JOURNAL OF CATALYSIS **102**, 199–206 (1986)

Effect of Alkaline Carbonate on the Dissociation of the C—O Bond in the Methanation over Ru/Al_2O_3 Catalyst

TOSHIAKI MORI,* AKIRA MIYAMOTO,†,[1] NAOKI TAKAHASHI,† HIROSHI NIIZUMA,†
TADASHI HATTORI,† AND YUICHI MURAKAMI†

*Government Industrial Research Institute (Nagoya), Hirate-cho, Kita-ku, Nagoya 462, Japan, and
†Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku,
Nagoya 464, Japan

Received March 4, 1985; revised December 19, 1985

By using a pulse microreactor in conjunction with an emissionless infrared diffuse reflectance spectrometer, the dynamics of adsorbed CO as well as produced CH_4 were measured and effects of alkaline carbonate were investigated for the surface reaction of methanation on Ru/Al_2O_3 catalyst. Alkaline carbonate added to the Ru catalyst decreased the rate constant for C—O bond dissociation, but scarcely affected the hydrogenation of the surface carbon species produced. Alkaline carbonate shifted the infrared absorption band of adsorbed CO to a lower frequency as a result of the increase in electron density in the Ru metal. It is concluded that the effect of alkaline carbonate is an electronic one whereby the C—O bond dissociation in the methanation is influenced. The suppressing effect of alkaline carbonate is discussed in terms of a proposed mechanism for the C—O bond dissociation which takes into account the electronic effect.

INTRODUCTION

A heterogeneous catalytic reaction is composed of various steps including adsorptions, surface reactions, and desorptions, and it is relevant to attempt to measure the rates for the individual steps involved in the overall reaction and also to investigate the effect of additives on these rates. It is well accepted that methanation and Fischer–Tropsch synthesis (FTS) are composed of several steps including the adsorption of H_2 and CO, the dissociation of the C—O bond of adsorbed CO to form surface carbon $[(CH_x)_{ad}]$ and oxygen $[(OH_y)_{ad}]$ species, and the hydrogenation of $(CH_x)_{ad}$ and $(OH_y)_{ad}$ to hydrocarbons with various numbers of carbon atoms and H_2O, respectively (*1–6*). There have been a great many studies about the effect of additives on the FTS and methanation (*7–10*). Alkali is one of the interesting additives for this reaction; it is known that the addition of alkali additives leads to a decrease in the catalytic activity and to selective formation of olefins and higher hydrocarbons (*11–23*). However, the effect of alkali additives has seldom been investigated for the individual steps involved in the FTS or the methanation.

We have proposed a pulse surface reaction rate analysis (PSRA) method for the measurement of the rate of a surface reaction and have demonstrated its use for various catalytic reactions (*24–30*). We have also developed the method by directly combining the PSRA apparatus with an emissionless infrared diffuse reflectance (EDR) spectrometer and a flame ionization detector (FID) in order to measure simultaneously the dynamics of surface species and product molecules (*31*). In the present study, the rate constants of surface reactions in methanation on alkali-doped Ru/Al_2O_3 catalyst, especially the processes of C—O bond dissociation and hydrogenation

---

[1] Present address: Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan.

0021-9517/86 $3.00

TABLE 1

Activation Energy and Preexponential Factor for Methanation and Amount of CO Adsorbed on the Catalyst

Alkaline carbonate	Content[a]	E (J/mol)	log[A (s^{-1})]	CO adsorbed (μmol/g)
Li_2CO_3	0.2	73.6	7.01	13.5
	2.0	68.2	6.39	11.8
	5.0	71.1	6.72	12.9
	10.0	77.4	7.51	9.4
	20.0	70.3	6.67	10.6
Na_2CO_3	0.2	82.2	8.11	11.4
	2.0	80.0	7.80	10.3
	5.0	73.2	6.60	10.5
	10.0	89.5	7.27	10.9
	20.0	92.0	8.31	11.9
K_2CO_3	0.2	78.7	7.79	12.5
	2.0	77.0	6.80	12.9
	5.0	84.5	7.86	14.7
	10.0	86.6	7.48	10.5
	20.0	98.7	8.30	12.2
None	—	72.4	7.15	14.5

[a] Alkaline metal/Ru (atomic ratio).

of $(CH_x)_{ad}$, were determined and the effect of alkaline carbonate on these processes was investigated on the basis of the rate constants thus determined. Alkaline carbonate was used as an additive because it is stable under the reaction conditions.

EXPERIMENTAL

Catalysts. Ru/Al_2O_3 catalyst (Ru loading, 0.5 wt%) was commercially obtained from Nippon Engelhardt Ltd. Alkali-doped Ru/Al_2O_3 catalysts were prepared by impregnating the Ru/Al_2O_3 with an aqueous solution of Li_2CO_3, Na_2CO_3, or K_2CO_3, followed by drying and subsequent reduction in flowing H_2 at 723 K for 3 h. The amount of CO adsorbed on the catalyst was determined by a conventional pulse adsorption method at room temperature, and the results are summarized in Table 1.

Apparatus and procedure. The PSRA apparatus used in this study was constructed by combining a pulse microreactor with a Jasco EDR-31 emissionless infrared diffuse reflectance spectrometer (*32*) and a flame ionization detector. The detail of the construction has been described elsewhere (*31*). The previously used PSRA-FID apparatus, a pulse microreactor directly combined with a FID (*27–30*), was also used.

The dynamics of adsorbed CO and of the CH_4 produced from the CO pulse were measured in a manner identical to that described previously (*31*). The rate constant for C—O bond dissociation to form $(CH_x)_{ad}$ was determined from the dynamics of adsorbed CO by using the Kubelka-Munk equation (*33*) and also from the dynamics of produced CH_4 according to the theory of the PSRA (*27–30*). Furthermore, the rate constant for hydrogenation of $(CH_x)_{ad}$ was determined from the dynamics of produced CH_4 in the manner described previously (*31*).

In situ IR absorption spectra were taken with the EDR under conditions of steady-state methanation and with partial pressure of CO = 1.82 kPa, partial pressure of H_2 = 99.5 kPa, total flow rate = 110 cm^3(STP)/min, and catalyst temperature = 393 K.

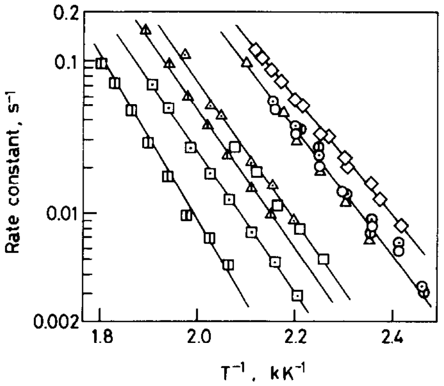

FIG. 1. Effect of alkaline carbonate on the rate constant for C—O bond dissociation in methanation over Ru/Al_2O_3 catalysts. (◇) Nondoped Ru/Al_2O_3. Alkali metal/Ru atomic ratio for alkali-doped Ru/Al_2O_3; (○) Li/Ru = 2.0, (⊙) Li/Ru = 10.0, (⦶) Li/Ru = 20.0, (△) Na/Ru = 2.0, (◬) Na/Ru = 10.0, (▲) Na/Ru = 20.0, (□) K/Ru = 2.0, (⊡) K/Ru = 10.0, (◫) K/Ru = 20.0.

RESULTS

Dynamics of Adsorbed CO and Produced CH_4

When a small CO pulse [usually 10 μl (STP)] was introduced to an alkali-doped Ru/Al_2O_3 catalyst via the H_2 carrier gas above 392 K, it was immediately adsorbed on the catalyst, exhibiting an IR absorption band at around 2040 cm^{-1}. This absorption band is assignable to linearly adsorbed CO on Ru metal (*31, 34–36*). The intensity of the IR band of linear CO gradually decreased with time due to its reaction with H_2 to produce CH_4. The FID response of produced CH_4 immediately increased and then gradually decreased with time, because the amount of CO adsorbed on the catalyst gradually decreased with time due to the methanation. The rate constants can be determined from these dynamics according to the method identical to that used for the nondoped Ru/Al_2O_3 catalyst (*31*). It was found that the rate constant for the C—O bond dissociation was much smaller than that for the hydrogenation of $(CH_x)_{ad}$.

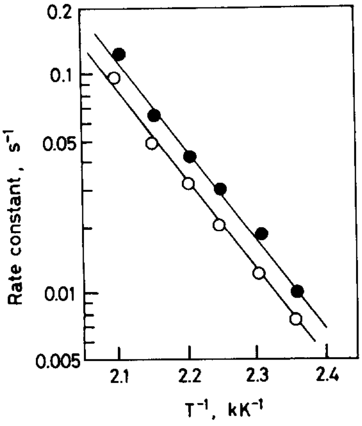

FIG. 2. Isotope effect on the rate constant for C—O bond dissociation in methanation over K_2CO_3-doped Ru/Al_2O_3 catalyst (K/Ru = 20.0). (○) in H_2, (●) in D_2.

Effect of Alkaline Carbonate on the Rate Constant for the C—O Bond Dissociation in Methanation

Figure 1 shows some typical results of the rate constant for C—O bond dissociation in the methanation over alkali-doped Ru/Al_2O_3 catalyst at various temperatures. The rate constants for nondoped catalyst are also shown in this figure. As shown, alkaline carbonate added to the Ru/Al_2O_3 catalyst markedly decreased the rate constant. The extent of the decrease became more significant with increasing the amount of the added alkaline carbonate and with the sequence $Li_2CO_3 < Na_2CO_3 < K_2CO_3$. The preexponential factor of the rate constant and the activation energy are summarized in Table 1. The activation energy increased in accordance with the decrease in the rate constant.

Isotope Effect on the Rate Constant for the C—O Bond Dissociation

The rate constant for the process of the C—O bond dissociation was also determined in flowing D_2. A typical example is shown in Fig. 2. As shown, the rate constant is larger in D_2 than in H_2, indicating that an inverse isotope effect exists in this process for the alkali-doped Ru/Al_2O_3 catalyst. The average value of the isotope effect

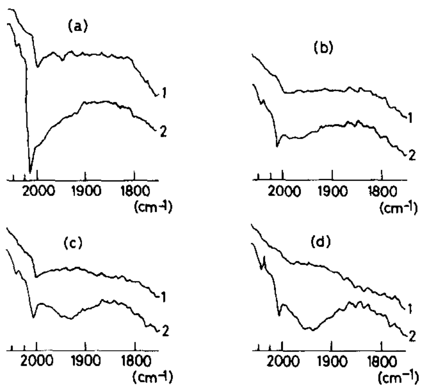

FIG. 3. Infrared spectra measured during steady-state methanation over nondoped and alkali-doped Ru/Al_2O_3 catalysts at 393 K. Dopants are: (a) none, (b) Li_2CO_3, (c) Na_2CO_3, and (d) K_2CO_3. Partial pressure of CO = 1.82 kPa, partial pressure of H_2 = 99.5 kPa, and total flow rate = 110 cm^3(STP)/min. Line 1 in each spectrum is the background taken in flowing H_2 alone.

is 0.78 for the K_2CO_3 doped Ru/Al_2O_3 catalyst.

IR Absorption Spectra Measured in the Steady-State Methanation

In situ IR absorption measurements of adsorbed CO during the steady-state methanation were carried out by using the EDR. Typical results are shown in Fig. 3. As shown, besides gaseous CO, linear CO was observed in the IR spectra at around 2050 cm^{-1} (*34–36*). The precise examination of the IR spectra revealed that the addition of alkaline carbonate to the Ru/Al_2O_3 catalyst resulted in a decrease in the wavenumber of linear CO, as shown in Fig. 4. The extent of the downshift in the wavenumber ($\Delta\nu_{CO}$) varied considerably among the catalysts studied; it was more pronounced for catalysts with a larger amount of added alkaline carbonate and with the sequence $Li_2CO_3 < Na_2CO_3 < K_2CO_3$.

Figure 3 also shows that the IR absorption band at around 1950 cm^{-1}, assignable to bridged CO, became more pronounced on alkali-doped Ru/Al_2O_3 catalyst. This is in accordance with the results obtained by Garfunkel *et al.* (*40*) and McClory and Gonzalez (*21*). It has, however, been found from the dynamic measurement of bridged CO that this species is less reactive with H_2 (*31*).

Correlation between the Rate Constant and the Band Shift

As shown in Figs. 1 and 4, during the methanation alkaline carbonate added to the Ru/Al_2O_3 catalyst greatly influenced the rate constant for the C—O bond dissociation and the IR absorption spectra. There seem to be some similarities in the features of the influence between them. With increasing the amount of added alkaline carbonate, and also in accordance with the sequence $Li_2CO_3 < Na_2CO_3 < K_2CO_3$, the rate constant decreased and the band shift became pronounced. Then the rate constant was tentatively plotted against the extent of the band shift ($\Delta\nu_{CO}$) (Fig. 5). Although there are significant variations in the rate constant and $\Delta\nu_{CO}$ among the catalysts, the rate constant is unequivocally related with $\Delta\nu_{CO}$ irrespective of the catalyst used, namely ln(rate constant) decreases linearly with $\Delta\nu_{CO}$.

DISCUSSION

Interaction between Alkaline Carbonate and Ru Metal in the Catalyst

The amount of added alkaline carbonate varies greatly; the maximum ratio of the al-

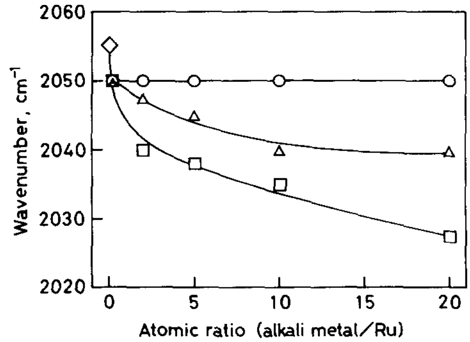

FIG. 4. Effect of alkaline carbonate on the wavenumber of linear CO. Dopants are: (◇) none, (○) Li_2CO_3, (△) Na_2CO_3, and (□) K_2CO_3.

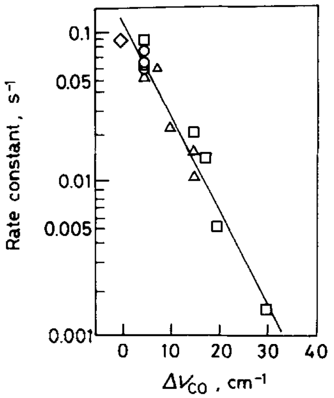

FIG. 5. Relationship between the rate constant for C—O bond dissociation at 465 K and the extent of downshift for the C—O stretching vibration of linear CO($\Delta\nu_{CO}$). Symbols are the same as those in Fig. 4.

kali metal to Ru reaches 20. However, as shown in Table 1, the amount of adsorbed CO hardly changed among the catalysts, suggesting that the added alkaline carbonate mainly exists on the alumina support, but not on the Ru metal. This may be ascribable to the acid–base interaction between the alkaline carbonate and the alumina support. Constancy of the amount of adsorbed CO was also observed for the alkali-doped Pd/Al_2O_3 catalyst (*37*) but is in clear contrast to the result obtained for the Ru/Al_2O_3 catalyst promoted with V, Nb, Mo, W, and Re oxides, where in spite of the small amount of these oxides (oxide metal/Ru = 1) the amount of adsorbed CO greatly decreased (*38*, *39*). It is therefore considered that the Ru metal in the catalyst is indirectly influenced through the modification of the acidic property of the alumina support with the added alkaline carbonate.

Effects of Alkaline Carbonate on the IR Spectra

As shown in Fig. 4, the wavenumber of linear CO shifted to a lower frequency by adding alkaline carbonate to the Ru/Al_2O_3 catalyst. This is in accordance with work in the literature (*20–22*, *40*). However, it should be noted that the band shift occurs in a quite regular fashion; its extent is larger with the amount of added alkaline carbonate and with the sequence $Li_2CO_3 < Na_2CO_3 < K_2CO_3$. It is well known that several effects can affect the IR absorption spectrum. For a downshift such as that in the present case, a decoupling of the CO dipole–dipole interaction due to a decrease in the amount of adsorbed CO (*41–48*), an increase in the electron density of the Ru metal (*20–22*, *40*, *49*), or an increase in the metal particle size (*50*, *51*) may be the possible effect. In the present case, however, the band shift seems not to be caused by the metal particle size effect, because there is not much difference in the amount of adsorbed CO among the catalysts examined, as shown in Table 1. The fact of the constancy in the amount of adsorbed CO may also exclude the decoupling effect from the possible effects for the downshift, because the extent of the dipole–dipole interaction is expected to be the same among the catalysts. In the steady-state reaction, however, the amount of adsorbed CO estimated from the IR spectra shown in Fig. 3 appears to be different from catalyst to catalyst. A recent surface science study also revealed an interesting interaction on Ru metal between CO and H_2 where H_2 blocked the adsorption of CO (*52*). If the decoupling effect is the main one for the band shift, the most significant shift should be observed on the Li-doped Ru/Al_2O_3 catalyst because of the smallest peak area which suggests the smallest amount of adsorbed CO. However, the experimental result in Fig. 4 shows that this is not the case. The blocking effect with H_2 is considered to be hardly operative in the steady-state reaction, because it is accepted that the CO hydrogenation over supported Group VIII metal catalysts shows a zero or slightly negative order dependence with respect to the CO partial pressure, which implies saturation coverage of the catalyst with CO (*53*). Moreover, it seems improbable that the monotonic correlation between the rate constant and $\Delta\nu_{CO}$ shown in Fig. 5 can reasonably be explained in terms of the decoupling effect.

It is known that alkali additives have electron-donor character even in the ionic state of alkaline metals, although the effect may be less than in the metallic state (*54*). The alumina support is acidic, so the Ru metal on it is in a slightly electron-deficient state. The alkaline carbonate added to the Ru/Al_2O_3 catalyst may reduce the acidic property of the alumina support, which results in the relative increase in the electron density in the Ru metal. The enrichment of electron density in the Ru metal should result in the weakening of the C—O bond due to the enhanced back-donation of electrons from the Ru metal to the antibonding 2π orbital of adsorbed CO molecule (*49*), which leads to the downshift of the IR absorption band of linear CO. Therefore, the extent of the band shift for linear CO($\Delta\nu_{CO}$) provides a measure of the increase in electron density in the Ru metal, as was the case for Pd/Al_2O_3 (*37*). As shown in Fig. 4, $\Delta\nu_{CO}$ became more pronounced with increasing the amount of added alkaline carbonate and with the sequence $Li_2CO_3 < Na_2CO_3 < K_2CO_3$. This may be rationalized on the basis of the difference in the ionization potential or electronegativity of alkaline carbonate; the order of the electronegativity is $Li_2CO_3 > Na_2CO_3 > K_2CO_3$, which leads to the order of the effectiveness of the added alkaline carbonate described above. It should, however, be noted that the effectiveness of alkaline carbonate on the Ru/Al_2O_3 catalyst markedly differs from that on the Pd/Al_2O_3 catalyst, where $\Delta\nu_{CO}$ increased with increasing the amount of added alkaline carbonate but their nature hardly affected $\Delta\nu_{CO}$ (*37*). Although further study is necessary for understanding the effect of alkaline carbonate, the electron configuration in the Ru atom different from that in the Pd atom may be responsible for the discrepancy in the effect of alkaline carbonate between these two supported metal catalysts. The number of vacant electron sites on the 4*d* orbital is 3 for Ru and 0 for Pd. The presence of the vacant electron sites seems to make the effect of alkaline carbonate sensitive, while the absence of such vacant sites does not. This is because the role of alkaline carbonate is considered to increase electron density in the metal by donating electron from the carbonate to the metal.

Effect of Alkaline Carbonate on the Rate Constant for the C—O Bond Dissociation in the Methanation

In the methanation over alkali-doped Ru/Al_2O_3 catalyst, the rate constant for the C—O bond dissociation was much smaller than that for the hydrogenation of the resultingly formed $(CH_x)_{ad}$ species. This indicates that the C—O bond dissociation is the rate-determining step, as is the case for the nondoped Ru/Al_2O_3 catalyst (*31*). It is concluded, therefore, that alkaline carbonate does not much influence the hydrogenation process of surface carbon species, which is in conflict with the conclusion recently obtained by McClory and Gonzalez (*21*). This may be due to the reaction conditions being different from those of McClory and Gonzalez; in the present case the reaction conditions are a hydrogen-rich atmosphere.

Figure 1 shows that the process of the C—O bond dissociation in the methanation is greatly affected by the amount of added alkaline carbonates as well as with their nature. This is again a marked contrast to methanation on alkali-doped Pd/Al_2O_3 catalyst, where this process is also influenced with the amount of added alkaline carbonates but not with their nature (*37*). Although this discrepancy is difficult to rationalize, it may possibly be explained as follows. Since Ru is one of the most active metals for methanation (*55*), and for C—O bond dissociation, it is sensitively influenced by the nature of the alkaline carbonate. Pd, on the other hand, is not so active for the C—O bond dissociation (*55, 56*) that the nature of alkaline carbonates is reflected in its activity.

According to the previous discussion, $\Delta\nu_{CO}$ can be regarded as a measure for the electronic state of the Ru metal. Therefore, the correlation shown in Fig. 5 indicates that the rate constant for the C—O bond dissociation is decreased on the Ru metal catalyst having higher electron density. Since, on such a Ru metal, the C—O bond is weakened due to the enhanced back-donation, this finding seems to be strange and is different from the conclusion obtained through recent experimental (*57, 58*) and theoretical (*59*) investigations about the effect of alkali additives which show that in the absence of H_2 the increase in electron density leads to an increase in the rate for the simple decomposition of the adsorbed CO molecule. However, the mechanism for the C—O bond dissociation in the CO hydrogenation is different from that in the absence of H_2 (*28–31, 37*).

Possible Reason for the Suppression of the C—O Bond Dissociation by Adding Alkaline Carbonate

We have established the mechanism for the process of C—O bond dissociation in the CO hydrogenation on the basis of the rate and the H_2–D_2 inverse isotope effect measured for this process. The C—O bond is rate-determiningly dissociated to surface carbon [$(CH_x)_{ad}$] and oxygen [$(OH_y)_{ad}$] species via the formation of an intermediate species like a partially hydrogenated CO, which is in equilibrium with adsorbed CO [$(CO)_{ad}$] (*28–31, 37*). On the Ru/Al_2O_3 catalyst, the hydroxycarbene [$(CHOH)_{ad}$] species is postulated to be formed as a plausible intermediate (*31*), viz.

$$\begin{aligned}(CO)_{ad} \rightleftharpoons (CHOH)_{ad} &\xrightarrow{\wedge} (CH_x)_{ad} \\ + (OH_y)_{ad} &\longrightarrow CH_4 + (H_2O) \qquad (1)\end{aligned}$$

This mechanism is also applicable to the C—O bond dissociation on alkali-doped Ru/Al_2O_3 catalyst, because, as shown in Fig. 2, the H_2–D_2 inverse isotope effect is observed in this process to an extent which is the same as that for the nondoped Ru/Al_2O_3 catalyst (0.78) (*31*). Furthermore, as shown in Table 1, the preexponential factor of the rate constant is also the same value as that for the nondoped catalyst (1.4×10^7 s^{-1}) (*31*). In the methanation over Ru/Al_2O_3 catalyst, the suppressing effect of alkaline carbonate on the C—O bond dissociation may be explained in terms of this mechanism. In Eq. (1), the possible factor by which the rate constant is determined is the equilibrium concentration of $(CHOH)_{ad}$. On the Ru surface with higher electron density, $(CO)_{ad}$ is more stabilized due to the resultant effect of the enhanced back-donation of electron from the Ru metal to the 2π orbital in $(CO)_{ad}$. Such stabilization may, however, not be expected for $(CHOH)_{ad}$. This leads to a decrease in the equilibrium concentration of $(CHOH)_{ad}$ and resultingly to a decrease in the rate constant for the C—O bond dissociation.

ACKNOWLEDGMENTS

This work was partially supported by a Grant-in-Aid for Energy Research from the Ministry of Education, Science and Culture, Japan (No. 59040015).

REFERENCES

1. Ponec, V., *Catal. Rev. Sci. Eng.* **18,** 151 (1978).
2. Bell, A. T., *Catal. Rev. Sci. Eng.* **23,** 203 (1981).
3. Biloen, P., and Sachtler, W. M. H., *in* "Advance in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 30, p. 165. Academic Press, New York, 1981.
4. Vannice, M. A., *in* "Catalysis-Science and Technology" (J. R. Anderson and M. Boudart, Eds.), Vol. 3, p. 139. Springer-Verlag, Berlin/Heidelberg/New York, 1982.
5. Ponec, V., "Catalysis," Vol. 5, p. 48. The Chemical Society, London, 1982.
6. Kelley, R. D., and Goodman, D. W., *in* "The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis" (D. A. King and D. P. Woodruff, Eds.), Chap. 10. Elsevier, Amsterdam, 1982.
7. Anderson, R. B., *in* "Catalysis" (P. H. Emmett, Ed.), Vol. 4. Reinhold, New York, 1956.
8. Denny, P. J., and Whan, D. A., "Catalysis," Vol. 2, p. 46. The Chemical Society, London, 1978.
9. Dry, M. E., *in* "Catalysis-Science and Technology" (J. R. Anderson and M. Boudart, Eds.), Vol. 1, p. 159. Springer-Verlag, Berlin/Heidelberg/New York, 1981.
10. King, G. L., Cusumano, J. A., and Garten, R. L., *Catal. Rev. Sci. Eng.* **23,** 233 (1981).
11. Dry, M. E., and Oosthuizer, G. J., *J. Catal.* **11,** 18 (1968).

12. Schoubye, P., *J. Catal.* **14,** 238 (1969).
13. Dry, M. E., Shingles, T., Boshoff, L., and Oosthuizer, G. J., *J. Catal.* **15,** 190 (1969).
14. Huang, C. P., and Richardson, J. T., *J. Catal.* **51,** 1 (1978).
15. McVicker, C. P., and Vannice, M. A., *J. Catal.* **63,** 25 (1980).
16. Kruissink, E. C., Pelt, H. L., Ross, J. R. H., and van Reijen, L. L., *Appl. Catal.* **1,** 23 (1981).
17. Okuhara, T., Kimura, T., Misono, M., and Yoneda, Y., *J. Chem. Soc. Chem. Commun.*, 1114 (1981).
18. Miura, H., and Gonzalez, R. D., *J. Catal.* **77,** 338 (1982).
19. Kagami, S., Naito, S., Kikuzono, Y., and Tamaru, K., *J. Chem. Soc. Chem. Commun.*, 256 (1983).
20. King, D. L., and Peri, J. B., *J. Catal.* **79,** 164 (1983).
21. McClory, M. M., and Gonzalez, R. D., *J. Catal.* **89,** 392 (1984).
22. Okuhara, T., Tamura, H., and Misono, M., *J. Catal.* **95,** 41 (1985).
23. Chuang, S. C., Goodwin, J. G., and Wender, I., *J. Catal.* **95,** 435 (1985).
24. Murakami, Y., *in* "Some Theoretical Problems of Catalysis" (T. Kwan, G. K. Boreskov, and K. Tamaru, Eds.), p. 203. University of Tokyo Press, Tokyo, 1973.
25. Hattori, T., and Murakami, Y., *Canad. J. Eng. Chem.* **52,** 601 (1974).
26. Hattori, T., Kanetake, K., and Murakami, Y., *Nippon Kagaku Kaishi,* 1957 (1977).
27. Mori, T., Masuda, H., Imai, H., and Murakami, Y., *Nippon Kagaku Kaishi,* 1449 (1979).
28. Mori, T., Masuda, H., Imai, H., Miyamoto, A., Baba, S., and Murakami, Y., *J. Phys. Chem.* **86,** 2753 (1982).
29. Mori, T., Masuda, H., Imai, H., Miyamoto, A., Hasebe, R., and Murakami, Y., *J. Phys. Chem.* **87,** 3648 (1983).
30. Niizuma, H., Hattori, T., Mori, T., Miyamoto, A., and Murakami, Y., *J. Phys. Chem.* **87,** 3562 (1983).
31. Mori, T., Miyamoto, A., Niizuma, H., Takahashi, N., Fukagaya, M., Hattori, T., and Murakami, Y., *J. Phys. Chem.* **90,** 109 (1986).
32. Niwa, M., Hattori, T., Takahashi, M., Shirai, K., Watanabe, M., and Murakami, Y., *Anal. Chem.* **51,** 46 (1979).
33. Kubelka, P., and Munk, F., *Z. Tech. Phys.* **12,** 593 (1931).
34. Brown, M. F., and Gonzalez, R. D., *J. Phys. Chem.* **80,** 1731 (1976).
35. Ekerdt, J. G., and Bell, A. T., *J. Catal.* **58,** 170 (1979).
36. Yamazaki, H., Kobori, Y., Naito, S., Onishi, T., and Tamaru, K., *J. Chem. Soc. Faraday Trans. 1* **77,** 2913 (1981).
37. Mori, T., Masuda, H., Imai, H., Miyamoto, A., Niizuma, H., Hattori, T., and Murakami, Y., *J. Mol. Catal.* **25,** 263 (1984).
38. Takahashi, N., Mori, T., Miyamoto, A., Hattori, T., and Murakami, Y., *Appl. Catal.*, **22,** 137 (1986).
39. Mori, T., Miyamoto, A., Takahashi, N., Fukagaya, M., Hattori, T., Murakami, Y. *J. Phys. Chem.*, in press.
40. Garfunkel, E. L., Crowell, J. E., and Somorjai, G. A., *J. Phys. Chem.* **86,** 310 (1982).
41. Eischens, R. P., Francis, S. A., and Pliskin, W. A., *J. Phys. Chem.* **86,** 310 (1956).
42. Hammaker, R. M., Francis, S. A., and Eischens, R. P., *Spectrochim. Acta* **21,** 1295 (1965).
43. Crossley, A., and King, D. A., *Surf. Sci.* **68,** 528 (1977).
44. Moskovits, M., and Hulse, J. E., *Surf. Sci.* **78,** 397 (1978).
45. Pfnur, H., Menzel, D., Hoffmann, F. M., Ortega, A., and Bradshaw, A. M., *Surf. Sci.* **93,** 431 (1980).
46. Crossley, A., and King, D. A., *Surf. Sci.* **95,** 131 (1980).
47. Stoop, F., Toolenaar, F. J. C. M., and Ponec, V., *J. Catal.* **73,** 50 (1982).
48. Toolenaar, F. J. C. M., Stoop, F., and Ponec, V., *J. Catal.* **82,** 1 (1983).
49. Blyholder, J., *J. Phys. Chem.* **68,** 2772 (1964).
50. Dalla Betta, R. A., *J. Phys. Chem.* **79,** 2519 (1975).
51. Toolenaar, F. J. C. M., Bastein, A. J. C. M., and Ponec, V., *J. Catal.* **82,** 35 (1983).
52. Peebles, D. E., Schreifels, J. A., and White, J. M., *Surf. Sci.* **116,** 117 (1982).
53. Vannice, M. A., *Catal. Rev. Sci. Eng.* **14,** 153 (1976).
54. Martin, G. A., *Stud. Surf. Sci. Catal.* **11,** 315 (1982).
55. Vannice, M. A., *J. Catal.* **37,** 449 (1975).
56. Rabo, J. A., Risch, A. P., and Poutsma, M. L., *J. Catal.* **53,** 295 (1978).
57. Benzinger, J., and Madix, R. J., *Surf. Sci.* **94,** 119 (1980).
58. Kiskinova, M. P., *Surf. Sci.* **111,** 584 (1981).
59. Tománek, K. D., and Bennemann, K. H., *Surf. Sci.* **127,** L111 (1983).