Industrial Chemistry Library, Volume 1

Progress in C_1 Chemistry in Japan

Edited by

The Research Association for C_1 Chemistry
Toranomon, Minato-ku, Tokyo 105, *Japan*

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Preface

The C1 Chemistry Project, officially called "Research and Development Program for New Technologies to Produce Basic Industrial Chemicals from Carbon Monoxide and Other Chemicals", was conducted over a period of seven years, from 1980 to 1986, as a project of the National Research and Development Program System of the Agency of Industrial Science and Technology of the Ministry of International Trade and Industry (MITI). The project was implemented with the close cooperation of the academic community, government laboratories and private industry and consisted of two parts: one to develop new technologies to synthesize chemicals from mono-carbon compounds and the other to develop new technologies to separate carbon monoxide and hydrogen using membranes. This volume gives an overview of the project and describes in detail the results in the development of catalysts and processes for the synthesis of basic chemicals.

Oil crises, occurring twice in the 1970's, made government and those in the chemical industry keenly aware of the total dependency of Japanese petrochemical industries on oil, a resource which is almost non-existent in Japan. The aim of the C1 Chemistry Project was to consolidate a base for the Japanese chemical industry enabling the use of any carbon resource which is cheap and easily available. From the technological viewpoint, the aim of the project

was to find new ways to synthesize chemicals of desired carbon numbers starting from the C_1 compounds, carbon monoxide, hydrogen and/or methanol obtainable from any carbon resource, instead of manufacturing chemicals using the high molecular hydrocarbons in oil as the starting material.

The Japanese chemical companies are still inferior in size and profitability compared to the gigantic multinational chemical companies of the U.S. and Europe. To develop the above technologies, joint research among companies and government cooperation were essential. This was the fundamental reason for the C_1 Chemistry Project.

The National Chemical Laboratory for Industry of MITI and the Research Association for C_1 Chemistry, which was established by 14 companies and a private research institute, conducted this project in very close cooperation and coordination with each other.

At the same time on the academic side, the Catalysis Society of Japan set up a Committee on C_1 Chemistry to encourage academic research and promote cooperative research activities among academic, government and private sectors. The committee held symposia on C_1 chemistry four times between 1984 and 1987.

I personally felt the necessity for promoting C_1 chemistry in general and urged the start of a cooperative research program in advance. Later, I was involved in this project as a member of the governmental review board which oversaw the research plan, budget and progress of the project and also chaired the committee of the Catalysis Society of Japan. At the same time, I strongly urged the publication of the results of this unique enterprise for the benefit those in concerned.

Although the results of the project have been made public in numerous reports and patents in Japanese, the Research Association for C_1 Chemistry decided to publish this book in English, first of all to make available our results, which we believe will become indispensable for the chemical industry, to the world at large, and second, to serve as a reference guide for researchers and planners in other countries concerning the management of a national project, providing details of cooperation among academia, government and private industry.

Chapter 1 deals with the progress of basic research at academic institutions and the National Chemical Laboratory for Industry, which supported the joint research of companies.

Chapters 2 through 7 are detailed reports on catalyst surveys, bench tests and process development of six synthetic processes of the project. As published previously in individual reports, the targets established at the beginning of the project were achieved for most of these processes. However, this volume also contains information of interest to readers which have not yet been made public. I know of no other document which contains such minute descriptions regarding background and insights in catalyst development, one of the most secret areas in corporate research and development.

In the course of the seven years of this project, economic conditions concerning oil and energy changed dramatically. The economic superiority of oil versus other carbon resources revived. Thus the fruits of the project, i.e. new catalysts and new processes, may not be commercialized in the immediate future. However, I am of the opinion that various findings in this project, e.g. experimental facts, hypotheses and rules deduced from experiments, are of great value in the research on catalysts and processes in areas other than those covered by this project. As pointed out earlier, I believe that the results of the project are extremely useful and relevant to the present time. For this reason, I think this volume is very valuable for researchers and companies. At the same time, it is the record of unique cooperative research. Within the limited and specific scope of the project, no secrets were withheld among the participating Japanese chemical companies, which ordinarily compete very fiercely with each other.

I thank the contributors who took the time from their very busy schedules to write and the staff of Kodansha Scientific who managed the publication.

Yukio Yoneda

Tokyo
Autumn 1988

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Chapter 1

General Review of C_1 Chemistry in Japan

1.1 Introduction

In Japan and throughout the world, C_1 chemistry was raised to an important and urgent target of research in the field of catalysis, homogeneous or heterogeneous, in academic as well as governmental institutions at the end of the 1970's when the oil shortage was a major concern. The number of research reports and symposiums on C_1 chemistry increased enormously with the trend lasting ten years.

The Catalysis Society of Japan responded the demand of the day by setting up a special committee for C_1 chemistry. The members of the committee worked hard to survey and discuss the existing problems and organized a number of symposiums concerning the field of C_1 chemistry and related areas. The activities of the committee were supported in part by the Research Association for C_1 Chemistry.

The following is a list of the topics of the symposiums, which were held under the auspices of the committee.

1. C_1 Chemistry (January 1981)
2. Feasibitities of the substitutes for Rh-catalysts in C_1 chemistry (June 1981)
3. Possibilities of novel reactions and novel catalysts in C_1 chemistry (September 1981)
4. Selectivity control in C_1 chemistry (January 1982)
5. Raw materials in C_1 chemistry (June 1982)
6. Zeolites--Possibility of zeolites superior to ZSM-5 (October 1982)
7. Recent development and future progress in C_1 chemistry (December 1982)
8. Do metal clusters open up new area in C_1-chemistry? (June 1984)
9. Recent development and future progress in technology for raw materials in C_1 chemistry (December 1984)
10. Selectivity control in FT synthesis (June 1984)
11. Zeolite catalysts--recent advances and developments (December 1984)
12. New catalysts and new technology in C_1 chemistry (March 1985)
13. Characteristics of Rh and Ru as catalysts (November 1985)
14. C_1 chemistry in the future (December 1986)

The hard work of the committee resulted in a monograph C_1 Chemistry in Japanese published in 1984 by Kodansha.[1)]

The Catalyst Society of Japan devoted its semiannual meeting in April 1981 to the subject. The number of participants exceeded 400.

Besides these activities, the committee and the Research Association for C_1 Chemistry sponsored four joint symposiums, which were very effective in transferring the knowledge accumulated in C_1 project to chemists at academic institutions and vice versa.

"Pan-pacific Synfuels Conference" was held in November 1982 under the auspices of the Japan Petroleum Institute. C_1 chemistry was one of the major topics of the symposium.[2)]

The following sections will summarize very brief by the works from academic institutions (section 1.2) and from the National

Chemical Laboratory for Industry (section 1.3) in the field of C_1 chemistry and related subjects. There is no doubt that what was accomplished contributed not only to C_1 chemistry itself, but also to the understanding of the chemistry of catalysis in general.

In this short overview, methane reactions such as the partial oxidation to ethylene or formaldehyde are not included, though the activation of methane was an important subject for discussion in the catalytic community in Japan throughout the period and become the subjects of active investigation by many scientists. The reader should refer to an excellent review by Otsuka on this topic.[3]

1.2 C_1 Chemistry at Academic Institutions

1.2.1 Fischer-Tropsch Synthesis

A number of works have been published on the production of hydrocarbons by the reaction of CO and H_2 over metal catalysts (FT synthesis). Most of them concern the factors controlling the activity and selectivity of the synthesis, and the mechanism of CO hydrogenation.

A. Effect of Particle Size of Metals

Fukushima *et al.*[4] studied the effect of the support and the metal dispersion on the FT synthesis over supported Ru catalysts. Under atmospheric conditions, the high dispersion catalyst was more active than the low conversion catalyst. The reverse effect of the dispersion was observed in the reaction under pressure (6 atm). The propagation probability α did not depend on the support, but on the dispersion. The low dispersion catalyst gave a higher value of α.

Okuhara *et al.*[5] prepared Ru/Al_2O_3 catalysts from $Ru_3(CO)_{12}$ and $RuCl_3$, and studied the effects of dispersion on the activity and selectivity in CO hydrogenation. Ru/Al_2O_3 catalysts prepared from $Ru_3(CO)_{12}$ showed high dispersion (> 80%) and were more active and selective for alkenes than the catalysts prepared from $RuCl_3$,

though the distribution of hydrocarbons produced was not sensitive to Ru dispersion. For each series of Ru/Al_2O_3, the turnover frequency increased as the dispersion decreased. This was explained by the poisoning effect of adsorbed CO of twin type, $Ru(CO)_2$, which was strongly held on the Ru surface.

Lin *et al.*[6] reported that the morphology of metal particles affected significantly the selectivity of CO hydrogenation. Thus, after the reduction of $RuCl_3$-impregnated alumina by H_2 at 723° K, Ru particles were aggregates of fine particles, and by subsequent oxidation at 773° K and reduction at 723° K, they changed to large single crystallites of Ru. Higher hydrocarbons were significantly formed over the former, and mostly methane over the latter.

Iwasawa *et al.*[7] reported that carbon monoxide was selectively converted to ethylene and propylene (> 80% of C_1-C_6 hydrocarbons produced) at 433° -447° K over SiO_2-supported Rh catalysts prereduced with a CO-H_2O mixture. Rh catalysts obtained by the pretreatment with a H_2-H_2O yielded ethanol and acetaldehyde in high selectivity at 453° K. On the other hand, a Rh catalyst prereduced with hydrogen gave methane as a major product. The authors suggested that a small surface Rh (I) cluster is the catalyst precursor for the selective formation of lower olefins.

B. Effect of Additives on Ru-Catalysts

Murakami and coworkers[8] reported that the addition of V, Mo, W or Re to Ru/Al_2O_3 increased the rate of C-O bond dissociation, while it decreased the rate constant for the hydrogenation of the surface CH_x species by the pulse surface rate analysis. By the same technique, they found that alkali carbonate added to the Ru catalyst decreased the rate constant for C-O bond dissociation, but that scarcely affected the hydrogenation of the surface carbon species. The addition of alkali carbonate shifted the infrared absorption band of adsorbed CO to a lower frequency as a result of the increase in the electron density in the metal.[9]

Misono and coworkers[10] studied the effect of additives in FT synthesis over alumina-supported Ru prepared from $Ru_3(CO)_{12}$. K increased alkene/alkane ratio and decreased the methane fraction, and the effect of P was opposite. The band shift of C-O stretching of

adsorbed CO molecules showed that K and P (or B) affects mainly the electronic state of Ru.

The addition of V suppressed methane formation with a slight decrease in the alkene/alkane ratio. From the comparison of the effect of V addition on the turnover frequency of CO hydrogenation with those on the turnover frequencies of benzene hydrogenation and ethane hydrogenolysis, they suggested that Ru particles were partially covered by V (or an oxide of V). Thus, the effects of V were ascribed to a geometric effect, e.g. ensemble effect, not to the electronic effect.

Misono and coworkers[11] also studied the effects of alkali metals added to silica-supported Ru catalysts on CO hydrogenation. As for the relative extents of the effects, the following trends are noted. The reaction rate decreased in the order of none > Li > Na > K ≈ Cs, while the selectivity to methane was in the order of none > Cs ≈ K > Na > Li.

The effect of Li was remarkable: the rate of methane formation decreased to 1/90 of the rate on non-doped catalyst, while the rate of C_{2^+} formation decreased only to 70%. From the infrared-band shift of adsorbed CO, electron microscopy and X-ray diffraction of the Ru particles and the change in the chemisorption capacity of H_2 and O_2, they concluded that Ru particles were partially covered by a compound of Li and that the suppression of methane formation by Li was due to a geometric effect.

Arai *et al.*[12] extensively studied CO hydrogenation over alloy catalysts, Fe-Co, Co-Ni, and Fe-Ni supported on TiO_2. The activities of alloy catalysts were higher than those of pure metal catalysts.

C. Effect of Supports

Kikuchi *et al.*[13] studied the effects of supports for Ru on the hydrogenation of CO and found that Ru supported on V_2O_3 and TiO_2 showed high activity for FT synthesis and low selectivity for methanation compared to Ru supported on Al_2O_3. The authors ascribed the characteristics of the two supports to the SMSI (strong metal-support interaction) effect.

Tamaru and coworkers[14] reported that the Rh/TiO_2 catalyst in

the SMSI state (after high temperature reduction) showed significantly lower activity than that after low temperature reduction and that the selectivity was changed in the SMSI state to higher hydrocarbons. It was also demonstrated by FT infrared spectroscopy that the SMSI state was destroyed by water produced during CO + H_2 reaction and the catalysts recovered the ability to adsorb gas as well as their catalytic activity.[15] Similar observations on Pt/TiO_2 were also reported by Kunimori *et al.*[16]

Kunimori *et al.*[17] found that the number of water molecules formed by H_2 treatment of Pt/TiO_2 at 773° K, which brought about SMSI, was of approximately the same magnitude as the number of Pt atoms in the catalyst. Based on this fact, they refuted the model invoking the stronger chemisorption of hydrogen on Pt metal, or the one involving the spillover and back-spillover of hydrogen as the major mechanism of SMSI. They also found that the hydrogen consumption during H_2 treatment of Pt/TiO_2 is proportional to the depression of H_2 chemisorption by the treatment, and that the oxygen consumption during oxygen treatment is proportional to increase of H_2 chemisorption.[18] They suggested the reversible redox cycle of TiO_2 by the treatments.

Kunimori *et al.* reported that activities for CO hydrogenation on Rh/Nb_2O_5 in the SMSI state were two orders of magnitude lower than in normal state.[19] The high temperature treatment of Rh/Nb_2O_5 in He as well as in H_2 caused marked decrease (by 10^3 in He, by 10^6 in H_2) in the catalytic activity for ethane hydrogenolysis. The authors noted that there is a subtle difference between Rh/Nb_2O_5 and Rh/TiO_2 systems.[20] The SMSI effect on the catalytic activities for CO hydrogenation on Rh/N_2O_5 and Pd/Nb_2O_5 was also reported.[21]

Kunimori *et al.*[22] found that an Nb_2O_5-modified Rh/SiO_2 catalyst(5.7wt% Nb_2O_5) exhibited SMSI behavior in ethane hydrogenolysis, the interaction being as strong as that in the Rh/Nb_2O_5 system. They suggested that the high-temperature reduction of Nb_2O_5-modified Rh catalysts leads to uniform covering of Rh surface with reduced niobia, NbO_x and the suppression of the catalytic activity with increasing reduction temperature is caused by a physical blockage of Rh surface site by NbO_x.

Iizuka *et al.*[23] studied the hydrogenation of CO and CO_2 over

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