[Review Paper]

Novel Reactions Catalyzed by Transition Metal Carbonyls

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Iron, cobalt, and ruthenium carbonyls show novel catalytic activities. The $\text{Fe}(\text{CO})_5/\text{S}$ system is an excellent catalyst precursor for coal liquefaction using carbon monoxide/water, syngas/water, and carbon monoxide/alcohol as hydrogen sources. The carbonyl trinuclear ferrate/ KOH /support system exhibits high catalytic activity with high selectivity for lower olefins in Fischer-Tropsch synthesis. Using $\text{Co}_2(\text{CO})_8/\text{N}$ -silylamine, a variety of cyclic ethers are smoothly carbonylated to give the corresponding siloxy amides. The Ru-catalyzed C-H bond activation of a variety of formyl groups is widely applicable for hydroamidation, hydroesterification, and hydroacylation of olefins using formamides, formates, and aldehydes, respectively. The $\text{Ru}_3(\text{CO})_{12}$ /carbon monoxide system is effective for deoxygenative transformation of oximes and nitroarenes. Ketoximes, amidoximes, and aldioximes are converted into ketimines, amidines, and aldimines, respectively. *N*-(2-Nitrobenzoyl)amide is converted into a quinazolinone derivative *via* a nitrene intermediate.

Transition metal carbonyls have been providing interesting chemistries, utterly different from those of the corresponding metal oxides and halides. Transition metals can take a variety of oxidation states in forming complexes. Metal oxides and halides are generally stable at high valent states. On the other hand, transition metals with low valent states are effectively stabilized by coordination of π -acids such as carbon monoxide to emerge, for example, as metal carbonyl derivatives. Moreover, metal carbonyls have enhanced solubility in organic solvents and volatility. Due to these properties, transition metal carbonyls afford a unique chemistry quite different from the chemistry of metal oxides and halides¹⁾. The metal carbonyls have been well utilized in the fields of organometallic chemistry, catalytic chemistry, and C_1 chemistry²⁾. Carbon monoxide itself has a great advantage because of high reactivity and availability from coal and natural gas. Carbon monoxide has been used mainly in two ways, a carbon building block and a reductant. Chemistry concerned with carbon monoxide would continuously receive much attention in the near future.

We have had much interest in effective utilization of carbon monoxide and transition metal carbonyls these decades. This paper deals with

our recent topics on transition metal carbonyls catalyzed novel reactions: (1) $\text{Fe}(\text{CO})_5$ -catalyzed coal liquefaction³⁻⁷⁾, (2) iron carbonyl-catalyzed Fischer-Tropsch synthesis⁸⁻¹¹⁾, (3) cobalt-catalyzed carbonylation of cyclic ethers using silylamines¹²⁻¹⁴⁾, (4) ruthenium-catalyzed C-H bond activation of formyl groups¹⁵⁻²¹⁾, and (5) ruthenium-catalyzed deoxygenative transformation of oximes²²⁻²⁴⁾ and nitroarenes²⁵⁾ with carbon monoxide. These reactions might exhibit novel findings for using carbon monoxide and its derivatives as useful building blocks and specific reductants.

1. Highly Active Catalysts for Coal Liquefaction Using Alternative Hydrogen Sources

The use of highly pressurized molecular hydrogen in coal liquefaction partly results in high cost of the process²⁶⁾. The development of a liquefaction process using alternative hydrogen sources to molecular hydrogen is of great current importance. Since 1921, the liquefaction of coal using carbon monoxide and water has been well investigated, and alkali metal hydroxides or carbonates and transition metal compounds have been reported to be active as catalysts^{27), 28)}. Few disposable iron-based catalysts with excellent activity, however, are known.

Here we demonstrate that $\text{Fe}(\text{CO})_5$ /sulfur com-

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Coal 2.0 g, 1-methylnaphthalene 4.0 mL, H₂O 1.1 g, CO 7.0 MPa, Fe(CO)₅ 1.0 mmol, sulfur 3.0 mmol, 1 h.

Fig. 1 Effect of Reaction Temperature on Liquefaction of Yallourn Coal

bination is one of the most effective catalysts for coal liquefaction using alternative hydrogen sources such as carbon monoxide/water, syngas/water, and carbon monoxide/alcohol. Moreover, high coal conversion and high oil yield achieved with carbon monoxide/water are comparable to those with molecular hydrogen.

1.1. Liquefaction of Coals Using Carbon Monoxide/Water with Fe(CO)₅/S Catalyst³⁾

Pentacarbonyliron/sulfur showed an excellent catalytic activity for liquefaction of coals by carbon monoxide and water. The maximum coal (Yallourn, C, 68.2; H, 4.5; ash, 1.1%) conversion was achieved at 360–375°C (Fig. 1). At high reaction temperatures, oil yields increased at the cost of AS and PA yields³⁾. Thermal cleavage of coal structures was considered to be depressed at lower temperatures, and at high temperatures, recombination of coal radicals into higher molecular substances seemed to occur. Both high coal conversion and high oil yield were achieved by two-staged reaction, first at 375°C for 60 min and then at 425°C for 60 min (Table 1). The presence of pyrrhotite was confirmed by XRD analysis. Thus, Fe(CO)₅/S would act as well dispersed pyrrhotite in the liquefaction reaction in which

only 0.3 MPa of hydrogen gas was detected in the gas phase after the reaction (375°C, 60 min, H₂O 1.1 g), suggesting that the active hydrogen species for liquefaction was not the molecular hydrogen formed *via* water gas shift reaction. The real active species from carbon monoxide/water is not yet clear.

1.2. Liquefaction of Coal Using Syngas/Water⁴⁾

The syngas/water system is effectively used for liquefaction of Yallourn coal with Fe(CO)₅/S. A high oil yield together with a high conversion of coal was achieved by the two-staged reaction (Table 1, Run 8). It should be noted that the coal conversion did not decrease as in the case of syngas/water but decreased in the case of carbon monoxide/water. The presence of molecular hydrogen in the case of syngas/water would prevent the recombination of fractions into coke at higher temperatures. In the case of syngas/water, there will be two hydrogen sources, molecular hydrogen itself and carbon monoxide/water. The two sources worked competitively, and both were eventually consumed. The hydrogen consumption decreased with increase in the amount of water. With more than 0.2 g of water (2.0 g of coal), the amount of carbon monoxide consumed exceeded that of hydrogen (Fig. 2). Thus, for liquefaction, syngas/water system works well as two competitive hydrogen sources, molecular hydrogen and carbon monoxide/water.

1.3. Liquefaction of Coal Using Carbon Monoxide/Alcohol⁵⁾

The liquefaction of Yallourn coal proceeds effectively with carbon monoxide/alcohol. Methanol, however, was not appropriate. Both the coal conversion and oil yield in methanol were lower than those in ethanol. Propanols (*n*- and *iso*-) were as effective as ethanol. Preferable reaction temperatures were around 400°C with Fe(CO)₅/S (Fig. 3). The two-staged heating, at 375°C for 60 min and 425°C for 60 min, resulted in high coal conversion (94.8 %) together with high oil yield (59.1 %). The mass balance of ethanol was as follows. In the run, at 375°C for 60 min, 60 mmol of ethanol was charged, and 25 mmol was

Table 1 Fe(CO)₅/Sulfur-catalyzed Liquefaction of Yallourn Coal in CO–Water and Syngas–Water Systems^{a)}

Run	Catalyst	H ₂ [MPa]	CO [MPa]	H ₂ O [g]	Temp. [°C]	Time [min]	Conv. [d.a.f.%]	Oil [d.a.f.%]	AS [d.a.f.%]	PA [d.a.f.%]
1	none	—	7.0	1.1	375	60	57.2	31.8	14.7	10.6
2	Fe ₂ O ₃ /S	—	7.0	1.1	375	60	75.4	32.3	23.9	19.2
3	Fe(CO) ₅ /S	—	7.0	1.1	375	60	95.6	37.0	27.4	31.2
4	Fe ₂ O ₃ /S	—	7.0	1.1	375+425	60+60	70.8	47.2	13.8	9.9
5	Fe(CO) ₅ /S	—	7.0	1.1	375+425	60+60	92.8	55.8	24.2	12.8
6	Fe(CO) ₅ /S	3.0	3.0	1.1	375	60	86.3	36.9	23.1	26.3
7	Fe(CO) ₅ /S	3.0	3.0	0.24	375	60	97.0	35.1	39.3	22.6
8	Fe(CO) ₅ /S	3.0	3.0	0.26	375+425	60+60	96.7	56.9	25.2	14.6

a) Coal 2.0 g, catalyst 1.0 mmol-atom-Fe, 1-methylnaphthalene 4.0 mL, sulfur 0.096 g (3.0 mmol).

Yallourn coal 2.0 g, 1-methylnaphthalene 4.0 ml, CO 3.0 MPa, H₂ 3.0 MPa, Fe(CO)₅ 1.0 mmol, sulfur 3.0 mmol, 375°C, 1 h.

Fig. 2 Effect of Water on Consumption of Hydrogen and Carbon Monoxide

Coal 2.0 g, Fe(CO)₅ 1.0 mmol, sulfur 3.0 mmol, 1-methylnaphthalene 4.0 ml, EtOH 60 mmol, CO 7.0 MPa, for 1 h.

Fig. 3 Effect of Reaction Temperature on Liquefaction of Yallourn Coal

consumed. In the gas phase, carbon dioxide (36 mmol), ethylene (1.8 mmol), and ethane (4.4 mmol) were detected. The amount of carbon dioxide from coal itself was estimated to be 9.1 mmol and the amount of hydrogen used for liquefaction

was estimated to be 2.0 wt% of d.a.f.coal. This amount of hydrogen is comparable to that transformed into coal in liquefaction using molecular hydrogen^{6),7)}. The ethanol consumed (25 mmol) gave only 1.8 mmol of ethylene and 4.4 mmol of ethane suggesting that ethanol did not behave only as a water-precursor for liquefaction. Of the amount of ethanol consumed, the oxygen appeared to be converted into carbon dioxide but about 20 mmol of the ethyl group was missing. This finding strongly suggests that ethylation of coal would occur with carbon monoxide/ethanol system although its reaction mechanism is not yet clear. The carbon monoxide/alcohol system clearly works well as a hydrogen source for coal liquefaction to give high coal conversion with high oil yield.

2. Fischer-Tropsch Synthesis Catalyzed by Supported [NEt₃H][HFe₃(CO)₁₁]-alkali Metal Hydroxide System^{8)~11)}

In Fischer-Tropsch synthesis, several attempts have been made to prepare catalysts from low valent transition metal carbonyls supported on metal oxides and these catalysts such as Fe₃(CO)₁₂/γ-Al₂O₃, K₂Fe(CO)₄/γ-Al₂O₃, Ru₃(CO)₁₂/γ-Al₂O₃, NaHRu₃(CO)₁₁/TiO₂, and Rh₆(CO)₁₆/NaY zeolite exhibited low catalytic activity often with rapid deactivation²⁹⁾. We found that catalysts derived from [NEt₃H][HFe₃(CO)₁₁]-alkali metal hydroxide on a support exhibit high and stable catalytic activity with high selectivity for light olefins. Although it is known that alkali metals as a co-catalyst have considerable effects on catalytic activity and olefin selectivity in Fischer-Tropsch synthesis³⁰⁾, few systematic studies on such effects of alkali metals have been made so far. A carbonyl ferrate, [NEt₃H][HFe₃(CO)₁₁] free from alkali metals, appears to be quite suitable for investigating the effects of alkali metals systematically.

A ferrates/KOH/γ-Al₂O₃ catalyst was very active for conversion of syngas into light olefins, ethylene

Table 2 Fischer-Tropsch Synthesis Using Ferrates/KOH/γ-Alumina^{a)}

Run	Ferrate ^{b)}	K/Fe ratio	Effective conv. ^{c)} [%]	Product distribution ^{d)} [carbon%]						
				C1	C2	C3	C4	C5	C6	C7+
1	Fe ₃	0	25(48)	25	15(24)	25(73)	15	8	5	7
2	Fe ₃	0.26	41(91)	19	12(29)	22(77)	16	10	8	14
3	Fe ₃	0.74	15(60)	16	14(83)	18(91)	14	10	10	18
4	Fe ₂	0.26	33(83)	20	12(19)	22(65)	16	11	7	12
5	Fe ₂	0.88	13(57)	13	15(85)	19(91)	15	10	9	20
6	Fe ₁	0.26	40(93)	21	11(15)	22(69)	15	10	7	14
7	Fe ₁	0.68	15(56)	15	14(85)	19(91)	16	11	9	16

a) $P_{\text{total}}=14 \text{ kg}\cdot\text{cm}^{-2}$, CO/H₂=1.0, $SI=2,300 \text{ h}^{-1}$, 320°C.

b) Fe, 10 wt%. Fe₃=[NEt₃H][HFe₃(CO)₁₁], Fe₂=[NEt₄][HFe₂(CO)₈], Fe₁=[NEt₄][HFe(CO)₄].

c) Conversion of CO to hydrocarbons. Total conversions are given in parentheses.

d) Selectivities for olefins are given in parentheses.

$P=14 \text{ kg/cm}^2$, $\text{CO}/\text{H}_2=1.0$, 320°C , $\text{Fe}=10 \text{ wt\%}$.
HY=HY Zeolite, NaY=NaY Zeolite.

Fig. 4 Effect of KOH on F-T Synthesis Using $[\text{NEt}_3\text{H}][\text{HFe}_3(\text{CO})_{11}]/\text{KOH}/\text{Support}$

and propylene (Table 2). Even without KOH, $[\text{NEt}_3\text{H}][\text{HFe}_3(\text{CO})_{11}]/\gamma\text{-Al}_2\text{O}_3$ itself (10 wt% Fe/support) exhibited some catalytic activity for Fischer-Tropsch synthesis. The addition of a small amount of KOH remarkably enhanced both catalytic activity and selectivity for olefins. At KOH 1.8 wt%/support (0.26 of K/Fe atom ratio), one-path conversion of carbon monoxide attained

the maximum, 91% with 41% effective conversion of carbon monoxide into hydrocarbons (Fig. 4). The catalytic activity and products selectivity remained high for 80 h without deactivation. Further addition of KOH resulted in a sharp decrease in activity. The preferable amount of KOH for maximal catalytic activity depended on the support, alumina and zeolites. γ -Alumina among the supports gave the highest activity. Mono- and dinuclear ferrates, $[\text{NEt}_4][\text{HFe}(\text{CO})_4]$ and $[\text{NEt}_4][\text{HFe}_2(\text{CO})_8]$, could be also used as catalyst precursors. The profile of catalytic activities by addition of KOH to these ferrates was similar to that in the trinuclear ferrate. Among these three ferrates, the trinuclear one was most stable and reproducible and easiest to handle. To our knowledge, this is the first example in which iron carbonyl complexes were used as highly active catalyst precursors in Fischer-Tropsch synthesis.

3. Cobalt-catalyzed Carbonylation of Cyclic Ethers Using *N*-Silylamines^{12)~14)}

Catalytic carbonylation of a variety of cyclic ethers with three, four, and five membered rings has been extensively studied. Only a few successful examples, however, have been given³¹⁾. One of such examples is the preparation of 1,3-diol derivatives from oxiranes with $\text{HSiR}_3/\text{CO}/\text{Co}_2(\text{CO})_8$ system. Although cobalt-catalyzed hydroformylation of olefins is well known, hydroformylation

Table 3 $\text{Co}_2(\text{CO})_8$ -Catalyzed Ring-opening Carbonylation of Oxiranes Using *N*-Silylamines under 1 atm of Carbon Monoxide at Room Temperature^{a)}

Run	<i>N</i> -Silylamine	Oxirane	Time [h]	Product	Isolated yield ^{b)} [%]
1	-CH ₂ NHSiMe ₃		24	-CH ₂ NH-C(=O)-CH ₂ -CH ₂ -OSiMe ₃	84
2	-CH ₂ NHSiMe ₃		50	-CH ₂ NH-C(=O)-CH ₂ -CH ₂ -OSiMe ₃	60
3	-CH ₂ NHSiMe ₃		24	-CH ₂ NH-C(=O)-CH ₂ -CH ₂ -OSiMe ₃	81
4	-CH ₂ NHSiMe ₃		24	-CH ₂ NH-C(=O)-CH ₂ -CH ₂ -OSiMe ₃	79
5	-CH ₂ NHSiMe ₃		48	-CH ₂ NH-C(=O)-CH ₂ -CH ₂ -OSiMe ₃	72
6	<i>n</i> -C ₈ H ₁₇ NHSiMe ₃		24	<i>n</i> -C ₈ H ₁₇ NH-C(=O)-CH ₂ -CH ₂ -OSiMe ₃	83
7	-CH ₂ N(CH ₃)SiMe ₃		24	-CH ₂ N(CH ₃)-C(=O)-CH ₂ -CH ₂ -OSiMe ₃	89

a) *N*-Silylamine (3.0 mmol), oxirane (4.5 mmol), $\text{Co}_2(\text{CO})_8$ (0.10 mmol), benzene (5.0 ml) under 1 atm of carbon monoxide (balloon) at room temperature.

b) Based on the amount of *N*-silylamine charged.

of oxiranes using syngas has faced with the difficulty of industrial development because of the occurrence of such severe side reactions as isomerization of oxiranes to ketones and aldehydes, dehydration of generated β -hydroxy aldehydes, and oligomerization of products such as α,β -unsaturated aldehydes³². These side reactions can get readily out of control, preventing hydroformylation of oxiranes from industrial application.

Catalytic carbonylation of cyclic ethers and acetals can be done without any difficulty by use of *N*-silylamines. In the presence of *N*-silylamines and $\text{Co}_2(\text{CO})_8$ catalyst, a variety of cyclic ethers, oxiranes, oxetane, and tetrahydrofurans were smoothly carbonylated to give the corresponding β , γ , and δ -siloxyamides in excellent yields, respectively (Eq. (1) and Table 3). The impor-

tance of *N*-silyl functionality is explicitly demonstrated by use of benzylamine instead of *N*-(trimethylsilyl)-benzylamine. Under the same reaction conditions, no carbonylation proceeded and the benzylamine was recovered unchanged. Strong oxophilicity of silicon (bond dissociation energy; Si-O 430-530 kJ·mol⁻¹, Si-N 305-330 kJ·mol⁻¹) might facilitate the ring opening followed by carbonylation. A plausible reaction scheme for epoxides is shown in Scheme 1. Dicobalt octacarbonyl is the only active catalyst precursor for these reactions and other transition metal carbonyls are totally inactive.

The *N* silylamine/ $\text{CO}/\text{Co}_2(\text{CO})_8$ system can be used for carbonylation of formaldehyde dialkyl acetals to give the corresponding 2-alkoxyacetam-

Scheme 1

ides in fairly good yields (Eq. (2)). In this reac-

tion, the addition of pyridine enhanced the catalytic activity highly.

4. Ruthenium-catalyzed Carbonylation with Formyl Derivatives —Selective C-H Bond Activation of Formyl Groups^{15)~21)}

Ruthenium complexes such as $\text{Ru}_3(\text{CO})_{12}$ and $\text{RuCl}_2(\text{PPh}_3)_3$ have been known to have poor catalytic activities for carbonylation reactions. In the course of our studies on carbonylation of olefins with ruthenium catalysts, we found that hydroamidation of olefins proceeded smoothly in the presence of *N*-alkylformamides and the catalytic amount of $\text{Ru}_3(\text{CO})_{12}$ that yielded the corresponding alkanamides in excellent yields (Eq. (3)). This is the first example of one-to-one

addition of formamides to olefins through C-H bond activation of the formyl group. This reaction is catalyzed only by ruthenium carbonyls.

This type of reaction is widely applicable to such formyl compounds as alkyl formates, formaldehyde, and aromatic aldehydes. Thus, by this procedure olefins are converted into a variety of carbonyl derivatives, amides, esters, aldehydes, and ketones using formyl compounds as versatile carbonyl sources for carbonylation (Eq. (4)). The

combination of olefins with aromatic aldehydes provides a novel method for preparation of unsymmetric ketones. This is the first example of an intermolecular hydroacylation between olefins and aldehydes. This reaction, however, is applicable only for aromatic aldehydes such as benzaldehyde, 2- or 3-thiophenecarboxaldehyde, and pyrrolecarboxaldehyde. Ethanal and propanal were decarbonylated to give mainly methane and ethane, respectively, in the reaction. A plausible

reaction mechanism of hydroacylation involves a C-H bond activation of the formyl groups as demonstrated in **Scheme 2**. Using benzaldehyde and olefin, the catalytic cycle to phenyl alkyl ketone goes through a benzoyl hydridocomplex as a key intermediate. This type of intermediate appears to be in equilibrium with a decarbonylated phenyl complex, since ketone with ^{12}C carbonyl is obtained starting even with ^{13}C benzaldehyde. So undesired decarbonylation such as benzaldehyde to benzene takes place considerably as a side reaction.

Alkyl formates can react with a variety of arenes in the presence of ruthenium catalysts to give alkylated products (Eq. (5)). This reaction pro-

ceeds *via* electrophilic substitution on the basis of *o*- and *p*-oriented selectivity. This is a novel type of Friedel-Crafts alkylation using alkyl formates and a ruthenium catalyst.

The combination, $\text{Ru}_3(\text{CO})_{12}$ /formyl derivatives, however, has a limited application to convert only olefins into carbonyl derivatives. $\text{RuCl}_2(\text{PPh}_3)_3$ can also activate the C-H bond of formamides and catalyze the reaction between formamides and amines or alcohols. The new combination, $\text{RuCl}_2(\text{PPh}_3)_3$ /formamide, converts amines and alcohols effectively into *N,N'*-diarylureas and carbamates, respectively (Eq. (6)). The present reaction offers a novel

method for phosgene-free and carbon monoxide-free synthesis of ureas and carbamates.

5. Ruthenium Complex-catalyzed Deoxygenative Transformation of Oximes²²⁾⁻²⁴⁾ and Nitroarenes²⁵⁾ Using Carbon Monoxide

Since organic compounds with an azomethine group ($\text{C}=\text{N}$) are both important as synthetic and biologic intermediates, various methods for construction of the azomethine group have been reported. Among the methods, the more attractive and simpler one appears to be the deoxygenation of oximes using transition metal complexes, such as TiCl_3 and $\text{Fe}(\text{CO})_5$, in which stoichiometric or a greater amount of the complexes is required^{32),33)}. Thus, catalytic deoxygenation of oximes has not yet been reported. We found that ruthenium complexes combined with carbon monoxide exhibit high catalytic activity for selective deoxygenation of ketoximes, amidoximes, and aldoximes.

Ketoximes were selectively transformed into the corresponding ketimines in presence of proper amount of $\text{Ru}_3(\text{CO})_{12}$ under carbon monoxide pressure. Propiophenone oxime was smoothly deoxygenated to ethyl phenyl ketimine in 100% yield together with carbon dioxide in 85% yield. Carbon monoxide functioned effectively as a deoxygenating reagent. Metal carbonyls such as $\text{Co}_2(\text{CO})_8$ and $\text{Rh}_6(\text{CO})_{16}$ also exhibited catalytic activities but with much lower selectivities for deoxygenation. The present method is applicable for different ketoximes, aromatic, aliphatic, and cyclic ones (**Table 4**). A plausible reaction mechanism is illustrated in **Scheme 3**. The first key step appears to be the O-H bond cleavage of ketoxime with a low valent ruthenium catalyst to form hydrido(oximato)ruthenium species fol-

Table 4 Ru₃(CO)₁₂-Catalyzed Deoxygenation of Various Ketoximes^{a)}

Run	Substrate	Product	Yield ^{b)} [%]
1	$\begin{array}{c} \text{C}_6\text{H}_5 \\ \text{C}_2\text{H}_5 \end{array} \text{C}=\text{N}-\text{OH}$	$\begin{array}{c} \text{C}_6\text{H}_5 \\ \text{C}_2\text{H}_5 \end{array} \text{C}=\text{N}-\text{H}$	(100)
2	$\begin{array}{c} \text{C}_6\text{H}_5 \\ i\text{-C}_3\text{H}_7 \end{array} \text{C}=\text{N}-\text{OH}$	$\begin{array}{c} \text{C}_6\text{H}_5 \\ i\text{-C}_3\text{H}_7 \end{array} \text{C}=\text{N}-\text{H}$	91
3	$\begin{array}{c} \text{C}_6\text{H}_5 \\ \text{C}_6\text{H}_5 \end{array} \text{C}=\text{N}-\text{OH}$	$\begin{array}{c} \text{C}_6\text{H}_5 \\ \text{C}_6\text{H}_5 \end{array} \text{C}=\text{N}-\text{H}$	82
4	$\begin{array}{c} 4\text{-ClC}_6\text{H}_4 \\ \text{CH}_3 \end{array} \text{C}=\text{N}-\text{OH}$	$\begin{array}{c} 4\text{-ClC}_6\text{H}_4 \\ \text{CH}_3 \end{array} \text{C}=\text{N}-\text{H}$	77
5			75
6 ^{c)}	$\begin{array}{c} n\text{-C}_4\text{H}_9 \\ n\text{-C}_4\text{H}_9 \end{array} \text{C}=\text{N}-\text{OH}$	$\begin{array}{c} n\text{-C}_4\text{H}_9 \\ n\text{-C}_4\text{H}_9 \end{array} \text{C}=\text{N}-\text{H}$	82

a) Oxime (5.0 mmol), Ru₃(CO)₁₂ (0.10 mmol), benzene (5.0 ml), CO (20 kg·cm⁻²) at 100°C for 4 h.

b) Isolated yield (GLC yield).

c) For 8 h.

Scheme 3

lowed by carbon monoxide insertion, decarboxylation, and reductive elimination.

Using the method, aromatic and heteroaromatic amidoximes were also deoxygenated into amidines in excellent yields (Eq. (7)). Aliphatic amidox-

(7)

imes, however, could not be employed for the reaction, yielding amidines only as minor products. When deoxygenation of aromatic amidoximes was carried out in the presence of 1,3-dicarbonyl compounds, acetylacetone and ethyl

acetoacetate, six-membered *N*-heterocycles, pyrimidines were obtained in excellent yields. The formation of amidines appears to be essential for *N*-heterocyclization.

Such aldoximes as heptanaloxime and benzaloxime were only dehydrated into the corresponding nitriles under the deoxygenation conditions used. Aldoximes, however, gave deoxygenated and further gave allylated products when the deoxygenation reaction was conducted in the presence of allylic carbonate (Eq. (8)). In this

(8)

reaction, aldoximes are firstly deoxygenated into aldimines, RCH=NH, and the generated aldimines are then sufficiently reactive for allylation with allylic carbonates *via* π -allylruthenium species.

The combination of ruthenium catalysts with carbon monoxide is applicable for deoxygenative *N*-heterocyclization of nitroarenes. We have developed *N*-heterocyclization using transition metal catalysts and *o*-substituted amino- and nitroarenes^{35)~38)}. Reductive *N*-heterocyclization of nitroarenes is considered to proceed *via* active nitrene species. We have found that Ru₃(CO)₁₂ selectively catalyzes reductive *N*-heterocyclization of *N*-(2-nitrobenzoyl)amides into 4(3*H*)-quinazolinone derivatives in excellent yields (Eq. (9)).

(9)

Since the starting compounds are easily derived from *o*-nitrobenzoic acid and amides, this method is widely applicable for construction of a quinazolinone nucleus.

In conclusion, we have succeeded in developing unique catalytic reactions which are characteristic of iron-, cobalt-, and rutheniumcarbonyls, respectively. The metal carbonyls using carbon monoxide, syngas, or formyl derivatives exhibit excellent performances in the transformation of a variety of substrates such as coal, syngas itself, cyclic ethers, alkenes, amines, oximes, and nitroarenes.

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要 旨

遷移金属カルボニルを用いる新規触媒反応の創出

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鉄, コバルトならびにルテニウムカルボニル錯体について, それぞれの金属の特性を生かした新規触媒反応を開発した。鉄カルボニルは, 石炭の直接液化反応において, 温和な条件で高い触媒活性を示し, 水素源として一酸化炭素/水, 一酸化炭素/アルコール, 合成ガス/水系をそれぞれ有効に利用できることを示した。カルボニル鉄酸塩/水酸化カリウム担持触媒は, 合成ガスからの低級オレフィン合成に高い活性を示し, 触媒活性は担体の種類によらず水酸化カリウムの添加量により強く影響された。コバルトカルボニル触媒は, シリルアミン存在下, 環

状エーテル類のカルボニル化反応に高い活性を示し, シロキシアミド類が得られた。ルテニウムカルボニル触媒は, ホルミル基 C-H 結合の活性化に高い活性を示し, ギ酸アミド, ギ酸エステル, アルデヒドを用いるオレフィンのヒドロアミド化, ヒドロエステル化, ヒドロアシル化などの反応を開発した。ルテニウムカルボニルは, 一酸化炭素を還元剤として用いるオキシム類ならびにニトロ芳香族の脱酸素還元反応に高い活性を示し, ケチミン, アミジンなどの新規合成法ならびにナイトレンをかき中間体とする合成反応を開発した。

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Keywords

Carbon monoxide, Carbonyl complex, Coal liquefaction, Fischer-Tropsch synthesis, Transition metal, Homogeneous catalysis