicted in Scheme, were synthesized according to the reported procedures: a salicylaldehyde derivative [13] or acetylacetone [14] was mixed with *o*-phenylenediamine or diethylenetriamine in 2 : 1 molar ratio in ethanol. The corresponding ligands L_1–L_5 were formed after refluxing of the resulting mixture at 60°C for 2 h. The cobalt(II) chelates $Co(L_1)$–$Co(L_5)$ were prepared by reacting of equimolar amounts of ligand and cobalt(II) acetate tetrahydrate in dichloromethane–methanol mixture (3 : 1, v/v), all the complexes were formed as dark green crystals. The ligands and complexes were characterized by IR, NMR and elemental analysis to determine their structures.

Catalytic Experiments

The redox carbonylation of aniline and nitrobenzene was carried out in 100 ml Teflon lined stainless autoclave equipped with a mechanic stirrer and a temperature controller. A mixture of accurately weighed aniline, nitrobenzene, catalyst, promoter and 30 ml of methanol was charged into reactor at room tempera-

Table 1. Redox carbonylation of nitrobenzene and aniline catalyzed by cobalt(II) complexes

Catalyst	Conversion, %		Yield, %		Selectivity to MPC, %
	Nitrobenzene	Aniline	MPC*	NMA**	
Co(saloph)	48.9	41.5	81.4	1.0	90.6
Co[$(NO_2)_2$saloph]	13.6	12.1	78.2	0.8	84.5
Co[$(OH)_2$saloph]	54.5	45.6	82.6	1.1	92.2
Co(AA_2ph)	33.4	30.6	80.6	1.0	85.4
Co(saldien)	6.4	5.7	77.1	0.8	83.2

Note. Reaction conditions: nitrobenzene—10 mmol, aniline—20 mmol, cobalt complex—0.2 mmol, PTS—0.2 mmol, CO—5 MPa, 170°C, 7 h.

$$*\text{Yield of MPC} = 1/3\frac{\text{moles of MPC}}{\text{moles of nitrobenzene converted}}\times 100.$$

$$**\text{ Yield of NMA} = \frac{\text{moles of NMA}}{\text{moles of aniline converted}}\times 100.$$

ture, the autoclave was sealed, purged with nitrogen for three times, and then pressurized with CO to the desired pressure. After being heated to the required reaction temperature, the autoclave was hold at this temperature for 7 h till the reaction was completed. After reaction, the autoclave was cooled to ambient temperature and the residue gas was released. The liquid samples were analyzed by GC using a HP-5 capillary column (30 m × 0.32 mm × 0.25 μm).

RESULTS AND DISCUSSION

Activities of Cobalt(II) Schiff Base Complexes

In the reaction of reduction carbonylation of $PhNO_2$ in the presence of methanol and various amounts of aniline, diphenyl urea is firstly formed, and then the alcoholysis of diphenyl urea by CH_3OH to form MPC take place nearly completely, in accordance with the data reported in the literature [15, 16]. Our experiments have shown that the optimal reaction time is 7 h. To make the comparison of the activities of various cobalt(II) complexes, all experiments were carried out as follows. 1.86 g of aniline (20 mmol), 1.23 g of nitrobenzene (10 mmol), Co(II) complexes with different ligands (0.2 mmol, 2 mol % in nitrobenzene) as catalysts, 0.2 mmol of *p*-toluenesulfonic acid (1 : 1 molar ratio to catalyst) and 30 ml of methanol were added at room temperature in the reactor. Then it was flushed with N_2 for three times and then pressurized with CO to 5 MPa. The reaction was allowed to proceed at 170°C for 7 h. The concentrations of the unreacted reactants and products in the liquid samples after reaction were determined by GC analysis using standard method, and the yield of carbamate regarding to nitrobenzene was calculated.

According to the GC analysis results, the desired product (methyl N-phenyl carbamate) is formed in dominant amount. N-methyl aniline (NMA) is a main byproduct of reductive and oxidative carbonylations, in accordance with data [17, 18], and it is formed by the methylation of aniline with methanol. Based on the stoichiometric relation in reaction (IV), the amount of aniline consumed must two times more than nitrobenzene consumed. However, as shown in Table 1, this relationship is really less than two. It can be explained that in the presence of an acidic promoter and reductive environment, some amount of nitrobenzene can be converted to aniline in accordance with the previous report [19], and this part of the formed aniline also contributes to aniline consumption:

$$PhNO_2 + 2CO + 2H^+ \longrightarrow PhNH_2 + 2CO_2. \quad (V)$$

It is also shown in Table 1 that the activities of the cobalt(II) Schiff base complexes depend on the nature of the ligand. The activities of the cobalt complexes with various ligands are increased in row: saldien < AA_2ph < saloph.

It is seen from Table 1 that the activity of Co[saldien] was very low, may be because that in the complexation sphere of the five coordinated Co[saldien] the cobalt(II) center ion is partly covered by the ligands and it reduces its reactivity to substrate. The comparison of saloph and the substituted saloph ligands indicates that the electronic and steric properties of the substituent in the modified saloph ligand strongly affect the reactivity of the corresponding cobalt(II) complexes, and this effect influences on the electron density of cobalt center as well as on the accessibility of axial position [19]. Among the three saloph-type ligands, the cobalt(II) complex with saloph ligand bearing electron-donating substituent, Co[$(OH)_2$saloph], showed the highest activity (54.5% of nitrobenzene conversion and 92.2% of selectivity to MPC). The cobalt(II) complex with saloph ligand bearing electron-withdrawing substituent, Co[$(NO_2)_2$saloph], showed the lowest catalytic activity. This fact indicates that the interaction of the cobalt with substrates is more favored by the modification of saloph ligand with electron-donating substituent.

The presence of acidic promoter has positive effect on the activity. When the reaction was conducted using non-promoted Co[$(OH)_2$saloph] as catalyst, a lower

Table 2. The pK_a values of different aromatic carboxylic acids and their effect on conversion and selectivity using a Co[$(OH)_2$saloph] catalyst

Promoter	pK_a^*	Conversion, %		Selectivity to MPC, %
		Nitrobenzene	Aniline	
–	–	38.2	28.5	73.3
Benzoic acid	4.19	50.3	40.3	90.6
2-Chlorobenzoic acid	2.89	40.5	32.7	89.3
Picolinic acid	5.52	11.3	9.1	82.6
p-Toluenesulfonic acid	1.70	54.5	45.6	92.2

Note: Reaction conditions: nitrobenzene—10 mmol, aniline—20 mmol, Co[$(OH)_2$saloph]—0.2 mmol, aromatic carboxylic acid—0.2 mmol, CO—5 MPa, 170°C, 7 h.
*All pK_a values measured in water at 25°C are taken from [20].

conversion of nitrobenzene (38.2%) and selectivity to MPC (73.3%) (Table 2) were obtained. On the one hand, owing to the proton transferring interaction between the aromatic carboxylic and nitrobenzene, a small quantity of nitrobenzene is converted to aniline, facilitating the carbonylation of aniline to MPC. On the other hand, the weak coordination of the aromatic carboxylic acid anion to Co center can stabilize the intermediate complexes formed during the reaction. According to the previous experimental results with using of various Schiff base cobalt(II) complexes, Co[$(OH)_2$saloph] was chosen as catalyst to investigate the effect of other reaction parameters.

The Promoter Effect

The correlation between the nature of the aromatic carboxylic acid and the performance of Co[$(OH)_2$saloph] was studied by the comparison of four aromatic carboxylic acids: benzoic acid, 2-chlorobenzoic acid, *p*-toluenesulfonic acid (PTS) and picolinic acid. The conversion and selectivity to carbamate as well as the pK_a value of the different acids are listed in Table 2.

As shown in Table 2, PTS shows the best promoting activity among the four acids giving 54.5% conversion of nitrobenzene and 92.2% selectivity to MPC. The catalytic activity of Co[$(OH)_2$saloph] is not strongly depended on the pK_a value of the acids. Among other aromatic carboxylic acids, only benzoic acid shows a comparative activity to PTS. 2-Chlorobenzoic acid is less effective than benzoic acid, this could be due to the larger steric hindrance of 2-chlorobenzoic acid. When picolinic acid was used as promoter, an apparent decrease in the activity of Co[$(OH)_2$saloph] was observed, a possible reason is that picolinic acid acts as a bidentate ligand which occupies two axial sites, and thus seriously hinders the accessibility of cobalt center.

It is also observed that azobenzene, a usual byproduct of reductive carbonylation, was not detected in all Co(II) Schiff base complex—carbonic acid systems. It seems that the acidic environment in this reaction system is not suitable for the formation of azobenzene.

The amount of promoter also affects the activity of Co[$(OH)_2$saloph]. To clarify this effect, a series of experiments with different content of promoting *p*-toluenesulfonic acid was conducted under the conditions described in experimental section. The profiles of the nitrobenzene conversion or selectivity of carbamate *vis* the acid/Co ratio are showed in Fig. 1.

It can be seen from Fig. 1 that the amount of PTS drastically affects the activity of Co[$(OH)_2$saloph]. When *p*-toluenesulfonic acid was added to catalytic system in low concentration, the conversion of nitrobenzene increased rapidly with the rise of the acid/Co ratio, and when this ratio is 1 : 1, it reached a maximum value (54.5%) under the reaction conditions. The further increase in acid/Co ratio in the range from 1.5 to 2.5 causes little change of nitrobenzene conversion, and when it increases up to 2.5, the conversion of nitrobenzene begins to decrease. This trend is probably associated with the fact that the pres-

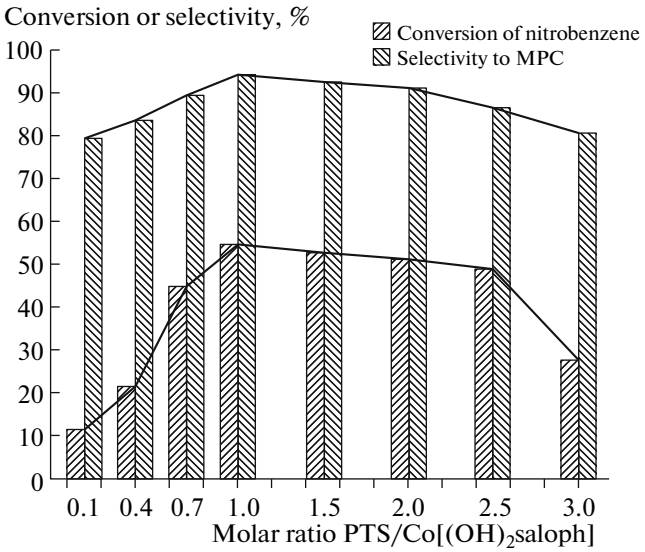

Fig. 1. The curves of the nitrobenzene conversion and selectivity of carbamate formation *vis* the acid/Co ratio.

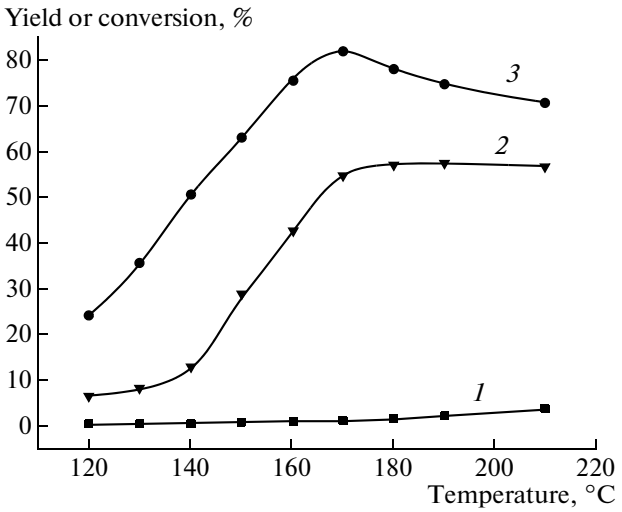

Fig. 2. Temperature effect on redox carbonylation of nitrobenzene and aniline catalyzed by Co[$(OH)_2$saloph]–PTS system: *1*—yield of NMA, *2*—conversion of nitrobenzene, *3*—yield of MPC. Reaction conditions: $PhNO_2$—10 mmol, $PhNH_2$—20 mmol, Co[$(OH)_2$saloph]—0.2 mmol, PTS—0.2 mmol, CO—5 MPa, time 7 h.

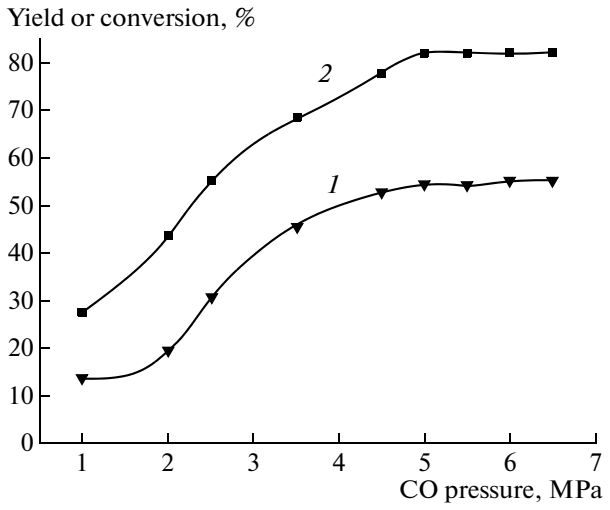

Fig. 3. CO pressure effect on the redox carbonylation of nitrobenzene and aniline catalyzed by Co[$(OH)_2$saloph]–PTS system: *1*—conversion of nitrobenzene, *2*—yield of MPC. Reaction conditions: $PhNO_2$—10 mmol, $PhNH_2$—20 mmol, Co[$(OH)_2$saloph]—0.2 mmol, PTS—0.2 mmol, temperature 170°C, time 7 h.

ence of excess of PTS can cause the protonation of aniline or the decomposition of the reactive complex.

The Effect of Reaction Temperature

Temperature also plays an important role in this reaction. To get insight to the effect of temperature the reaction was operated at various temperatures in Co[$(OH)_2$saloph]–PTS catalytic system. The results are shown in Fig. 2.

From 120 to 140°C nitrobenzene conversion and selectivity to MPC are low and increased slowly with the rise of temperature. When the temperature was raised up to 150°C, nitrobenzene conversion as well as MPC yield increased steeply and reached a maximum value at about 170°C. With the further raising of temperature, the yield of MPC began to decrease and the increasing of N-methyl aniline fraction in products is observed. It is caused by the quick increasing of contribution of aniline methylation side reaction at higher temperature [15]:

$$PhNH_2 + MeOH \longrightarrow PhNHMe + H_2O. \qquad (VI)$$

The Effect of CO Pressure

The effect of CO pressure on the reaction was studied at 170°C using Co[$(OH)_2$saloph] –PTS system as catalyst. It is noted that a relative high CO pressure is required for this reaction. When CO pressure is below 2 MPa, the reaction of MPC formation is slow. In the range of 2–5 MPa the conversion of nitrobenzene and yield of MPC increase steadily with CO pressure, the further increase in CO pressure above 6 MPa has no appreciable effect on the nitrobenzene conversion and MPC yield (Fig. 3).

Thus, in this paper, the composite catalytic system of various cobalt(II) Schiff base complexes and an aromatic carboxylic acid was applied as catalyst for the redox carbonylation of nitrobenzene and aniline. It is found that the Co(II) complex with saloph-type ligand showed better reactivity than Co(II) complex with saldien and AA_2en, affording higher conversion of nitrobenzene and yield of methyl N-phenyl carbamate. The suitable coordinating capability of the ligand with Co(II) center is required for the cobalt(II) Schiff base complexes with good catalytic activity, and too strong complexation of saldien is account for the low activity of Co(saldien). The electronic properties of the substituent on the saloph ligand have an important effect on the activity of the cobalt complexes, Co[$(OH)_2$saloph] is most effective among the three cobalt complexes with saloph-type ligands. The carboxylic acid in this catalytic system improved the activity of Co[$(OH)_2$saloph], and the promoting effect of a carboxylic acid is correlated to its capability of stabilizing various cobalt intermediate complexes. The comparison of the carboxylic acids indicates that *p*-toluenesulfonic acid has the best promoting effect.

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REFERENCES

1. Kim, H.S., Kim, Y.J., Lee, H., Lee, S.D., and Chin, C.S., *J. Catal.*, 1999, vol. 184, p. 526.
2. Shi, F., Deng, Y.Q., SiMa, T.L., and Yang, H.Z., *J. Catal.*, 2001, vol. 203, p. 525.
3. Tafesh, A.M. and Weiguny, J., *Chem. Rev.*, 1996, vol. 96, p. 2035.
4. Förster, S. and Rieker, A., *J. Org. Chem.*, 1996, vol. 61, p. 3320.
5. Delledonne, D., Rivetti, F., and Romano, U., *J. Organomet. Chem.*, 1995, vol. 488, p. C15.
6. Kureshy, R.J., Khan, N.H., Abdi, S.H.R., Patel, S.T., and Jasra, R.V., *Tetrahedron: Asymmetry*, 2001, vol. 12, p. 433.
7. Jacobsen, E.N., *Acc. Chem. Res.*, 2000, vol. 33, p. 421.
8. Aoyama, H., Tokunaga, M., Hiraiwa, S.I., Shirogane, Y., Obora, Y., and Tsuji, Y., *Org. Lett.*, 2004, vol. 6, p. 509.
9. Chen, L.J., Bao, J., Mei, F.M., and Li, G.X., *Catal. Commun.*, 2008, vol. 9, p. 658.
10. Li, G.X., Chen, L.J., Bao, J., and Mei, F.M., *Appl. Catal., A*, 2008, vol. 346, p. 134.
11. Chen, L.J., Mei, F.M., and Li, G.X., *Catal. Commun.*, 2009, vol. 10, p. 981.
12. Mei, H., Mei, F.M., and Li, G.X., *Xiandai Huagong / Modern Chemical Industry*, 2006, vol. 26, no. 5, p. 35.
13. Chen, D. and Martell, A.E., *Inorg. Chem.*, 1987, vol. 26, p. 1026.
14. Hill, H.A.O., Morallee, K.G., Pellizer, G., Mestroni, G., and Costa, G., *J. Organomet. Chem.*, 1968, vol. 11, p. 167.
15. Chuang, S.S.C., Kondurn, M.V., Chi, Y., and Toochinda, P., *Stud. Surf. Sci. Catal.*, 2000, vol. 130, p. 737.
16. Macho, V., Kralik, M., and Halmo, F., *J. Mol. Catal. A.: Chem.*, 1996, vol. 109, p. 119.
17. Bei, Ch. and Steven, S.C.C., *J. Mol. Catal. A.: Chem.*, 2003, vol. 195, p. 37.
18. Gasperini, M., Ragaini, F., Cenini, S., and Gallo, E., *J. Mol. Catal. A.: Chem.*, 2003, vol. 204–205, p. 107.
19. Huber, A., Müller, L., Elias, H., Klement, R., and Valko, M., *Eur. J. Inorg. Chem.*, 2005, no. 8, p. 1459.
20. *Lange's Chemistry Handbook*, Dean, J.A., Ed., New York: McGraw-Hill, 1999, 15th ed.