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Differential Pressure and FAB MS Studies of the Adsorption and Reaction of CO on Slightly Hydrated $(Fe,Cr)_3O_4$ Catalysts

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An apparatus for studying adsorption and adsorbate reaction quantities by means of a differential pressure method (DPM) to an accuracy of about 1.3×10^{-8} mol has been designed. Adsorption of CO and reaction of the adsorbate on slightly hydrated $(Fe,Cr)_3O_4$ catalyst have been studied by means of DPM and fast atom bombardment mass spectroscopy (FAB MS) at P_{CO} = 6–9 Torr (1 Torr = 133.3 N m^{-2}) and T = 473–633 K. It has been established that CO interacts with hydroxylated $(Fe,Cr)_3O_4$ to form carbonaceous species on the surface, in which the number of carbon atoms increases when the contact time of CO with $(Fe,Cr)_3O_4$ is increased; no elemental carbon was deposited. It has also been found that compared to the bulk composition, while the chromium content is not markedly enriched at the surface of $(Fe,Cr)_3O_4$, it is enriched at the subsurface. © 1988 Academic Press, Inc.

INTRODUCTION

Metals and metal oxides are often important catalysts, for example, shift catalysts for hydrogen production in ammonia synthesis, catalysts for CO hydrogenation, and the like. In studies of reactions involving CO, disproportionation to CO_2 and elemental carbon are possible and may pose problems in the use of such catalysts. It was thus of interest to examine the interaction of CO with the mixed-metal oxide $(Fe,Cr)_3O_4$, some important surface properties of which have been established in an earlier study (*1*).

Hydrocarbon decomposition and carbon monoxide disproportionation can be catalyzed by iron, cobalt, or nickel in the range 473–1073 K (*2*), and mechanisms for the disproportionation have been proposed. Sacco and Reid (*3*) discovered that H_2 and CO_2 reacted to form H_2O, CH_4, CO, and carbon when they were exposed to iron at 800–900 K and 1 bar pressure, and the magnetite (Fe_3O_4) and wustite (Fe_xO), which formed during the reaction, inhibited carbon deposition. Renshaw *et al.* (*4*) found that for both Fe and Si–Fe, the active catalytic species for the disproportionation of CO was a *p*-type oxide. In most instances this oxide was γ-Fe_2O_3 which was presumably stabilized at temperatures up to 600°C by an underlying Fe_3O_4 lattice. Having studied the chemical nature of the carbonaceous deposits on iron after CO hydrogenation by means of AES and XPS, Bonzel and Krebs (*5*) have suggested that the CH_x phase consists mostly of CH species. It is not easy to say what the precise value of x is because the C 1*s* binding energy does not vary sensitively with x. However, fast atom bombardment mass spectroscopy (FAB MS) (*6*, *7*) can be used to reveal the nature of such carbonaceous deposits.

In order to study adsorption of CO and possible disproportionation and/or carbon deposition, an apparatus using a differential pressure method (DPM) has been designed to measure changes of gas quantity as small as 1.3×10^{-8} mol. FAB MS was used to determine the species on the $(Fe,Cr)_3O_4$ surface after CO had been adsorbed on and had possibly reacted with it, and to investigate the surface composition.

In the earlier study (*1*), pretreatment of the $(Fe,Cr)_3O_4$ at 773 K yielded anhydrous material. In the present work the maximum

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pretreatment temperature was 633 K, which leaves a known trace of H_2O, approximately a monolayer, as calculated from the earlier data (*1*, *8*).

EXPERIMENTAL

Materials

The samples of carbon free $(Fe,Cr)_2O_3$ were prepared by a mixed precipitation method. A. R. grade reagents of $FeSO_4 \cdot 7H_2O$, H_2SO_4, CrO_3, $NH_3 \cdot H_2O$, and NH_4NO_3 were used. In the H_2/H_2O gas mixture with partial pressure ratio P_{H_2}/P_{H_2O} equal to 4, at 673 K and atmospheric pressure, $(Fe,Cr)_2O_3$ were reduced to $(Fe,Cr)_3O_4$ (*9*). During the preparation, care was taken to prevent any contamination by carbon-containing substances. The prepared samples were kept in a nitrogen atmosphere.

CO was purified by passing cylinder CO through silica gel and soda–asbestos drying towers to remove H_2O and CO_2, a 5-Å molecular sieve tower to remove H_2O, and a 105 and 401 deoxidizing catalyst tower to remove O_2. This was followed by liquefying the CO in a trap at liquid nitrogen temperature, for low-temperature fractionation. The liquid CO was then vaporized and introduced into an evacuated spherical glass reservoir. The pressure of this purified CO was 520 Torr.

Apparatus, Method, and the Principle of the Differential Pressure Method

The apparatus using the DPM to examine adsorption and reaction is shown schematically in Fig. 1. The volume of the gas storage tube, 2, is several times larger than that of the reaction tube, 1. The liquid in the U-type differential pressure meter, 3, is No. 275 methyl silicon oil, of density 1.08 g cm^{-3}, determined at 30°C (ambient temperature).

The gas at low pressure is considered ideal. The equivalent volume V_1 of the left part of the apparatus, in which the reaction tube is located and kept at a fixed higher temperature, is determined. It equals the volume of a given quantity of gas at its pressure but at a lower temperature being equal to that of the right part of the apparatus, where the gas storage tube is located. In such a way the adsorption and reaction properties of a gas on a sample can be determined.

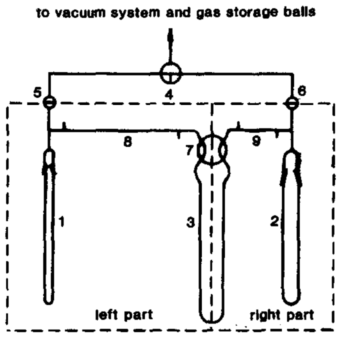

FIG. 1. Schematic diagram of the apparatus using the DPM. (1) Reaction tube, (2) gas storage tube, (3) U-type silicon oil differential pressure meter, (4) three-way stopcock, (5, 6) two-way stopcocks, (7) four-way stopcock, (8, 9) thermostatic tubes.

When a fixed quantity of a gas is introduced into the right part, its pressure P_2 is determined while the left part is under vacuum. By turning the four-way stopcock, 7, the pressures of both parts are in equilibrium. After that, the four-way stopcock is fixed at a position that enables one to measure differential pressure so that the progress of adsorption and reaction is inferred from the variation of differential pressure, and the total quantity of both adsorption and reaction can be calculated. Each manipulation takes several seconds.

The equivalent volume v_1 is obtained by plotting according to the equation

$$\Delta P = P_2 - P = \frac{V_1}{V_1 + V_2} P_2, \qquad (1)$$

where P is the pressure of the gas when its volume changes from V_2 to $V_1 + V_2$, where V_2 is the volume of the right part.

X-ray diffraction patterns of the catalysts were taken with a Shimadzu model XD-3A diffractometer, using Fe$K\alpha$ radiation. FAB mass spectra were recorded with a VG analytical model VG ZAB-HS GC/MS (single focus, V. accel. 7.910 kV, 1 mA, Argon atom, response time 0.3 ms).

RESULTS AND DISCUSSION

Results of XRD

Four catalyst samples named Fe–Cr-5, -10, -15, and -20, of which the original weight percents of $Cr_2O_3/(Cr_2O_3 + Fe_2O_3)$ were 5, 10, 15, and 20 wt%, respectively, were prepared. X-ray diffraction (XRD) analysis of the catalysts showed that the samples were $(Fe,Cr)_3O_4$. After CO adsorption in the DPM experiment, the XRD observations remained unchanged, leading to the conclusion that the magnitude structure of samples was maintained and that no carbon deposition (within the limits of the technique) was indicated.

Determination of Adsorption and Extent of Disproportionation of CO on $(Fe,Cr)_3O_4$ by DPM

From the observed rates of adsorption indicated by $d\Delta h/dt$ it may be confidently assumed that little adsorption occurs during the rapid initial dosing.

It was suitable to use methyl silicon oil as an indicator liquid in the U-type manometer because of its low density (1.08 g cm^{-3}), its very low vapor pressure at room temperature, and its inertness to the catalyst. With an accuracy of the scale on the U-type manometer of about 0.2 mm, and an effective volume of the left part of 15.15 cm^3, the accuracy of detection would be 1.3×10^{-8} mol. With the 0.5 g of solid sample usually used, the sensitivity is high (2.6×10^{-8} mol g^{-1}).

Figure 2 shows the relationships between differential pressure, Δh (expressed as centimeters silicon oil), and time, $t(h)$, for CO adsorbed on $(Fe,Cr)_3O_4$. P_{CO} is the pressure of CO after 8 h adsorption. For the adsorption temperatures 473, 533, 573, 633, and 673 K, the pressures of CO are 6.19, 6.04, 6.19, 8.26, and 8.97 Torr, respectively. The curves show that after adsorption for about 3 h, the system is at or very near adsorption equilibrium; there is no detectable disproportionation. From approximate estimates of surface areas of similar samples, the amount of CO adsorbed per unit area is (very roughly) $2.3–0.6 \times 10^{-7}$ mol m^{-2}.

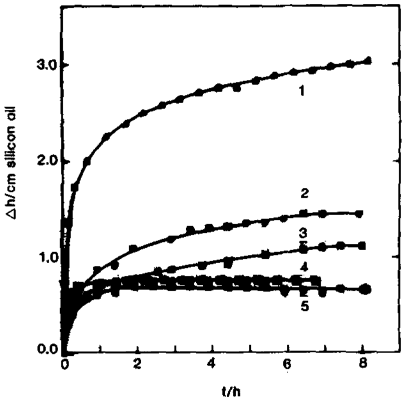

FIG. 2. Relationships of $\Delta h–t$ for CO adsorbed on $(Fe,Cr)_3O_4$ (Fe–Cr-20 sample). Adsorption temperature (K): (1) 473, (2) 533, (3) 573, (4) 633, (5) 673. Equilibrium pressure P_{CO} (Torr): (1) 6.19, (2) 6.04, (3) 6.19, (4) 8.26, (5) 8.97.

The results of Renshaw *et al.* (*4*) showed that a linear rate of carbon formation was established from the disproportionation reaction of CO. Their experiments were conducted at a total gas pressure of 1 atm (1 atm = 101325 N m^{-2}) which is higher than the pressure in our experiment. However, Jagannathan *et al.* (*10*) studied the interaction of carbon monoxide with surfaces of Fe, Co, and Ni by XPS and concluded that at 300 K, the disproportionation reaction was prominent up to exposures of 10^3 L (1 L = 10^{-6} Torr s) giving rise to high surface concentrations of carbon. But the pressure in our experiment lies between the pressures used in the two studies referred to above. If the disproportionation reaction of CO were to occur, the $\Delta h–t$ relationships would tend to the horizontal at values of Δh not less than about 6 cm silicon oil, which is half of the initial pressure of CO and is much greater than the horizontal values of Δh shown in Fig. 2. Thus Fig. 2 shows essentially the adsorption properties of CO on $(Fe,Cr)_3O_4$. We note, first, that the higher the adsorption temperature, the shorter the time to reach equilibrium. This means that activation energy is necessary for the adsorption of CO on $(Fe,Cr)_3O_4$. Second, the higher the adsorption temperature, the smaller the adsorption quantity at equilibrium. It is related to the larger rate of desorption of CO at higher temperatures (as can be deduced from Ref. (*11*)) in its effect on the equilibrium constant for adsorption and desorption.

Results of FAB MS Experiments

Both before and after adsorption of CO on the $(Fe,Cr)_3O_4$ Fe–Cr-15 catalyst, FAB mass spectra were recorded. The results were as follows.

(*A*) Figure 3 shows that after $(Fe,Cr)_3O_4$ has been pretreated by CO adsorption for 8 h, the peak heights of $^{52}Cr^+$ and $^{56}Fe^+$ and their ratio, $^{52}Cr^+/^{56}Fe^+$, depend on the time of Ar atom bombardment. The peak heights of $^{56}Fe^+$ and $^{52}Cr^+$ varied regularly as the surface sputtering proceeded: During the first 3 min of the Ar atom bombardment the peak height of $^{52}Cr^+$ increased smoothly until it reached a steady state value, while at the same time the peak height of $^{56}Fe^+$ decreased smoothly to another steady value. For two $(Fe,Cr)_3O_4$ samples, one subjected to CO adsorption for 24 h, the other free of CO adsorption, the same FAB mass spectra were obtained. Kubsh *et al.* (*12*) studied $(Fe,Cr)_3O_4$ by ESCA, their results indicating that the surface of this homogeneous solid solution is enriched in chromium, compared to the bulk composition. In contrast, the results of FAB mass spectra in our experiments indicate that while the surface content of chromium is not markedly enriched, remarkably, in the subsurface of $(Fe,Cr)_3O_4$, the content of chromium *is* enriched.

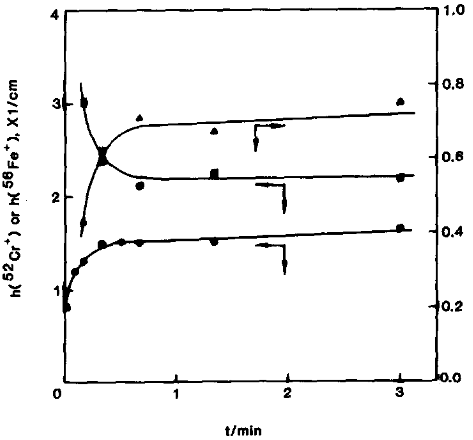

FIG. 3. Relationships of $h(^{52}Cr^+)$–t, $h(^{56}Fe^+)$–t, and $h(^{52}Cr^+)/h(^{56}Fe^+)$–$t$, where $h(^{52}Cr^+)$, $h(^{56}Fe^+)$, $h(^{52}Cr^+)/h(^{56}Fe^+)$, and t represent the peak height of $^{52}Cr^+$, the peak height of $^{56}Fe^+$, the ratio of the peak heights, and the time of Ar atom bombarding of $(Fe,Cr)_3O_4$, respectively. (○) $h(^{52}Cr^+)$–t, (□) $h(^{56}Fe^+)$–t, (△) $h(^{52}Cr^+)/h(^{56}Fe^+)$–$t$.

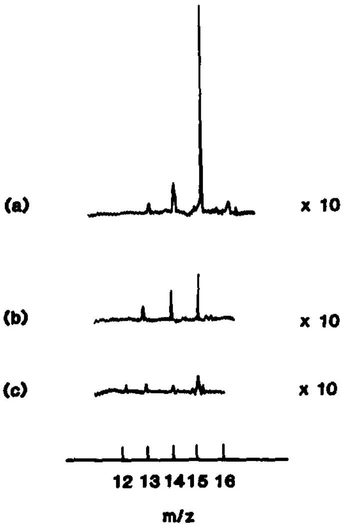

FIG. 4. Positive-ion FAB mass spectra of the $(Fe,Cr)_3O_4$ sample, $m/z = 12$–16. (a) After the sample with CO adsorbed at 633 K for 24 h; Ar atom bombardment time <1 s. (b) After the sample with CO adsorbed at 633 K for 8 h; Ar atom bombardment time <1 s. (c) Without CO adsorption; Ar atom bombardment time <1 s. ("Ar atom bombardment time <1 s" means that the spectrum was recorded just at the beginning of the bombardment.

(*B*) The FAB mass spectra show that a layer of carbonaceous species appeared on the surface of $(Fe,Cr)_3O_4$ after contact with CO. Figure 4 shows the positive-ion FAB mass spectra of the $(Fe,Cr)_3O_4$ sample, $m/z = 12$–16. Three spectra were recorded as Ar atoms started bombarding the sample (within less than 1 s). The spectrum (c) which was taken from the sample without CO adsorption shows very small peaks which may be regarded as the background of the signals of the sample. Both spectra (b) and (a) were taken from samples after CO adsorption for 8 and 24 h, respectively. It is evident that the amount of carbonaceous species increases with the time of CO adsorption at 633 K, and the order of CH_x content is $CH_3 > CH_2 > CH$. Clearly, FAB MS is better able than either AES or XPS to distinguish the carbonaceous species, and the results from FAB MS are the most reliable.

(*C*) We consider the source of hydrogen in the carbonaceous species: The $(Fe,Cr)_3O_4$ was prepared by reducing $(Fe,Cr)_2O_3$ in a gas mixture of $H_2 : H_2O = 4 : 1$ at 633 K. If the surface pretreatment was carried out at this temperature before CO adsorption, it is known that adsorbed water could not be totally desorbed (*1*). The hydroxylated surface must then afford the hydrogen for the carbonaceous species.

Figure 5 shows the positive-ion FAB mass spectrum of the $(Fe,Cr)_3O_4$ sample, *m/z* = 67–77, and the negative-ion FAB mass spectrum of the $(Fe,Cr)_3O_4$ sample, *m/z* = 15–18. Figure 5a is the positive-ion FAB mass spectrum of the sample with CO adsorbed at 633 K for 8 h. There exist two main peaks at *m/z* of 69 and 73. In the positive-ion FAB mass spectra of both the sample with CO adsorbed at 633 K for 24 h and the sample without CO adsorption, there also exist two similar main peaks. Figure 5b is the negative-ion FAB mass spectrum of the sample with CO adsorbed at 633 K for 24 h, which shows that even after Ar atom bombardment for 20 min there still exist two peaks of *m/z* 16 and 17. These facts, in combination with the observation that the heights of the two peaks with *m/z* 69 and 73 varied regularly with the time of Ar atom bombardment (the longer the bombardment time, the lower the two peaks synchronously), lead us to conclude that the peaks of *m/z* 69 and 73 represent $(^{52}CrOH)^+$ and $(^{56}FeOH)^+$, and the peaks of *m/z* 16 and 17 denote O^- and OH^-, respectively. These facts thus establish that the residual water dissociatively adsorbed on the surface of the catalyst was the source of hydrogen in the carbonaceous species.

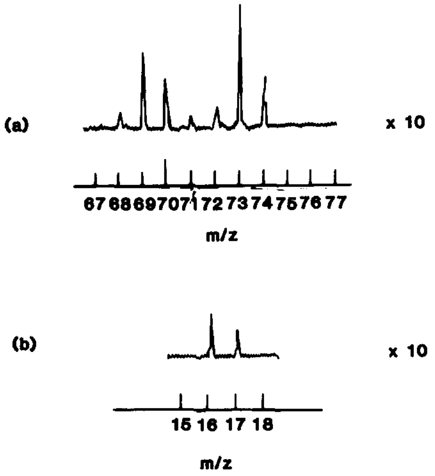

FIG. 5. Positive-ion FAB mass spectrum of the $(Fe,Cr)_3O_4$ sample, *m/z* = 67–77, and negative-ion FAB mass spectrum of the $(Fe,Cr)_3O_4$ sample, *m/z* = 15–18. (a) Positive-ion FAB mass spectrum of the sample with CO adsorbed at 633 K for 8 h; Ar atom bombardment time = 20 s. (b) Negative-ion FAB mass spectrum of the sample with CO adsorbed at 633 K for 24 h; Ar atom bombardment time = 20 min.

(*D*) FAB MS has been used to investigate the effect of the time of interaction of CO with $(Fe,Cr)_3O_4$ on the kinds and populations of the carbonaceous species. The results showed that after interaction at 633 K for 8 h, the major carbonaceous species were C_1–C_3, and after interaction lasting 24 h at 633 K, a large number of carbonaceous species with more than three carbon atoms was formed (see Fig. 6). Similar results were obtained by temperature-programmed desorption mass spectrography. All of the facts showed that in the course of interaction of CO with $(Fe,Cr)_3O_4$ carbonaceous species formed on the surface of $(Fe,Cr)_3O_4$ and developed from lower carbon number to higher carbon number.

(*E*) In all these FAB MS experiments no C^+ signal was ever found. This implies that there is no carbon deposit formed on the

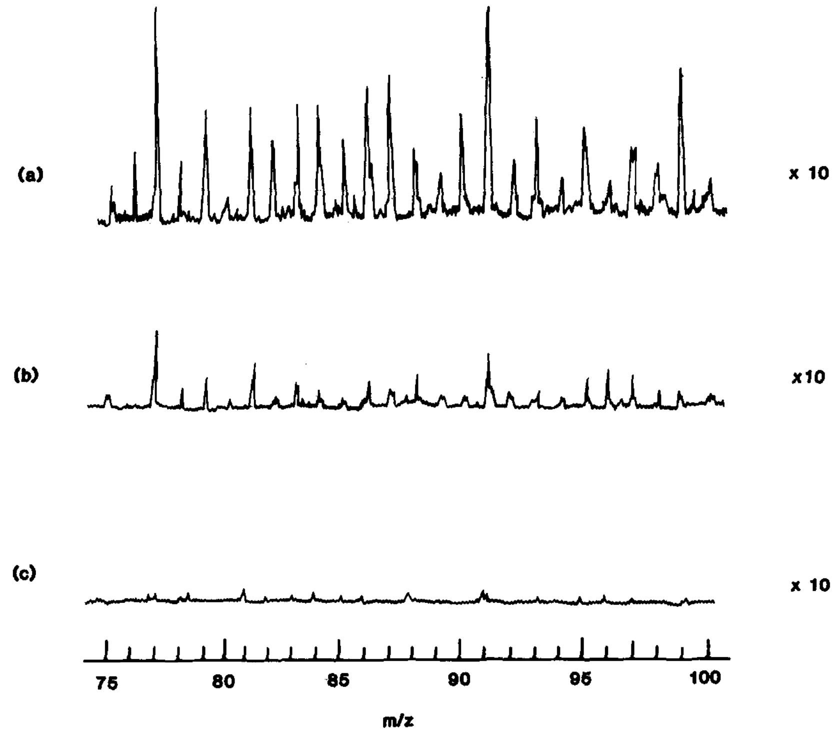

FIG. 6. The effect of the time of interaction between CO and $(Fe,Cr)_3O_4$ on the kinds and populations of the carbonaceous species. (a) Positive-ion spectrum of the sample with CO adsorbed at 633 K for 24 h; Ar atom bombardment time <1 s. (b) Positive-ion spectrum of the sample, with CO adsorbed at 633 K for 24 h, Ar atom bombardment time = 10 s. (c) Positive-ion spectrum of the sample, with CO adsorbed at 633 K for 8 h, Ar atom bombardment time = 10 s.

surface under the conditions of this study.

(*F*) The $K_p = (P^2_{CO}/P_{CO_2})$ of the reaction $C + CO_2 = 2CO$ at 673 K is 9×10^{-5}, and it is lower at 633 K. If the total pressure $(P_{CO} + P_{CO_2})$ is 8.97 Torr when equilibrium is reached, then P_{CO_2}/P_{CO} must be 10.96, ≈ 11. The results of our FAB MS experiment are given in Table 1.

TABLE 1

Peak Heights (a.u.) for *m/z* 28 and 44 in FAB MS Experiment

m/z	$(Fe,Cr)_3O_4$ with CO adsorbed at 633 K for 24 h signals (×1)	$(Fe,Cr)_3O_4$ with CO adsorbed at 633 K for 8 h signals (×10)	$(Fe,Cr)_3O_4$ without CO adsorption signals (×10)
28	4.1	6.0	3.9
44	6.9	7.1	6.8

Note. Ar atom bombardment time <1 s. The peak height ratios of 44/28 of the adsorbate on the catalysts' surfaces are 6.9/4.1, 7.1/6.0, 6.8/3.9 = 1.7, 1.2, 1.7. They are far smaller than 11, and the ratio of the peak height of the sample with CO adsorbed for 24 h is the same as the ratio of the peak height of the sample without CO adsorption. This establishes that no disproportionation of CO has occurred.

CONCLUSIONS

(i) At P_{CO} = 6–9 Torr and T = 473–673 K, CO interacts with hydroxylated $(Fe,Cr)_3O_4$ surface to form carbonaceous species, but no carbon deposit has been found.

(ii) The surface content of chromium in $(Fe,Cr)_3O_4$ is not markedly enriched, compared to the bulk composition, but at the subsurface of $(Fe,Cr)_3O_4$ the content of chromium is enriched.

(iii) Owing to the interaction of CO with $(Fe,Cr)_3O_4$, carbonaceous species formed on the surface of $(Fe,Cr)_3O_4$ and developed from lower carbon number to higher carbon number with increasing duration of CO exposure.

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REFERENCES

1. Yang, Shang-run, Liu, Xian-de, and Fu, Xian-cai, *J. Nanjing Univ. Nat. Sci. Ed.* **21**(4), 649 (1985).

2. Audier, M., Coulon, M., and Bonnetain, L., *Carbon* **17,** 391 (1979).

3. Sacco, A., Jr., and Reid, R. C., *Carbon* **17,** 459 (1979).

4. Renshaw, G. D., Roscoe, C., and Walker, P. L., Jr., *J. Catal.* **18,** 164 (1970).

5. Bonzel, H. P., and Krebs, H. J., *Surf. Sci.* **91,** 499 (1980).

6. Barber, M., Bordoli, R. S., Elliott, G. J., Sedgwick, R. D., and Tyler, A. N., *Anal. Chem.* **54,** 645A (1982).

7. Devienne, F. M., and Roustan, J.-C., *Org. Mass Spectrom.* **17,** 173 (1982).

8. Yang, Shang-run, Liu, Li, and Fu, Xian-cai, "Program and Abstracts for Second China–U.S.–Japan Symposium on Heterogeneous Catalysis, July 1–3, 1985." University of California, Berkeley, CA, C-29.

9. Yang, Shang-run, Xu, Wei-xing, and Fu, Xian-cai, *J. Nanjing Univ. Nat. Sci. Ed.* **21**(2), 285 (1985).

10. Jagannathan, K., Srinivasan, A., Hegde, M. S., and Rao, C. N. R., *Surf. Sci.* **99,** 309 (1980).

11. (a) Yang, Shang-run, *J. Catal. (China)* **4,** 57 (1983); (b) *Acta Physicochim. Sin.* **3,** 313 (1987).

12. Kubsh, J. E., Chen, Y., and Dumesic, J. A., *J. Catal.* **71,** 192 (1981).