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Difference in the selectivity of CO and CO_2 methanation reactions

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Abstract

CO and CO_2 methanation at steady states and under transient states was conducted over Ni, Ni/Al_2O_3, Ni/SiO_2 and Ru/SiO_2. The CO_2 methanation proceeded highly selectively as compared with the CO methanation. In the CO methanation, weakly adsorbed CO retarded the hydrogenation of surface carbon species. In the CO_2 methanation, the retardation was absent. The selectivity for the CO_2 methanation was estimated from the selectivity for the CO methanation, the extent of the retardation and the ratio of the steady state rates of these reactions. The selectivity estimated was in fair agreement with that experimentally obtained.

Keywords: CO methanation; CO_2 methanation; Selectivity of methanation

1. Introduction

CO and CO_2 methanation reactions proceed over various transition metal catalysts. A number of papers related to these reactions have been published. It has been widely accepted that both of these reactions proceed through the hydrogenation of surface carbon species, C(a), formed by the dissociation of strongly adsorbed CO [1–15]. However, the activity and selectivity for CO_2 methanation are markedly different from those for CO methanation [13–19]. CO_2 methanation proceeded highly selectively as compared with CO methanation. Several authors [5,8,10] suggested that the higher selectivity observed in the CO_2 methanation was attributed to a lower amount of C(a) species present in this reaction. However, it is still uncertain what causes the difference in the selectivity.

It was previously shown [13–15] that in the CO methanation weakly adsorbed CO and strongly adsorbed CO were present along with C(a) species, and that the weakly adsorbed CO retarded the hydrogenation of C(a) to methane in the course of the reaction. On the other hand, the amount of the weakly adsorbed CO was found to be negligible in the course of the CO_2 methanation. The retardation by the weakly adsorbed CO caused the difference in the rate of methane formation and in the amount of C(a). It may be speculated that this retardation causes the difference in the selectivity.

In the present study, CO and CO_2 methanation at steady states and under transient states was carried out over Ni, Ni/Al_2O_3, Ni/SiO_2 and Ru/SiO_2. On the basis of the results of the steady state reactions and on analysis of methane formation under the transient states, the selectivity of CO_2 is estimated and compared with that experimentally obtained. It is shown that the difference in the methane selectivity is primarily ascribed to the presence or the absence of the weakly adsorbed CO in the course of these reactions.

2. Experimental

CO and CO_2 methanation was carried over Ni, 8.2 wt.% Ni/SiO_2, 8.2 wt.% Ni/Al_2O_3, 5.0 wt.% Ru/SiO_2 catalysts. Ni catalyst was prepared by decomposition of basic nickel carbonate (Wako Pure Chemical Industry Ltd., extra pure grade) at 773 K in air and by subsequent H_2 reduction at 873 K for 13 h. The Ni/Al_2O_3, Ni/SiO_2 and Ru/SiO_2 catalysts were prepared by impregnation of Al_2O_3 (JRC-ALO-4, supplied by the Catalysis Society of Japan) or SiO_2 (Gaschro Kogyo Inc.) with a solution of nickel nitrate or ruthenium chloride (Wako Pure Chemical Industry Ltd., extra pure grade). The supported catalysts were dried in air at 383 K overnight and then reduced with 1 atm (1 atm = 101.3 kPa) of H_2. The H_2 reduction was carried out at 800 K for 40 h for Ni/SiO_2 and Ni/Al_2O_3, and at 723 K for 13 h for Ru/SiO_2. The number of surface metal atoms was determined by H_2 adsorption at room temperature (Table 1).

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Table 1
Dispersion of metal in the catalysts

Catalyst	Number of surface metal atoms (μmol/g cat)	Dispersion (%)
Ni	222	1.67
8.2 wt% Ni/Al_2O_3	259	24.5
8.2 wt.% Ni/SiO_2	143	14.1
5.0 wt.% Ru/SiO_2	75	15.8

Methanation reactions were carried out in a flow reactor at atmospheric pressure. For the reactions under the transient states, the gas composition in the inlet stream was changed stepwise and gases in the outflow were analyzed at selected times by gas chromatography. The total flow rate was kept at 100 cm^3 NTP min^{-1}. Helium was used as a diluent.

Temperature programmed reaction was carried out in a stream of H_2–He mixture ($H_2 = 0.3$ atm) at a total flow rate of 200 cm^3 NTP min^{-1}. After a stream of the mixture of CO–H_2 or CO_2–H_2 was fed over the catalyst at a given temperature for 2 h, the stream was switched to that of helium and the catalyst was rapidly cooled to room temperature. The temperature programmed reaction run was then started at a heating rate of 5 K min^{-1}. Gaseous components at the outlet from the reactor were determined by gas chromatography.

XPS spectra of Ni/Al_2O_3 were measured on an ESCALAB-Mk2 (V.G. Scientific) with Al Kα radiation. A sample of the catalyst was placed in a reaction chamber from which the catalyst could be transferred to the analysis chamber without exposure to air.

3. Results and discussion

3.1. CO and CO_2 methanation at steady states and under transient states

Table 2 summarizes the results of CO and CO_2 methanation reactions at steady states. Methanation of CO_2 proceeds with selectivities above 99% whereas that of CO proceeds with selectivities of 40–90%. Ethane was formed as the byproduct in the former reaction while both saturated and unsaturated C_2–C_5 hydrocarbons were produced as the byproducts in the latter reaction. Over Ni, Ni/Al_2O_3 and Ru/SiO_2, the methanation of CO_2 proceeds more rapidly than that of CO. Over Ni/SiO_2, the rate of the CO_2 methanation is slower than that of the CO methanation, although the former reaction proceeds more selectively than the latter reaction as observed over the other catalysts.

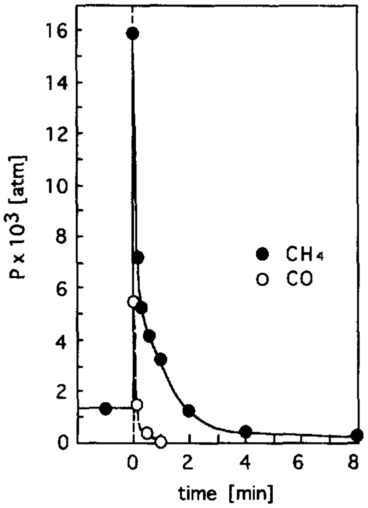

Fig. 1. Variation of the outlet partial pressures of methane and CO with time over Ni/Al_2O_3. A stream of CO–H_2 (CO: 0.1 atm, H_2: 0.9 atm) was switched to that of H_2–He (H_2: 0.9 atm) at a steady state of the reaction at 473 K.

XPS spectra of Ni/Al_2O_3 were measured before and after the CO and CO_2 methanation reactions were carried out. The spectra showed that the state of the Ni surface was the same regardless of the gases in the inflow. Hence, the difference in the rate and the selectivity was governed by the kinetics of the reactions.

Fig. 1 shows how the outlet partial pressures of methane and CO vary when a mixture of CO–H_2 (CO: 0.1 atm, H_2: 0.9 atm) is switched to that of H_2–He (H_2: 0.9 atm) at the steady state of the reaction over Ni/Al_2O_3. On the stepwise change of the feed gas mixture to H_2–He, CO in the outflow decreases instantly to 5.3% of the value at the steady state and then falls off at a slower rate, showing that weakly adsorbed CO desorbs rapidly. Simultaneously, the outlet par-

Table 2
Steady state rates and selectivity of CO and CO_2 methanation reactions[a]

Catalyst	CO–H_2			CO_2–H_2			r'/r
	X^b (%)	r^c	S^d (%)	X^b (%)	r'^c	S'^d (%)	
Ni	1.24	2.1	40.3	2.28	9.4	99.8	4.6
Ni/Al_2O_3	2.09	26.6	62.2	2.60	53.3	99.4	2.0
Ni/SiO_2	1.36	9.8	88.2	1.0	8.2	99.8	0.84
Ru/SiO_2	0.94	5.7	74.2	3.2	26.2	99.4	4.6

[a] $CO = CO_2 = 0.1$ atm, $H_2 = 0.9$ atm, $T = 473$ K.
[b] Conversion of CO or CO_2.
[c] Rate of the methane formation in μmol/min/g cat.
[d] Amount of CO or CO_2 converted to methane/total amount of CO or CO_2 converted to hydrocarbons.

Table 3
Extent of the enhancement of methane formation under the transient state

Catalyst	R^a
Ni	20.3
Ni/Al_2O_3	12.1
Ni/SiO_2	4.8
Ru/SiO_2	9.6

[a] Ratio of methane formation at maximum under the transient state to that at the steady state.

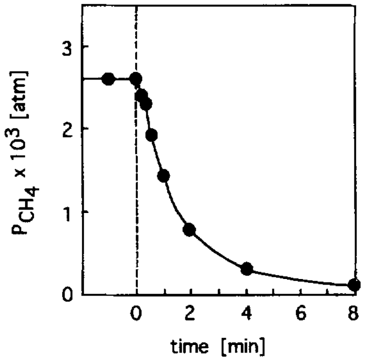

Fig. 2. Variation of the outlet partial pressure of methane with time over Ni/Al_2O_3. A stream of CO_2–H_2 (CO_2: 0.1 atm, H_2: 0.9 atm) was switched to that of H_2–He (H_2: 0.9 atm) at a steady state of the reaction at 473 K.

tial pressure of methane reaches rapidly about 12 times that at the steady state, falling off with time.

Over the other catalysts, similar results were obtained. Upon switching the mixture of CO–H_2 to that of H_2–He, the outlet partial pressure of methane increased rapidly and then decreased with time. However, the extent of the increase of the methane formation under the transient state depended on the catalyst used. Table 3 lists the ratio of the outlet partial pressure of methane at the maximum in the stream of the H_2–He mixture to that at the steady state of the methanation, R. The ratio varies by the catalyst used, ranging from 4.8 to 20.3.

Fig. 2 shows how the outlet partial pressure of methane varies when a mixture of CO_2–H_2 (CO_2: 0.1 atm, H_2: 0.9 atm) is switched to that of H_2–He (H_2: 0.9 atm) at the steady state of the reaction over Ni/Al_2O_3. CO was undetected in the effluent both at the steady state and under the transient state. In contrast with the CO methanation, no enhancement of the methane formation is observed. Upon the switch of the CO_2–H_2 mixture to H_2–He, the outlet partial pressure of methane decreases with time in a monotonic manner.

Similar results were obtained over the other catalysts. No enhancement of the methane formation was observed in the CO_2 methanation under the transient states.

Temperature programmed reaction runs were carried out over the catalysts subjected to the CO and CO_2 methanation reactions. It was found that strongly adsorbed CO and C(a) species were produced in both of these reactions [13–15]. The amount of C(a) species was determined on analysis of the response curves in a similar way employed in the previous study [13]. Table 4 summarizes the amounts of C(a) species present in the CO and the CO_2 methanation. It shows that the amount of C(a) present in the CO methanation is 2–6 times that present in the CO_2 methanation.

Table 4
Amount of C(a) species present in the CO and CO_2 methanation reactions

Catalyst	V^a	V'^b	V/V'
Ni	53.3	10.9	4.9
Ni/Al_2O_3	75.0	12.3	6.1
Ni/SiO_2	20.0	3.7	5.4
Ru/SiO_2	13.1	6.2	2.1

[a] In CO methanation, in μmol/g cat.
[b] In CO_2 methanation, in μmol/g cat.

As discussed previously [13,15], weakly adsorbed CO present in the CO methanation retarded the hydrogenation of C(a) species which was the intermediate for the methane formation, and this retardation caused the higher amount of C(a) in the CO methanation. The extent of the retardation is defined as the ratio of the rate of the hydrogenation of C(a) to methane in the absence of the weakly adsorbed CO to that in the presence of the weakly adsorbed CO. Since the weakly adsorbed CO desorbed rapidly upon switching of the CO–H_2 mixture to H_2–He and consequently the retardation disappeared, the methane formation increased rapidly at the initial period under the transient state, falling off with time. Therefore, the extent of the retardation could be estimated from the reciprocal of the extent of the increase under the transient state, $1/R$.

As Fig. 2 shows, no enhancement of the methane formation is observed in the CO_2 methanation under the transient state, meaning that the retardation is absent in this reaction.

It was previously shown [13] that, in a stream of hydrogen, the rate constant of the hydrogenation of C(a) formed in CO methanation is the same as that of the hydrogenation of C(a) formed in CO_2 methanation at a constant partial pressure of hydrogen. As described above, the hydrogenation of C(a) is retarded by the weakly adsorbed CO to the extent of $1/R$ in the course of the CO methanation, while the retardation is absent in the CO_2 methanation. Hence, the rate constant of the hydrogenation of C(a) in the former reaction, k, is related to that in the latter reaction, k', as follows:

$$k=k'/R \qquad (1)$$

On the other hand, a steady state rate of the CO methanation, r, and that of the CO_2 methanation, r', are represented respectively as

$$r=kV \qquad (2)$$

and

$$r'=k'V' \qquad (3)$$

where V and V' are the amount of C(a) present in the CO methanation and in the CO_2 methanation, respectively. By substituting Eq. (1) into Eq. (3), an expression for the ratio of the rate of the CO methanation to that of the CO_2 methanation is obtained as

$$r/r' = (1/R)(V/V') \tag{4}$$

From this equation, we can readily understand the difference in the rate of these reactions in terms of the extent of the retardation, $1/R$, and the ratio of the amounts of C(a) species, V/V'.

Over Ni, Ni/Al_2O_3 and Ru/SiO_2, the amounts of C(a) present in the CO methanation were respectively 4.9, 6.1 and 2.1 times that in the CO_2 methanation (Table 4). However, the extent of the retardation in the CO methanation was 1/20, 1/12 and 1/9.6 respectively over Ni, Ni/Al_2O_3 and Ru/SiO_2 (Table 3). As a result, the CO methanation proceeded at a slower rate than the CO_2 methanation over these catalysts. On the other hand, over Ni/SiO_2 the amount of C(a) species present in the CO methanation was 5.4 times that in the CO_2 methanation (Table 4) and the extent of the retardation was 1/4.8 (Table 3). Hence, the CO methanation proceeded faster than the CO_2 methanation over this catalyst.

3.2. *Difference in the selectivity of CO and CO_2 methanation*

As discussed above, the retardation by the weakly adsorbed CO results in the difference in the rates of the CO_2 methanation and the CO methanation. In this section, we show that the selectivity of the CO_2 methanation can be estimated from that of the CO methanation on the basis of the retardation.

It is widely accepted that the surface carbon species are hydrogenated stepwise through CH, CH_2 and CH_3 species to methane in the course of the CO methanation [4,20–27]. It has been also proposed that higher hydrocarbons produced in this reaction are formed via polymerization of CH_2 species in which the insertion of CH_2 into the metal–carbon bond of CH_3 species is the initiation step of the polymerization [4,20,28,29].

For simplification of the following discussion on the formation of higher hydrocarbons, it is assumed that one kind of surface CH_x ($x = 0$–3) species takes part in both the initiation and the polymerization, and termination of chain growth occurs via hydrogenation of alkyl intermediate (Fig. 3). This mechanism is similar to that employed by several authors [30–32]. Hence, the mass balance of the CH_x species gives expressions for the probability of the chain propagation, P, and the steady state rate of the methane formation respectively as

$$P = k_pV_1/(k_pV_1 + k_t) \tag{5}$$

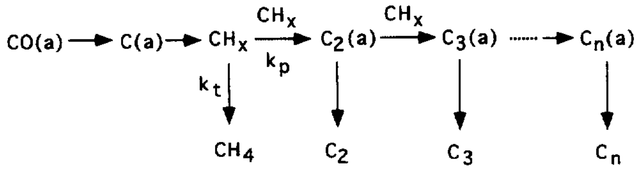

Fig. 3. A scheme for the formation of hydrocarbons.

and

$$r = k_tV_1 = kV \tag{6}$$

where k_p and k_t represent the rate constants of the propagation and the termination, respectively, and V_1 is the amount of CH_x species. On the assumption that P is independent of the chain length, the selectivity for methane formation, S, which is the fraction of C(a) converted to methane, can be represented [33] as

$$S = (1-P)^2 \tag{7}$$

Similar equations are obtained for CO_2 methanation. In this reaction, the probability of chain propagation, P', the steady state rate of the methane formation, r', and the selectivity for methane, S', can be expressed respectively as

$$P' = k_p'V_1'/(k_p'V_1' + k_t') \tag{8}$$

$$r' = k_t'V_1' = k'V' \tag{9}$$

and

$$S' = (1-P')^2 \tag{10}$$

where k_p' and k_t' are the rate constants of the propagation and the termination, respectively, and V_1' is the amount of the CH_x species.

Assuming that the hydrogenation of CH_x is retarded by the weakly adsorbed CO to the same extent as that of C(a) species and the step of the propagation is unaffected by the presence of the weakly adsorbed CO, we obtain

$$k_t = k_t'/R \tag{11}$$

and

$$k_p = k_p' \tag{12}$$

Eqs. (5) and (8) can be rewritten respectively as

$$k_pV_1/k_t = P/(1-P) \tag{13}$$

and

$$k_p'V_1'/k_t' = P'/(1-P') \tag{14}$$

Substitution of Eqs. (11) and (12) into Eq. (14) results in

$$P'/(1-P') = R^{-1}k_pV_1'/k_t \tag{15}$$

which, on comparison with Eq. (13), gives

$$P'/(1-P') = R^{-1}(V_1'/V_1)P/(1-P) \tag{16}$$

or

$$1-P' = [1 + R^{-1}(V_1'/V_1)P/(1-P)]^{-1} \tag{17}$$

On the other hand, Eqs. (6), (9) and (11) give an expression for the ratio of the steady state rate of CO methanation to that of CO_2 methanation as

$$r/r' = V_1/(RV_1') \tag{18}$$

Substituting Eq. (17) into Eq. (10) and rewriting V_1'/V_1 by use of Eq. (18) yield an expression of the selectivity for the CO_2 methanation as

Table 5
Comparison of the selectivity of CO_2 methanation observed with that estimated

Catalyst	Selectivity (%)	
	Observed	Estimated
Ni	99.8	98.8
Ni/Al_2O_3	99.4	99.3
Ni/SiO_2	99.8	99.5
Ru/SiO_2	99.4	98.4

$$S' = [1 + R^{-2}(r'/r)P/(1-P)]^{-2} \qquad (19)$$

The value of P is obtained from the selectivity for the CO methanation experimentally observed by using Eq. (7), and the values of R and r'/r are experimentally obtained. Hence, the selectivity for the CO_2 methanation is estimated from Eq. (19).

Table 5 compares the selectivity for the CO_2 methanation thus estimated with that observed. It shows that the selectivity for the CO_2 methanation estimated is in fair agreement with that observed.

If only the difference in the amount of C(a) was taken into account, as several authors previously suggested [5,8,10], the value of R in Eq. (17) would be equalized to 1 and the selectivity for the CO_2 methanation estimated from Eqs. (17) and (10) would be 80.1, 89.7, 97.6, 86.3% for Ni, Ni/Al_2O_3, Ni/SiO_2 and Ru/SiO_2, respectively. In a similar manner, if only the retardation of the weakly adsorbed CO was taken into account, the selectivity for the CO_2 methanation estimated would be 95.0, 95.7, 97.4, 96.7% respectively for Ni, Ni/Al_2O_3, Ni/SiO_2 and Ru/SiO_2. In these cases, the selectivity estimated deviated from that observed. It was clear that the difference in the selectivity of the CO and CO_2 methanation can be accounted for in terms of both of the retardation by the weakly adsorbed CO and the difference in the amount of C(a) species present in these reactions. Since the retardation by the weakly adsorbed CO caused the difference in the amount of C(a) species present in the CO and CO_2 methanation, it was concluded that the difference in the selectivity of these reactions was primarily attributed to the presence or the absence of the weakly adsorbed CO in the course of these reactions.

Appendix A. Nomenclature

k	rate constant of the hydrogenation of C(a) to methane for CO methanation (min^{-1})
k'	rate constant of the hydrogenation of C(a) to methane for CO_2 methanation (min^{-1})
k_p	rate constant of propagation in CO methanation (min^{-1})
k_p'	rate constant of propagation in CO_2 methanation (min^{-1})
k_t	rate constant of termination in CO methanation (min^{-1})
k_t'	rate constant of termination in CO_2 methanation (min^{-1})
r	steady state rate of CO methanation (mol/(min g cat))
r'	steady state rate of CO_2 methanation (mol/(min g cat))
P	probability of chain propagation in CO methanation
P'	probability of chain propagation in CO_2 methanation
R	ratio of the outlet partial pressure of methane at the steady state to that at maximum under the transient state
S	selectivity of CO methanation (%)
S'	selectivity of CO_2 methanation (%)
V	amount of C(a) formed in CO methanation (mol/g cat)
V'	amount of C(a) formed in CO_2 methanation (mol/g cat)
V_t	amount of CH_x species formed in CO methanation (mol/g cat)
V_t'	amount of CH_x species formed in CO_2 methanation (mol/g cat)

References

[1] M. Araki, V. Ponec, J. Catal. 44 (1976) 439.
[2] J.A. Rabo, A.P. Risch, M.L. Poutsma, J. Catal. 53 (1978) 295.
[3] J.G. McCarty, H. Wise, J. Catal. 57 (1979) 406.
[4] P. Biloen, J.N. Helle, W.H.M. Sachtler, J. Catal. 58 (1979) 95.
[5] J.L. Falconer, A.E. Zagli, J. Catal. 62 (1980) 280.
[6] D.W. Goodman, R.D. Kelly, T.E. Madey, J.T. Yates Jr., J. Catal. 63 (1980) 226.
[7] E. Zagli, J.L. Falconer, J. Catal. 69 (1981) 1.
[8] F. Solymosi, A. Erdohelyi, T. Bansagi, J. Catal. 68 (1981) 371.
[9] N.W. Cant, A.T. Bell, J. Catal. 73 (1982) 257.
[10] D.E. Peebles, D.W. Goodman, J.M. White, J. Phys. Chem. 87 (1983) 4378.
[11] S.Z. Ozdogan, P.D. Gochis, J.L. Falconer, J. Catal. 83 (1983) 257.
[12] M.A. Henderson, S.D. Worley, J. Chem. Phys. 89 (1985) 1417.
[13] S. Fujita, H. Terunuma, M. Nakamura, N. Takezawa, Ind. Eng. Chem. Res. 29 (1991) 1146.
[14] S. Fujita, M. Nakamura, N. Takezawa, React. Kinet. Catal. Lett. 49 (1993) 39.
[15] S. Fujita, M. Nakamura, T. Doi, N. Takezawa, Appl. Catal. A 104 (1993) 87.
[16] G.A. Mills, F.W. Steffgen, Catal. Rev. 8 (1973) 159.
[17] R. Bardet, Y. Trambouze, C.R.H, Acad. Sci. Seances Ser. C 288 (1979) 101.
[18] F. Solymoji, A. Erdohelyi, J. Mol. Catal. 6 (1980) 471.
[19] T. Iizuka, Y Tanaka, K. Tanabe, J. Catal. 76 (1982) 1.
[20] C.S. Kellner, A.T. Bell, J. Catal. 70 (1980) 418.
[21] A.J. Baker, A.T. Bell, J. Catal. 78 (1982) 165.
[22] C.J. Wang, J.G. Ekerdt, J. Catal. 80 (1983) 172.
[23] W. Erley, P.H. McBreen, H. Ibach, J. Catal. 84 (1983) 229.
[24] M.A. Barteau, P. Feoulner, R Stengel, J.Q. Broughton, D. Menzel, J. Catal. 94 (1985) 51–59.
[25] J.J.C. Geerlings, M.C. Zonnevylle, C.P.M. de Groot, Surf. Sci. 241 (1991) 302.
[26] J.J.C. Geerlings, M.C. Zonnevylle, C.P.M. de Groot, Surf. Sci. 241 (1991) 315.

[27] H. He, J. Nakamura, K. Tanaka, Catal. Lett. 16 (1992) 407.
[28] R.C. Brady, R. Pettit, J. Am. Chem. Soc. 102 (1980) 6181.
[29] R.C. Brady, R. Pettit, J. Am. Chem. Soc. 103 (1981) 1287.
[30] F.M. Dautzenberg, J.N. Helle, R.A. van Santen, H. Verbeek, J. Catal. 50 (1977) 8.
[31] R.A. Anderson, The Fischer-Tropsch Synthesis, Academic Press, New York, 1983.
[32] C.A. Mims, J.J. Krajewski, K.D. Rose, M.T. Melchior, Catal. Lett. 7 (1990) 119.
[33] R.J. Madon, J. Catal. 57 (1979) 183.