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# Possibility of Direct Conversion of $CH_4$ and $CO_2$ to High-Value Products

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**The possibilities of low-temperature activation of $CH_4$ and hydrogenation of $CO_2$ were analyzed, and the feasibility of the direct conversion of $CH_4$ and $CO_2$ to oxygenated compounds by means of a two-step reaction sequence at low temperature was studied. Preliminary experimental results show that the interaction of $CH_4$ adspecies with $CO_2$ on Cu–Co-based catalysts can produce various compounds such as alcohol, aldehyde, ketone, carboxylic acid, and cyclopentane derivatives. The product composition and distribution depend greatly on the way in which the feed is introduced, but acetic acid and a cyclopentane derivative are produced according to the three methods studied. The optimum temperature is 250°C and the optimum Cu/Co ratio is 5 for acetic acid production. FTIR measurements confirmed the formation of $CH_x$ and $CH_xO$ over the catalysts used.** © 2001 Academic Press

*Key Words:* **methane; carbon dioxide; Cu–Co catalysts; two-step reaction; acetic acid.**

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## 1. INTRODUCTION

Conversion and utilization of $CO_2$ as well as of $CH_4$ are important subjects in the field of $C_1$ chemistry. Converting $CO_2$ is desirable because of its greenhouse effect. Due to the large $CH_4$ reserves in the world and its economic and environmental superiority to coal, it may become the main source of energy and chemical feedstock after petroleum. Conversion of $CO_2$ requires consumption of hydrogen, while that of $CH_4$ requires oxygen. Therefore, the conversion of $CH_4$ and $CO_2$ together is an ideal combination of an oxygenation reaction and a reduction reaction.

Basically, there are three routes for the chemical use of methane. The first is the so-called indirect route, in which methane is converted into syngas in the presence of water (steam reforming), $CO_2$ (carbon dioxide reforming), or oxygen (partial oxidation); and the resultant syngas can be used in the traditional way. The second route is direct coupling in the presence of oxygen (oxidative coupling of methane) or hydrogen (two-step polymerization). The third route is the conversion of methane directly to oxygenates ($CH_3OH$, $CH_2O$), methane chlorides, or HCN in the presence of oxygen, $Cl_2$, and HCl or ammonia respectively.

When the existing technology is applied, $CO_2$ and $CH_4$ are converted in an indirect method. First, $CO_2$ and $CH_4$ are converted into CO and $H_2$ by reforming at high temperature (generally $>800°C$); then CO and $H_2$ are further transformed to oxygenates or to higher hydrocarbons through the Fischer–Tropsch reaction at lower temperature ($\sim 320°C$). This indirect method appears to be inefficient, since all of the hydrogen in the methane is stripped in the first step and then subsequently reintroduced in the second. Moreover, reforming requires a large energy input, but only part of the energy is recovered in the second step. The temperature differential further exacerbates the heat transfer problem of the process (1).

Our laboratory is trying to develop a technology by means of which methane and $CO_2$ can be converted directly to high-value chemicals at low temperature (100–400°C). An outline of the proposed research is given in Fig. 1.

The present study was conducted to determine whether direct low-temperature conversion of $CH_4$–$CO_2$ occurs in a two-step reaction sequence with the aim of developing oxygenates, such as acetic acid.

Direct low-temperature conversion of $CH_4$–$CO_2$ has been studied in only a few cases (2–6). Raskó and Solymosi (2, 3) observed that $CH_3$ adspecies (from azomethane) reacted rapidly with $CO_2$ to CO, $CH_2O$, and $CH_3O$ at low temperature over $TiO_2$ and $Rh/SiO_2$ catalysts. Fujiwara *et al.* (4) reported that high yields of acetic acid resulted from the direct reaction of $CH_4$ with $CO_2$ by means of homogeneous catalysis at 80°C using a $Pd(OAc)_2/Cu(OAc)_2/K_2S_2O_8$/TFA catalyst, which created a new way of synthesizing acetic acid and using $CH_4$. Yan *et al.* (5) investigated the direct carbonylation of $CH_4$ by means of a two-step method and observed the formation of ethanal and ethanol. In their patent (6), Freund *et al.* claimed to have developed a method of manufacturing acetic acid from $CH_4$ and $CO_2$ using VIIB or VIII metal-supported $Al_2O_3$ or $SiO_2$ catalysts at 100–600°C, but they did not give specific examples. Generally speaking, all low-temperature reactions involving $CH_4$ and $CO_2$ are

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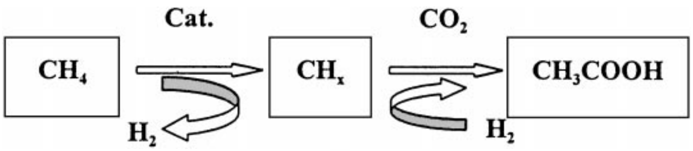

**FIG. 1.** Profile of direct synthesis of acetic acid from $CO_2$ and $CH_4$.

thermodynamically unfavorable (1); thus, it is necessary to adopt unconventional methods. Recent publications (1, 7, 8) have shown that activation of $CH_4$ to $CH_x$ ($x = 0$, 1, 2, or 3) at low temperature over certain metal catalysts is not especially difficult. The key difficulty is achieving low-temperature conversion of $CH_4$ by using $CH_x$ species to avoid high operating temperatures, high-energy consumption, and coke deposition of the existing conversion method of $CH_4$. The C–H bond energy of $CH_4$ is equal to the H–H bond energy. Moreover, the activation of $CH_4$ produces the same intermediate ($CH_x$) as the hydrogenation of $CO_2$:

$$CH_4 \xrightarrow{\text{Catalyst}} CH_x \xrightarrow{CO_2} \text{oxygenates}, \qquad [1]$$

$$CO_2 \xrightarrow{H_2} CH_x \xrightarrow{CO_2} \text{oxygenates}. \qquad [2]$$

Accordingly, it is reasonable to study the possibility of low-temperature conversions of $CH_4$ and $CO_2$ using the catalysts for hydrogenation of $CO_2$.

## 2. METHODS

### 2.1. *Catalysts*

A series of copper–cobalt-based catalysts with Cu/Co ratios from 0.3 to 6 were used in this work. These catalysts are generally used in the hydrogenation of $CO_2$ and CO and can activate $CH_4$ as well as insert $CO_x$ ($x = 1$ or 2). The preparation method is described in detail in the literature (9). To ensure that the oxygen contained in the products comes from $CO_2$ rather than from crystal lattice oxygen, we did not add nonreducible oxides to some catalysts.

### 2.2. *$CH_4$–$CO_2$ Temperature-Programmed Surface Reaction ($CH_4$–$CO_2$ TPSR)*

The temperature-programmed surface reaction (TPSR) of $CH_4$–$CO_2$ was carried out using a TP-5000 apparatus (Xianquan Instrument, Tianjin) with a thermal conductivity detector. A sample of 100 mg was first treated with a reducing gas of 10% $H_2/N_2$ at a flow rate of 20 ml/min in a temperature-programmed manner. The final temperature was 400°C. After treatment, the sample was exposed at 350°C to a 10% $CH_4$/Ar flow for 10 min and then to pure Ar for 5 min. Thereafter, the reactor temperature was decreased to 50°C. A mixture of 10% $CO_2$ in Ar or 10% $CO_2$ and 5% $H_2$ in Ar was passed over the catalyst from 50 to 600°C at 15°C/min.

### 2.3. *Reaction Procedure*

The catalyst (2.5 g) was placed in a continuous fixed-bed flow reactor. Before the reaction, the catalyst was reduced *in situ* with 10% $H_2/N_2$ at the same temperature used in the TPSR. After reduction, the catalyst was fed at normal pressure alternatively with $CH_4$ or $CO_2$ at the given temperatures. The products were collected in a trap cooled with ice-water or absorbed by a 0.1 N NaOH solution and analyzed by means of gas chromatography (GC 6890 A/5973 MSD) and ion chromatography (Dinox-500, Dinox, United States), respectively. The composition of the outlet gas was analyzed on a GC-9A gas chromatograph (Shimadzu, Japan) fitted with a thermal conductivity detector. The feed gases, such as $CH_4$, $CO_2$, Ar, and $H_2$ were provided by the Beijing Analysis Instrument Plant and by the Taiyuan Iron and Steel Company. The feed gases did not contain $C_{2+}$ compounds detectable by chromatography.

### 2.4. *Catalyst Characterization*

The fresh and used catalysts were both diluted with KBr, and IR spectra were measured with an FTS-165 FTIR instrument (Bio-Rad, Richmond, CA).

## 3. RESULTS AND DISCUSSION

### 3.1. *$CH_4$–$CO_2$ TPSR*

The catalysts with Cu/Co ratios from 0.3 to 6 (referred to as CC03 to CC6) were investigated by means of TPSR. Figure 2 shows a typical $CH_4$–$CO_2$ TPSR profile. The operating conditions were described in Section 2 and are also in the caption to Fig. 2. The figure shows clearly that there is a sharp peak at about 200°C. A similar pattern was

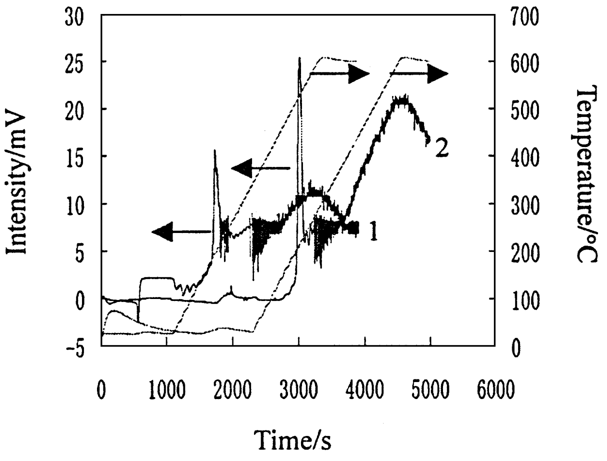

**FIG. 2.** Temperature-programmed surface reaction of adsorbed $CH_4$ with $CO_2$ on catalyst CC5. Flow 10% $CH_4$/Ar for 10 min and Ar for 5 min at 350°C, followed by a decrease in temperature to 50°C, and then (1) flow 10% $CO_2$/Ar from 50 to 600°C at 15°C/min, (2) flow 10% $CO_2$/5% $H_2$/Ar from 50 to 600°C at 15°C/min.

obtained when $CO_2$ was replaced by $CO_2/H_2$ to react with $CH_4$ adspecies, with the result that the intensity of this peak increased. This shows, on one hand, that the same reactions occur with both $CH_{x(ad)}/CO_2$ and $CH_{x(ad)}/CO_2/H_2$ and, on the other hand, that $H_2$ is beneficial to the reactions. Several investigations (1, 7, 8) have demonstrated that adsorption of $CH_4$ on the catalyst surface is a process of dehydrogenation, and that this process is enhanced with adsorption time and cleaning with a diluting gas after the adsorption. Thus, in the pure $CO_2$ reaction with $CH_x$ species to acetic acid, after cleaning with a diluting gas, performed in the absence of hydrogen, adding hydrogen to the reaction represents a clear advantage.

### *3.2. Activity and Selectivity*

Figure 3 shows the production of acetic acid over the typical Cu–Co catalysts and its dependence on reaction temperatures. All reactions were carried out at normal pressure and under isothermal conditions. The products were collected in the alkaline solution and analyzed by ion chromatography. The catalysts were alternatively exposed to a $CH_4$ flow of 50 ml/min for 5 min and a $CO_2$ flow of 75 ml/min for 10 min. The product of 20 cycles was collected for analysis. Figure 3 shows that the rate of acetic acid formation increases with increasing Cu/Co ratio and operatiing temperature, and reaches a maximum at a Cu/Co ratio of 5 and a temperature of 250°C. This result is consistent with that of the TPSR.

Formic acid is a primary side product that can be detected by ion chromatography. The production of formic acid is interesting, because unlike acetic acid, formic acid was not obtained for any catalyst at 250°C, the temperature at which the most acetic acid was produced (Fig. 4). The cause is unclear at this time. Generally speaking, a higher reaction temperature is favorable.

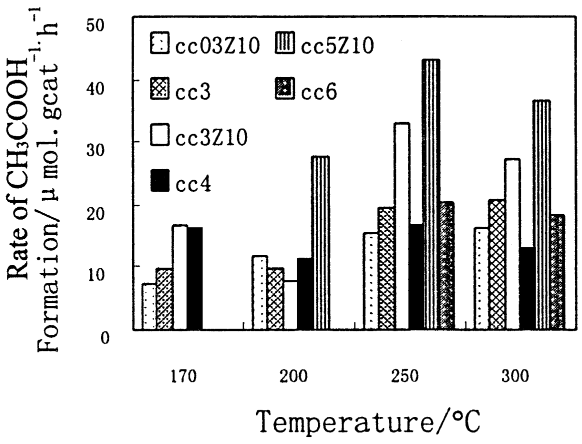

**FIG. 3.** Comparison of Cu–Co catalyst activities to acetic acid (the rate refers to 20 × 15 min, Z = Zr).

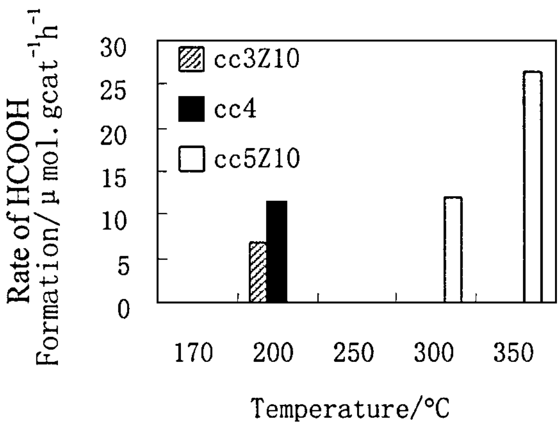

**FIG. 4.** Comparison of Cu–Co Catalyst activities to formic acid (the rate refers to 20 × 15 min, Z = Zr).

The liquid product, collected in the trap cooled with an ice-water mixture, was analyzed by GC-MS. Methanol, formaldehyde, butanone, methyl furan, and two cyclopentane derivatives were present in the liquid product together with formic and acetic acids. When the method of introducing feed was changed, the composition and distribution of the product also changed considerably.

The first feed (feed consisted alternatively of 50 ml/min $CH_4$ for 5 min and 75 ml/min $CO_2$ for 10 min, both at 200°C, and cleaned with diluting gas for 5–10 min at the gas switch interval) produced mainly $C_1$–$C_4$ alcohols (48%), two cyclopentane derivatives (44%), and some acetic acid (5.6%). The second feed ($CH_4$ and $CO_2$ fed alternatively as described above, but no cleaning in the gas switch interval) gave mainly formic acid (36%) and compounds such as butanone (2.40%) and $\alpha,\beta$-butenone (trace), and methyl furan (5.50%) in addition to methanol (21%), acetic acid (28%), and a cyclopentane derivative (3.4%). The third feeding method ($CH_4$ and $CO_2$ fed simultaneously under the same conditions as the first feed except temperature was 350°C) produced only formaldehyde (68%), a cyclopentane derivative (21%), and acetic acid (12%). No liquid product was obtained at a reaction temperature of 200°C held for 6 h. Because the third procedure is thermodynamically constrained, the formation of acetic acid is noteworthy. A similar result, observed by FTIR, has been reported (10). From the GC-MS analysis, the second type of feed results in the primary side products of methanol and formic acid.

The composition and distribution of the products, as well as the formation of cyclopentane derivatives, change with the type of feed, thus supporting to a great extent the occurrence of carbon-chain growth as the first step of the reaction (11). This is because cyclopentane is one of the primary products with high carbon chains in the homologation of $CH_4$ through an isothermal two-step reaction. $CH_4$ adspecies can become dehydrogenated and polymerized during the cleaning with diluted gas, which results in a larger quantity of the products with higher carbon chains in the first type of feed.

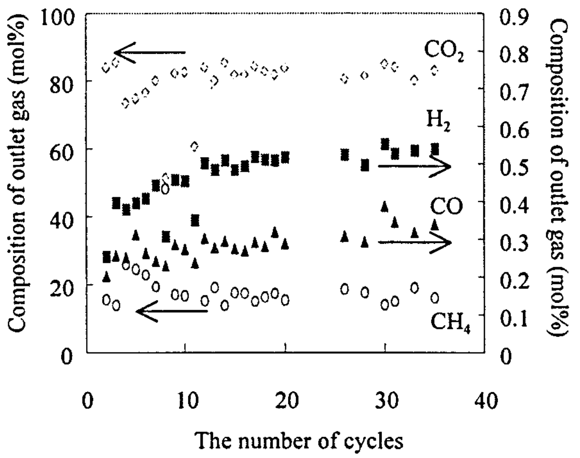

**FIG. 5.** Composition of outlet gas 3 min after feeding $CH_4$ in each reaction cycle.

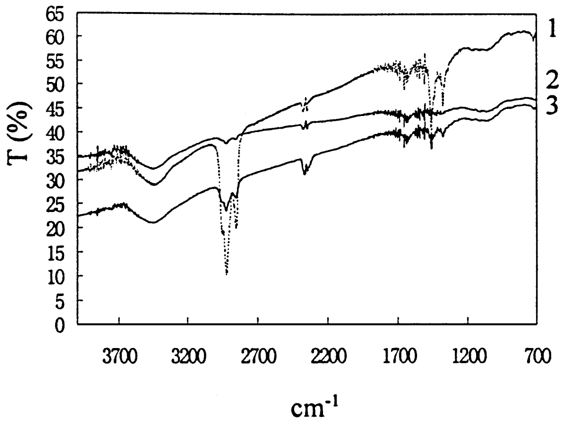

**FIG. 7.** FTIR spectra of the used catalysts: (1) $CH_4$ and $CO_2$ fed simultaneously, (2) $CH_4$ and $CO_2$ fed alternatively, (3) hydrogenation of $CO_2$.

### *3.3. The Outlet Gas*

Checking the hydrogen formation during the feeding of $CH_4$ and comparing the amount of $CO_2$ in the outlet gas during feeding with $CO_2$ after and before exposure of the catalyst to a $CH_4$ flow, information about catalyst performance can be obtained. This is because hydrogen formation represents the degree of $CH_4$ activation, and the change in $CO_2$ produced in the outlet gas during feeding with $CO_2$ reflects the extent of the $CO_2$ reaction with the $CH_4$ adspecies. As shown in Fig. 5, hydrogen formation is approximately constant after 10 cycles of feeding $CH_4$. This reveals that catalyst performance remained steady during the period of observation.

Figure 6 shows that the amount of $CO_2$ outlet gas changes with reaction time for the CC5 catalyst. The upper curves (Fig. 6), which represent the $CO_2$ adsorption curves, are those of the $CO_2$ outlet gas introduced after the catalyst had been cleaned with Ar for 20 min following a complete cycle. The lower curves, representing the $CH_4$–$CO_2$ reaction, are those of the $CO_2$ outlet gas introduced after the catalyst had been exposed to a $CH_4$ flow and then cleaned with Ar for 10 min. These two groups of experiments were carried out alternatively. The results show that the amount of $CO_2$ in the outlet gas changes more when $CH_4$ adsorption occurs, indicating that $CO_2$ reacts with the $CH_4$ adspecies and that the activity of the catalysts did not decrease during the period investigated.

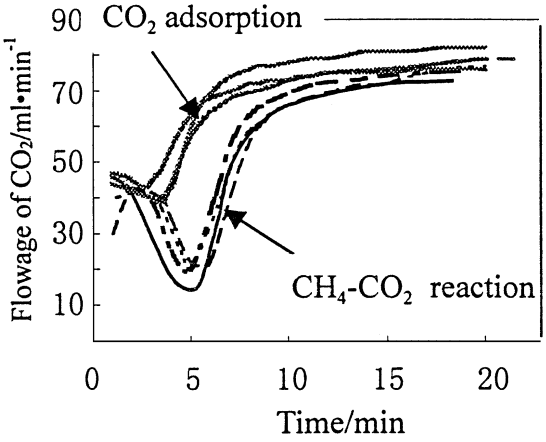

**FIG. 6.** Change of $CO_2$ outlet gas with reaction time.

### *3.4. FTIR Measurements*

FTIR measurements of the used catalysts (Fig. 7) show that, as well as $CO_2$ adsorption peaks at 2365 and 2340 $cm^{-1}$, strong C–H peaks appeared at 2952, 2922, and 2853 $cm^{-1}$, which are very close to those observed for $CH_3$ (from azomethane) adsorbed (2960, 2922, and 2854 $cm^{-1}$) on $Rh/SiO_2$ (2) and $TiO_2$ (3). The peak at 2922 $cm^{-1}$ can be attributed to $CH_3$ adspecies (2, 3, 12), and the peaks at 2952 and 2853 $cm^{-1}$ correspond to adsorbed $CH_3O$ (2, 3). An identical FTIR spectrum was obtained when the catalyst was used for hydrogenation of $CO_2$ (curve 3). Comparing the peak intensity at 2800 to 3000 $cm^{-1}$ and the three types of feed, the highest intensity was found when using simultaneous feeds, followed by the intensity during the hydrogenation of $CO_2$, and the lowest intensity was found when using the alternative method of feeding. Because nearly all of the reactions for the synthesis of oxygenates from $CH_4$ and $CO_2$ are thermodynamically unfavorable at low temperature, $CH_x$ species produced in the simultaneous feed cannot react effectively with $CO_2$ to products. Therefore, it is reasonable that the peaks at 2800 to 3000 $cm^{-1}$ are stronger. On the contrary, when $CH_4$ and $CO_2$ are fed alternatively, the produced $CH_x$ can react effectively with $CO_2$ and convert into products (a two-step reaction sequence can overcome the thermodynamic limitations). In addition, FTIR measurements of the catalysts after the reaction with $CO_2$ reflect the concentration of the $CH_x$ adspecies remaining on the catalyst surface. This explains why the intensity of the obtained peak was lower. This suggests that $CH_4$ may be activated effectively on the surface of Cu–Co-based catalysts, even in the presence of $CO_2$; i.e., the presence of $CO_2(CH_4 : CO_2 = 1 : 1.1)$ does not greatly affect the ability of the catalysts to activate $CH_4$. It is obvious that the alternative feed method can result in the effective conversion of $CH_4$ and $CO_2$ at low temperatures.

## 4. CONCLUSIONS

The results indicate that the direct conversion of $CH_4$ and $CO_2$ to high-value products is possible. The main obstacle is presented by thermodynamics rather than kinetics. The thermodynamic limitions can be circumvented by the periodic operation of a catalyst.

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## REFERENCES

1. Guczi, L., Van Santen, R. A., and Sarma, K. V., *Catal. Rev.-Sci. Eng.* **38**, 249 (1996).
2. Raskó, J., and Solymosi, F., *Catal. Lett.* **46**, 153 (1997).
3. Raskó, J., and Solymosi, F., *Catal. Lett.* **54**, 49 (1998).
4. Fujiwara, Y., Taniguchi, Y., Takaki, K., Kurioka, M., Jintoku, T., and Kitamura, T., *Stud. Surf. Catal.* **107**, 275 (1997).
5. Yan, Z., Xu, J., and Shen, S., *Tianranqi Huagong* **22**, 37 (1997).
6. Freund, H.-J., Wambach, J., and Seiferth, O., and Dillmann, B., Patent DE 4428566C1, Germany, 1995.
7. Tanaka, K.-I., *J. Chem. Soc. Chem. Commun.*, 938 (1982).
8. Pareja, P., Molina, S., Amariglio, A., and Amariglio, H., *Appl. Catal. A* **168**, 298 (1998).
9. Huang, W., Xie, K., Li, X., Li, Y., and Yin, L., *in* "Greenhouse Gas Control Technologies" (B. Eliassion, P. W. F. Riemer, and A.Wokaum, Eds.), p. 361. Elsevier, Amsterdam, 1998.
10. James, J., and Makarand, R., International Patent WO 99/59952, United States, 1999.
11. Amariglio, H., Pareja, P., and Amariglio, A., *Catal. Today* **25**, 113 (1995).
12. Driessen, M. D., and Grassian, V. H., *J. Catal.* **161**, 810 (1996).