Liquid Phase Hydrogenation of Carbon Monoxide (Part 2) Catalytic Properties of Ultrafine Particles Composed of Iron, Cobalt, and Nickel

Hiroyuki ITOH*, Eiichi KIKUCHI, and Yoshiro MORITA

Department of Applied Chemistry, School of Science and
Engineering, Waseda University
3-4-1 Okubo, Shinjuku-ku, Tokyo 160

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Liquid phase hydrogenation of carbon monoxide (Fischer-Tropsch synthesis) was investigated with ultrafine particles (UFP) composed of iron, cobalt and nickel as catalysts, which were prepared by vapor phase reduction of their metal chlorides and were passivated by gradual oxidation. The catalysts composed mainly of iron showed high catalytic activity and oxygenate selectivity. Although aggregation of UFP caused deterioration of activity and oxygenates selectivity, the deterioration could be recovered by ultrasonic irradiation. Addition of colloidal potassium to UFP catalysts effectively modified the active sites on the UFP to yield higher molecular weight products. On addition of potassium, the oxide phase formed in the UFP during passivation procedures disappeared at an early stage of reaction, and the aggregation of the catalyst particles was suppressed.

1. Introduction

Hydrogenation of carbon monoxide (Fischer-Tropsch synthesis) is accompanied by a large heat evolution. Consequently, local superheating of the catalyst surface is usually inevitable in the gas phase synthesis. To improve heat transfer, Kölbel et al.¹⁾ have proposed liquid phase synthesis using a slurry reactor where the liquid carrier efficiently removes the heat of reaction. Their catalysts were promoted iron granules of 30 μm on the average. It is expected that the use of smaller catalyst particles will bring about higher yields in the liquid phase synthesis.

The term "ultrafine particle (UFP)" is used to represent the materials in which the particle size is less than 0.1 μm . In such materials, relatively high proportions of the atoms are located on or close to the surface, and there is a high density of potential bonding sites. So, the properties of the UFP surface are quite different from those of the bulk material. From this point of view, it awakens a wide interest in the application of UFP to various

fields of science and industry. Preparation of UFP may be accomplished either by breaking-down or building-up;²⁾ however, in either case, it is very important to stop the process at the required particle size. The UFP's used in this study were prepared by hydrogen reduction of chloride vapors, and they were nonporous spheres.³⁾

Many of the currently used catalysts, e.g., precipitated or Raney type catalysts, are porous with relatively large internal surface areas. Though, in these catalysts, a large surface area can be achieved without difficulty in handling of fine particles, diffusion of the reactants or that of the products in the catalyst pores will be fairly slow, so that only the mouth of the catalyst pores will be available for rapid reactions. Therefore, the use of a nonporous and high surface area catalyst may be advantageous. Though there are some studies reported on catalysis by UFP,^{4),5)} its application to Fischer-Tropsch synthesis is not one of them.

The objective of this study is to determine the catalytic activity and selectivity of UFP catalysts for the liquid phase Fischer-Tropsch synthesis. It is almost impossible to use UFP in the gas phase synthesis, since to hold the UFP in a fixed catalyst

* To whom correspondence should be addressed.

bed is difficult, and it will easily sinter during the exothermic synthesis. Dispersion of UFP in a liquid carrier to form a suspension is effective against sintering of UFP catalysts.

In general, addition of alkaline promoters to iron catalysts is very effective for the Fischer-Tropsch synthesis.⁶⁾ However, to our knowledge, alkali promotion has not been applied to UFP catalysts. So, the procedure for and effects of potassium promotion on UFP catalysts were also investigated.

2. Experimental

2.1 Apparatus and Procedure

Hydrogenation of carbon monoxide was carried out in a high pressure, circulating flow system previously described.⁷⁾ Syngas ($H_2/CO=1$), fed to the bottom of the reactor, reacted on the catalyst suspended in the liquid carrier (cetane). The gas was partly recycled by using a solenoid pump, and the catalyst particles were agitated in the liquid carrier by the recycling gas. Concentration of the catalyst was adjusted to be 1.6 wt%. An ultrasonic generator (Nihonseiki, US-300) was used to prepare a suspension of the UFP catalyst as follows: the UFP catalyst in cetane was irradiated with ultrasonic (20 kHz, 85 W) for 10 min at room temperature.

The procedure for potassium addition to a UFP catalyst is shown in **Fig. 1**. The procedure used in the present work was the application of the extremely easy and rapid method for formation of colloidal potassium developed by Luche et al.⁸⁾ When potassium metal pieces in dried cetane were exposed to ultrasonic irradiation at room temperature, a silvery blue color developed rapidly, and after a few minutes the metallic pieces disappeared. A very fine suspension of potassium thus obtained settled very slowly on standing. Potassium-promoted UFP catalysts were prepared

by addition of a predetermined amount of colloidal potassium to the catalyst suspension.

2.2 Catalysts

Five kinds of UFP catalysts and a precipitated catalyst composed of iron, cobalt, and nickel were used in the present work.

The UFP catalysts listed in **Table 1** were prepared by hydrogen reduction of the chlorides in vapor phase at ca. 1,000°C. The unreacted chlorides were washed out with water in an inert gas atmosphere. The catalysts were passivated by gradual oxidation in a controlled atmosphere to avoid violent oxidation when exposed to the air. Consequently, the surface of the UFP catalysts was covered with oxide layers. Transmission electron microscopic (TEM) observations showed the aggregation of fine metal particles as shown in **Fig. 2**. The average size of the primary particles measured by TEM, and the BET surface area of the UFP catalysts are listed in **Table 2**. The specific surface areas were roughly in agreement with the values calculated on the assumption that the particles were nonporous spheres.

Table 1 Composition of UFP Catalysts

Catalyst	Chemical Composition (wt%)				XRD Analysis
	Fe	Co	Ni	O	
A	79.2	1.0	2.0	Balance	α -Fe, Fe_3O_4
B	1.2	81.2	10.4	Balance	Co(cubic)
C	1.2	1.8	69.4	Balance	Ni
D	72.2	14.2	1.4	Balance	α -Fe, Fe_3O_4
E	47.6	2.8	39.8	Balance	Ni, Fe_3O_4 , γ -(FeNi)

Table 2 Particle Sizes and Specific Surface Areas of UFP Catalysts

Catalyst	Particle Size (Å)		BET Area (m ² /g)
	TEM	BET*	
A	4.8×10^2	6.0×10^2	12.6
B	3.6×10^2	4.2×10^2	16.0
C	5.9×10^2	6.1×10^2	11.2
D	4.0×10^2	4.8×10^2	15.4
E	4.3×10^2	4.8×10^2	14.9

* Assuming nonporous spheres

Fig. 1 Procedure for Potassium Promotion

Fig. 2 Transmission Electron Micrograph of Catalyst C

Fig. 3 Product Distributions and Reaction Rates on Various UFP Catalysts

A precipitated catalyst having the same composition as that of catalyst D was prepared from aqueous nitrates using KOH aqueous solution as the precipitant. Details of the procedure are as follows: aqueous nitrates of the metals (92 g-metal/l) and KOH aqueous solution (ca. 5 N) were boiled separately, and the KOH solution was added rapidly to the aqueous nitrates. The resulting pH was about 8.0. After 30 minutes of ripening, the precipitate was filtered and washed with hot water. The catalyst thus prepared was calcined at 350°C for 6 hr, then crushed to fine particles, smaller than 200 mesh (74 μ m), and activated in a stream of H₂ at 300°C for 6 hr. The X-ray diffraction pattern for this catalyst after these treatments showed that the crystalline composition of the catalyst was almost the same as that of catalyst D. The BET surface area of the precipitated catalyst was 16.1 m²/g.

3. Results and Discussion

Liquid phase hydrogenation of carbon monoxide was investigated at 220°C and 30 atm using various UFP catalysts. **Figure 3** shows the product distribution and average reaction rate for the initial 6 hr of run. Catalysts A and D, composed mainly of iron showed high catalytic activity and selectivity for oxygenated organic compounds (mostly alcohols). Catalyst D with a composition of 82.2Fe-16.2Co-1.6Ni was the most active and selective for oxygenates. On the other hand, paraffinic lower molecular weight products were formed

Reaction conditions : temperature, 220°C ; pressure, 30 atm ; H₂/CO, 1 mol/mol ; W/F, 1,060 g-cat.min/CO-mol

Fig. 4 Catalytic Activities with Time on Stream

predominantly on catalysts C and E which contained a large amount of nickel. Hydrocracking of cetane (liquid carrier) also took place on these catalysts under the reaction conditions due to the high hydrogenation activity of nickel.

Catalytic activities and selectivities of TiO₂-supported Fe-Co-Ni alloy catalysts have been investigated by Arai et al.^{9),10)} They have reported that activities of the alloy catalysts are

greater than those of pure metal catalysts, and that selectivities of the alloys relative to the pure metals shift to forming higher molecular weights. Though we have not investigated catalysis of pure metal UFP, the effect of alloying may also appear in this work. The relation between activity and composition of our UFP catalysts was not in agreement with the results reported by Arai et al. It is not clear, at present, whether the difference is caused predominantly by the difference in the reaction conditions or in the catalyst type.

Variations in the catalytic activity expressed by the level of CO conversion with time on stream are shown in **Fig. 4**. Activities of catalysts B and D decreased with time on stream. Similar deterioration patterns, which are not shown here, were observed with catalysts C and E. On the other

hand, the activity of catalyst A increased significantly in the initial 3 hr period. The X-ray diffraction studies on fresh and used catalyst A indicated that Fe_3O_4 in the fresh catalyst decreased in the course of activity enhancement. This result suggests that catalytic activity increase with time on stream if an easily-reducible catalyst is used.

In the remaining work of this study, the behavior of catalyst D, which shows the highest catalytic activity, will be discussed in more detail.

Figure 5a shows the variation in the catalytic activity and in the oxygenates selectivity of catalyst D as a function of time on stream. Both the catalytic activity and oxygenate selectivity decreased with time on stream. Aggregation of catalyst particles was visible in the liquid carrier after deactivation. The catalyst slurry after use in the

Catalyst : catalyst D. Reaction conditions : temperature, 220°C ; pressure, 30 atm ; H_2/CO , 1 mol/mol ; W/F, 1,060 g-cat.min/ CO -mol

Fig. 5 Effects of Ultrasonic Irradiation on CO Conversion and Oxygenate Content in Product

Reaction conditions : temperature, 220°C ; pressure, 30 atm ; H_2/CO , 1 mol/mol ; W/F, 1,060(a), 3,710(b) g-cat.min/ CO -mol. Catalyst composition ; Fe : Co : Ni = 82.2 : 16.2 : 1.6 (weight ratio).
 ▨, olefin ; ▤, alcohol ; ▤, aldehyde and ketone

Fig. 6 Product Distributions and Reaction Rates over UFP (catalyst D) and Precipitated Catalysts

first run was taken out from the reactor and was treated under ultrasonic irradiation (20 kHz, 85 W) for 1 hr at room temperature. This treatment was found to be effective for redispersion of UFP, since the sedimentation velocity of the UFP was reduced by this treatment. The ultrasonicated slurry was reused in the reaction. As shown in **Fig. 5b**, the levels of catalytic activity and oxygenates selectivity of catalyst D were restored almost to those of the fresh catalyst; however they decreased again with time on stream as in the first run. Thus, aggregation of fine catalyst particles is considered to be the cause of deactivation and decrease in the oxygenate selectivity.

Reaction conditions : temperature, 220°C ; pressure, 30 atm ; H_2/CO , 1 mol/mol. Catalyst : catalyst D. K addition : ○, none ; △, 1 wt% of catalyst

Fig. 7 Mass Distributions (C-%) of Hydrocarbon Products on Carbon Number Fractions

Figure 6 shows the rate of CO conversion and distribution of the products eluted from the reactor at various stages of reaction compared to the results obtained on the precipitated catalyst. The products formed on the deactivated UFP (in 5–6 hr on stream) were similar to those formed on the precipitated catalyst. When the catalytic activity was recovered by ultrasonic irradiation, the product distribution also shifted close to that observed on the fresh catalyst.

Effects of potassium promotion to UFP catalysts were investigated using catalyst D. **Figure 7** shows the effect on hydrocarbon distribution. The average molecular weight of the products formed on the promoted UFP catalyst was significantly higher than that formed on the unpromoted catalyst. Thus, the method employed in the present work to modify the UFP catalyst by colloidal

Reaction conditions : temperature, 220°C ; pressure, 30 atm ; H_2/CO , 1 mol/mol ; W/F, 500 g-cat.min/ CO -mol. Catalyst : catalyst D. K addition : ○, none ; △, 1 wt% of catalyst.

Fig. 8 Effect of Potassium Addition on Catalytic Activity Change

Reaction conditions : temperature, 220°C ; pressure, 30 atm ; H_2/CO , 1 mol/mol ; W/F, 500 g-cat.min/ CO -mol. Catalyst : catalyst D. K addition : 1 wt% of catalyst

Fig. 9 Effect of Ultrasonic Irradiation on CO Conversion

Reaction conditions : temperature, 220°C ; pressure, 30 atm ; H_2/CO , 1 mol/mol ; W/F, 1,060 g-cat. min/ CO -mol ; time, 6 hr

Fig. 10 X-ray Diffraction Patterns of Fresh and Used Catalyst D

potassium is valid for changing the nature of active sites; the modified sites yield higher molecular weight hydrocarbons.

Figure 8 illustrates the variation in catalytic activities of promoted and unpromoted UFP catalysts as a function of time on stream. Though the initial activity of the promoted catalyst was lower than that of the unpromoted catalyst, deactivation was suppressed by addition of potassium. The catalyst suspension used for 6 hr was treated by ultrasonic irradiation for 1 hr at room temperature, and was reused in the synthesis. Although the activity of the unpromoted catalyst was recovered by such ultrasonic treatment, the activity of the promoted catalyst was unaffected as shown in **Fig. 9**. This result shows that aggregation of UFP was avoided by potassium addition.

The X-ray diffraction patterns for fresh and used catalysts are shown in **Fig. 10**. The pattern

for the unpromoted used catalyst indicates that the oxide phase formed in the fresh catalyst during passivation procedures remained after reaction. On the other hand, in the case of the promoted UFP catalyst, the oxide phase disappeared during the reaction. Furthermore, X-ray diffraction measurements on the promoted catalyst at several stages of reaction showed that the oxide phase was carburized to form Fe_2C at an early stage of reaction (less than 1 hr on stream). Therefore, it is considered that composition of the UFP catalysts play a key role in aggregation behavior. Though the cause of slow deactivation observed in **Fig. 9** cannot be explained precisely at present, it may be attributed to the change in the surface state or to the sintering of the UFP.

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要 旨

一酸化炭素の液相接触水素化（第 2 報）鉄、コバルト、ニッケル系超微粒子の触媒特性

伊藤 宏行, 菊地 英一, 森田 義郎

早稲田大学理工学部応用化学科, 160 東京都新宿区大久保 3-4-1

塩化物の気相還元法により調製された Fe, Co, Ni 系超微粒子 (UFP) を触媒として, 液相法による一酸化炭素の水素化反応 (F-T 合成) を行い, UFP の触媒特性およびカリウムの添加効果について検討した。

反応は試作したスラリー床式高压流通循環反応装置⁷⁾を用いて行い, 循環ガスで触媒 (1 g) を分散媒 (セタン, 80 ml) に懸濁した。UFP 触媒の分散には超音波破壊機を用い, カリウムの添加は Fig. 1 に示したように, 金属カリウムの懸濁液の所定量を触媒のスラリーに添加することにより行った。また, 通常の実験条件は温度 220°C, 圧力 30 atm, 供給 H₂/CO 比 1 とした。

使用した触媒は塩化物の気相還元法により調製し, 徐酸化処理した Fe, Co Ni 系複合金属 UFP (Fig. 2) であり, その組成および平均粒子径, 比表面積はそれぞれ Tables 1, 2 に示した。また, 比較のために使用した共沈法による沈殿触媒は各金属硝酸塩の混合水溶液を用い, KOH 水溶液を沈殿剤として調製した。得られた沈殿は焼成後粉碎し, H₂ 気流中 300°C, 6 hr 活性化処理した。

各 UFP 触媒を用いて 6 hr の反応を行ったときの平均の活性および生成物分布を Fig. 3 に示した。Fe の割合が高い触媒 A, D は高い活性および含酸素化合物 (主としてアルコール) 選択性を示した。特に触媒 D は最も高活性であり, 含酸素化合物選択性も高かった。CO 転化率の経時変化を Fig. 4 に示した。触媒 C および E は図中の触媒 B, D と同様に劣化した。触媒 A は反応開始後 3 hr 活性が上昇した。この差異は反応条件下での触媒表面の還元の見易さによるものと考えられる。

特に触媒 D の活性が高いことから, 以下触媒 D について検

討した。Fig. 5a には活性および含酸素化合物選択性の経時変化を示した。反応時間とともに活性, 含酸素化合物の選択性とも低下した。反応後の触媒には粒子の凝集がみられたが, 超音波照射により再分散された。このとき活性, 含酸素化合物選択性はともに回復し, 新触媒の場合と同様な経時変化を示した (Fig. 5b)。Fig. 6 には触媒 D を用いて反応を行ったときの初期と劣化後の活性および生成物分布を触媒 D と同一組成の沈殿触媒と比較して示した。劣化後の UFP 触媒上の生成物分布は沈殿触媒のものによく類似していたが, 超音波照射により活性が回復するとともに生成物分布も新触媒のものに近づいた。

さらに, UFP 触媒のカリウムによる修飾について検討した。カリウムを添加した UFP 触媒で生成する炭化水素の分布は無添加のものに比べ高分子量側に移行しており (Fig. 7), 本方法で添加したカリウムの懸濁液が UFP 触媒上の活性点を有効に修飾していることが明らかになった。Fig. 8 にはカリウム添加の有無による活性の経時変化の差を示した。カリウムを添加することにより, 反応初期の活性は低くなったが, 活性劣化は抑制された。このとき, 6 hr の反応に使用した後の触媒に超音波照射しても活性の変化はみられなかった (Fig. 9)。また, 新触媒および反応後の触媒の X 線回折図 (Fig. 10) を比較すると, カリウム無添加の場合徐酸化処理で生成した酸化物は 6 hr の反応後の触媒中にも存在するが, カリウムを添加した場合酸化物は反応中に消失した。さらに反応の各段階で X 線回折測定を行うと, カリウムを添加した場合反応の初期 (< 1 hr) において酸化物が炭化物に変化していることが明らかになった。これらの結果から, UFP 触媒の組成がその凝集挙動に大きく影響していると考えられる。

Keywords

Carbon monoxide, Fischer-Tropsch synthesis, Hydrogenation, Liquid phase reaction, Metal catalyst, Ultrafine particle