JOURNAL OF CATALYSIS **170,** 54–61 (1997)
ARTICLE NO. CA971723

A Kinetic and *in Situ* XRD Study of Carbon Reactions Catalyzed by Nickel, Cobalt, Molybdenum, and Their Mixtures

I. F. Silva, D. W. McKee, and L. S. Lobo

Departamento de Quimica, FCT/Universidade Nova de Lisboa, 2825 Monte de Caparica, Portugal

Received January 12, 1996; revised March 21, 1997; accepted April 10, 1997

The kinetics of oxidation and hydrogenation of ground charcoal in the presence of nickel, cobalt, and molybdenum catalysts have been studied using a microbalance and *in situ* X-ray diffraction to identify the phases present during the reactions. Nickel and cobalt were found to be better catalysts than molybdenum for the oxidation of carbon. However, addition of molybdenum to the other metals resulted in increased catalytic activity, probably because of decreased crystal growth or sintering of the active phases. The promoting effect of molybdenum was less clear in the case of carbon hydrogenation, which took place in two distinct temperature ranges (between 773 and 973 K and above 1023 K) with nickel catalysts. Possible mechanisms of the catalyzed reactions are discussed.

INTRODUCTION

Many studies have been carried out on the catalytic effects of nickel and cobalt in carbon gasification reactions (1–3). It is known, for example, that during the Ni-catalyzed hydrogenation of carbon, methane formation attains maximum values in different temperature ranges (4, 5). This is not clearly understood and the behavior of the nickel catalyst appears to depend on factors such as catalyst loading, heat treatment of the sample, carbon oxygen group content, dispersion, and chemical state of the catalyst (6, 7). The addition of inactive oxides, such as CaO or MgO, has been found to promote the catalytic activity of nickel in the hydrogasification of carbon (8), especially in the low-temperature region (9). Less is known about the behavior of molybdenum as a catalyst in these reactions, although the oxide has been reported to be active in carbon oxidation (10).

This paper describes the results of a study of the comparative catalytic behavior of the three metal oxides and their mixtures in carbon oxidation and hydrogenation, using both microbalance and *in situ* X-ray diffraction (XRD) techniques. The results complement those of previous investigations in which either molybdenum oxide catalyst was mixed with activated carbon (11) or carbon samples were impregnated or mixed with cobalt, nickel, and molybdenum salts (12) and the resultant reactivity toward oxygen was studied. This investigation was undertaken to explore the potential of *in situ* XRD technique as a means of determining the nature of catalytically active species present during carbon gasification reactions. It was hoped that the method would shed light on the mode of action of oxide catalysts in these reactions.

EXPERIMENTAL

Carbon Sample

A charcoal sample with an area of 605 $m^2\ g^{-1}$ and a pore volume of 0.68 $cm^3\ g^{-1}$ was used in this study. The charcoal was ground to an average particle diameter in the range 6–50 μm.

Catalyst Preparation

The MoO_3 catalyst was prepared by calcination of ammonium molybdate at 873 K for 6 h. The oxide was then ground in a mortar with the ground charcoal to give a mixture containing 2.5 wt% Mo. Similarly, samples containing Ni and Co were prepared by physical mixing of the charcoal with the ground metal nitrates, followed by heat treatment in a stream of air or hydrogen at 573 K for 30 min to convert the salts to oxides.

Samples of charcoal with Ni–Mo and Co–Mo oxides were prepared by mixing the charcoal with MoO_3 and Ni or Co nitrates in different ratios and subsequently heating in a stream of air or hydrogen at 573 K. Samples used for the XRD experiments contained 5% metal by weight.

Kinetic Measurements

The kinetic measurements were carried out in a C.I. Electronics microbalance operated isothermally, with continuous recording of changes in weight. Details of the geometry of the crucible and gas flow pattern have been reported previously (11). A constant gas flow of 3.5 cm^3/s was used throughout, ensuring the absence of mass transfer limitations over a wide range of temperature. The purity of gases was 99.99, 99.95, and 99.99% for nitrogen, air, and

0021-9517/97 $25.00

hydrogen, respectively. Before use, the gases were passed through a molecular sieve bed to remove water. The total gas pressure used was always 1 bar (0.1 MPa). For comparison purposes, initial rates obtained at initial burn-off were used in the case of hydrogenation and the rates at 20% burn-off in the case of the much faster carbon oxidation reaction. Constant rates of gasification were generally obtained up to 50% burn-off of the carbon. The gasification rates at each temperature were derived from the relation: rate (s^{-1}) = $(-\Delta w/\Delta t)/w_0$, were w_0 is the initial weight of the sample. Reaction orders were obtained at constant temperature, diluting air or hydrogen with nitrogen. Oxygen and hydrogen partial pressures varied from 1 bar down to 6.6×10^{-3} bar. The slope of the plot of ln(rate) versus ln(gas partial pressure) gave the reaction order.

XRD Studies

In situ XRD measurements were conducted in a Rigaku D/MCX IIC diffractometer with a Cu$K\alpha$ radiation source (45 kV, 35 mA) and a high-temperature chamber. The samples were compacted on a platinum support mounted vertically. Air or hydrogen was passed over the sample at 2.5 cm^3/s; the chamber was first flushed with the reactant gas at room temperature for 30 min before the measurements were carried out. The oxygen and hydrogen partial pressures used were 0.21 and 0.07 bar (0.021 and 0.007 MPa), respectively.

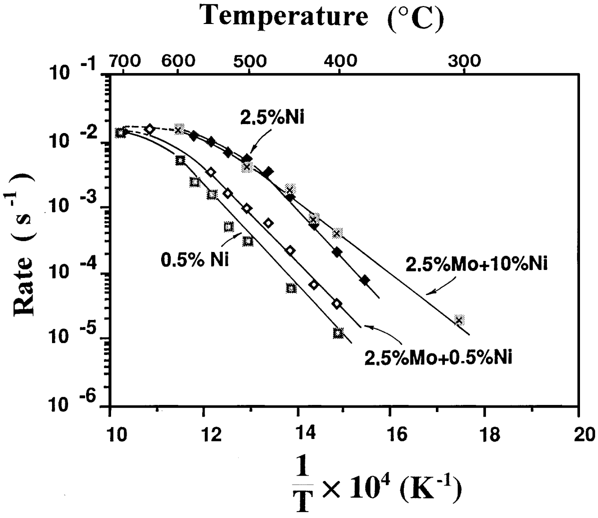


FIG. 1. Logarithmic plot of rate of gasification in air for charcoal samples containing Mo, Ni, and mixed Mo–Ni catalysts ($P_{O_2} = 0.21$ bar) as a function of reciprocal temperature.

RESULTS AND DISCUSSION

Carbon Oxidation

In previous studies carried out at 773 K with Ni, Co, and Mo catalysts (11, 12), the activity of these catalysts in carbon oxidation reached a plateau above 2.5 wt% metal. Figures 1 and 2 illustrate the effects of temperature on catalyzed oxidation rates of charcoal in the temperature range 573–973 K. The Arrhenius plot for the 2.5% Mo sample was identical with that for 0.5% Ni. The apparent activation energies for the uncatalyzed and catalyzed reactions (573–973 K) vary between 170 ± 1 and 83 ± 9 kJ mol^{-1}. Reactions orders with respect to O_2 were evaluated at 773 K. Zero order was observed with Co and Co + Mo samples, and 0.7 order was observed in the other cases. The activation energy is reduced to a very low value when external diffusion controls the reaction rate. This latter case was observed in the present work at temperatures above 873 K.

In contrast to the results reported by Baker and Sherwood (13), nickel was an active catalyst for the oxidation of charcoal, although the activity was found to decrease after 35% burn-off. Cobalt was generally more active than nickel or molybdenum at temperatures below 873 K (Fig. 2). With cobalt, the catalyzed oxidation took place in two distinct temperature ranges, i.e., one between 573 and 648 K and a different process above 673 K. Similar behavior was observed by Oh and Baker (14) who correlated the different patterns of activity with the existence of different chemical states of the catalyst. However, in a previous study of the effects of cobalt (12) in which the catalyst was added by impregnation, this two-stage effect was not observed.

In this study, nickel oxide was found to be a more active catalyst for the reaction of carbon with oxygen than molybdenum oxide. This disagrees with the findings of Baker who has argued that catalytic activity in this reaction can be inversely correlated with the tendency of the metal to form carbides (15). In contrast, vanadium is a strong carbide former and its oxides are very active catalysts for the C–O_2 reaction (1). It seems more likely that catalytic activity in

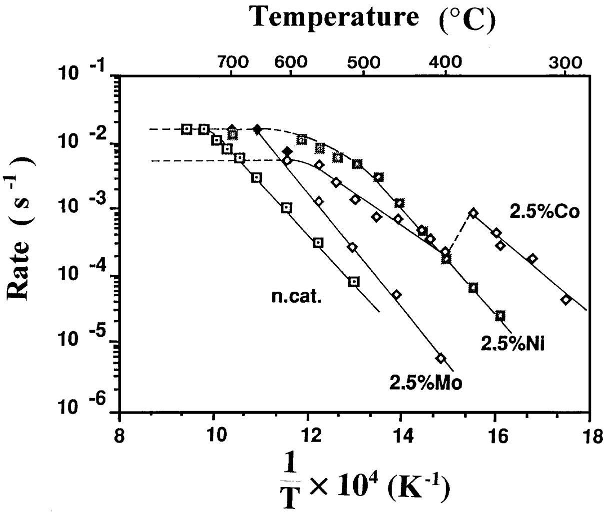


FIG. 2. Comparison of rates of gasification in air for charcoal samples containing Ni, Co, and Mo catalysts ($P_{O_2} = 0.21$ bar) as a function of reciprocal temperature.

this case is related to the ability of the oxide to be reduced by carbon and undergo redox reactions on the carbon surface (1).

For reaction temperatures above 723 K a decline in activity was observed above 50% burn-off for the 0.5% Ni sample. However, the mixed catalyst 2.5Mo + 0.5Ni exhibited no decline in activity up to at least 70% burn-off. This finding suggests that the presence of molybdenum oxide helped to reduce the occurrence of sintering of the nickel oxide particles. A comparison of the activity of the various catalysts in air (723 K) showed that the mixed catalysts Mo + Ni and Mo + Co were both more active than expected from the additive effects of the separate components. These results also suggested that the presence of the molybdenum oxide phase promoted and helped to maintain a high degree of dispersion of the active nickel or cobalt oxide particles.

In situ XRD measurements carried out in nitrogen (298–1023 K) showed that NiO and cobalt oxide (Co_3O_4/CoO) were reduced by carbon to metallic Ni and Co, and that MoO_3 was reduced to MoO_2.

Thus MoO_3 was reduced by carbon to MoO_2 above 773 K; $Ni(NO_3)_2 \cdot 6H_2O$ decomposed at 573 K to form small crystals of NiO (∼3.6 nm) as determined from X-ray line broadening. Above 723 K, NiO was reduced to Ni metal by reaction with carbon. $Co(NO_3)_2 \cdot 6H_2O$ decomposed at 573 K to form both Co_3O_4 and CoO. Above 723 K both oxides were reduced by carbon to Co metal.

These reduction reactions are thermodynamically favored and calculations of the standard free energy changes (ΔG°_{773} kJ/mol) for reduction of the oxides by carbon and for reoxidation with air at 773 K are summarized in Table 1 (20).

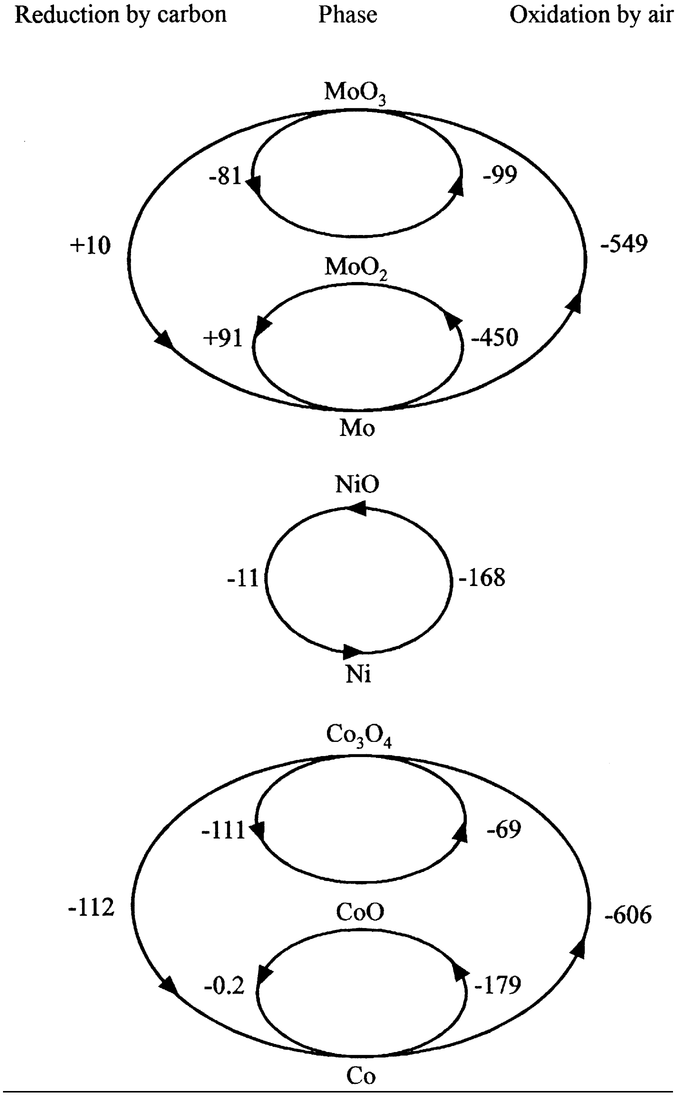
As CO is the primary gaseous product of carbon oxidation, the only reactions considered were of the following types:

$$\begin{array}{ll} \text{Reduction} & \\ \quad\text{by carbon} & M_xO_{y+1}(s) + C(s) = M_xO_y(s) + CO(g) \\ & M_xO_y(s) + yC(s) = xM(s) + yCO(g) \\ \text{Oxidation} & xM(s) + y/2O_2(g) = M_xO_y(s) \\ & M_xO_y(s) + 1/2O_2(g) = M_xO_{y+1}(s) \end{array}$$

As with other oxide systems (10), the catalytic effects of Co_3O_4 and MoO_3 can be explained by the occurrence of redox processes of these types in which the oxide particles are reduced by reaction with the carbon at points of contact with the charcoal substrate to form the lower oxides CoO and MoO_2. Reoxidation to form the higher oxide subsequently occurs on contact with ambient oxygen.The results of the free energy calculations indicate that, although NiO can be reduced to the metallic state by reaction with carbon at 773 K, reduction of CoO and MoO_2 to the metals is unlikely. These results were generally confirmed by the XRD data.

TABLE 1

Standard Free Energies (ΔG° kJ mol^{-1}) for Possible Redox Reactions at 773 K



Thus, *in situ* X-ray results obtained in air under reaction conditions (298–803 K) showed that MoO_3 was reduced to MoO_2 above 673 K. Along with MoO_3 and MoO_2 a nonstoichiometric oxide ($Mo_{17}O_{47}$) was detected. This oxide was converted to Mo_4O_{11} (10).

Similar results have been reported by other authors (16). With nickel, only NiO was detected during the reaction. In the case of cobalt, both Co_3O_4 and CoO may be present under reaction conditions. Thus in each case, redox reactions were possible and quite probably explained the catalytic effects.

The XRD pattern obtained in air for the charcoal sample containing 5%Mo + 5%Co as catalyst (Fig. 3) shows that melting of $Co(NO_3)_2 \cdot 6H_2O$ occurs at 423 K and that

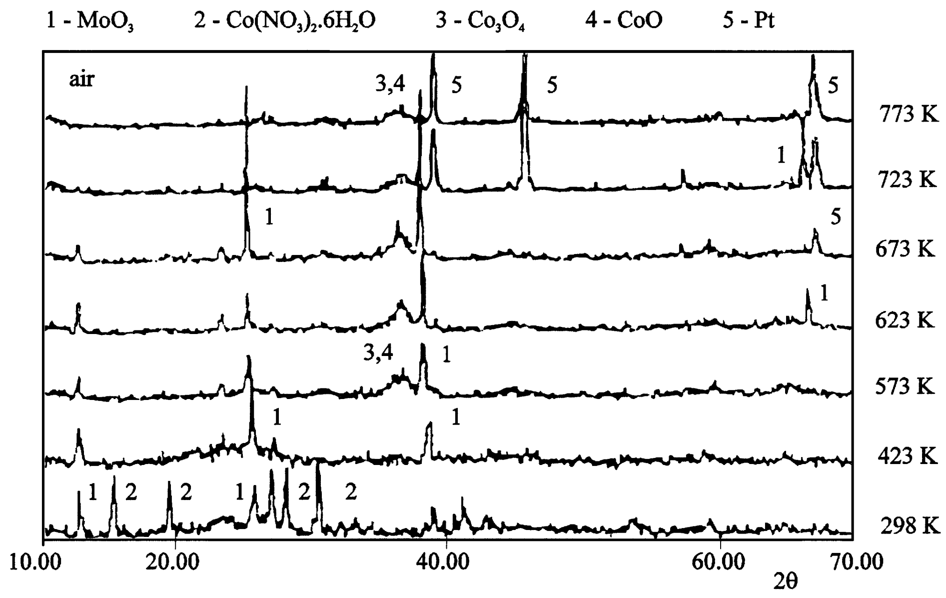


FIG. 3. *In situ* X-ray diffractograms obtained on heating 5%Mo + 5%Co–charcoal in air at various temperatures.

it decomposes at 573 K to form Co_3O_4 and CoO. The peaks generally showed shifts to lower 2θ with increasing temperature which reflected expansion of the crystal lattices. Pt peaks which appeared in the spectra at high temperatures resulted from exposure of the sample holder to the X-ray beam as the carbon burnt away.

No evidence of a new phase responsible for the "synergistic" effect was observed for Mo + Co, but above 673 K the intensity of the peak corresponding to Co_3O_4/CoO ($2\theta \approx 37^\circ$) decreases as the temperature increases, suggesting melting of the catalyst.

A liquid-like state does not exhibit reflections, so it may be that only the larger crystals are observed by XRD and that the particles responsible for gasification (the droplets) are not detected.

Carbon Hydrogenation

Several transition metals catalyze the reaction of carbon with hydrogen and maxima in the rates of production of methane have been observed in two or more temperature regions (4, 5). Figure 4 shows Arrhenius plots for this reaction as catalyzed by Ni, Co, and Mo in the range 973–1173 K.

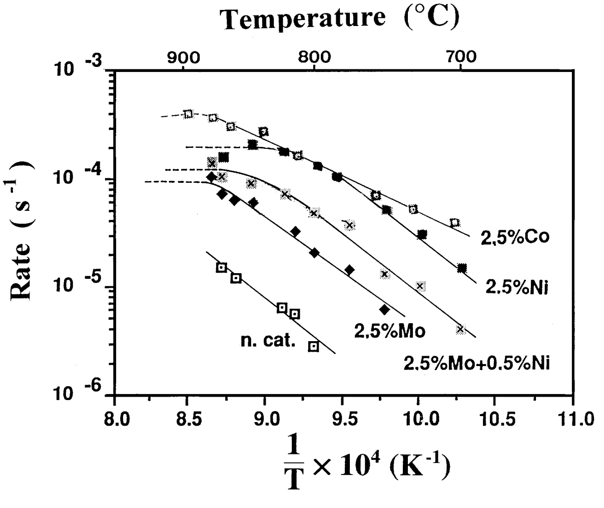


FIG. 4. Logarithmic plot of rate of gasification in hydrogen (P_{H_2} = 1 bar) for charcoal samples containing Ni, Co, and Mo catalysts between 973 and 1173 K as a function of reciprocal temperature.

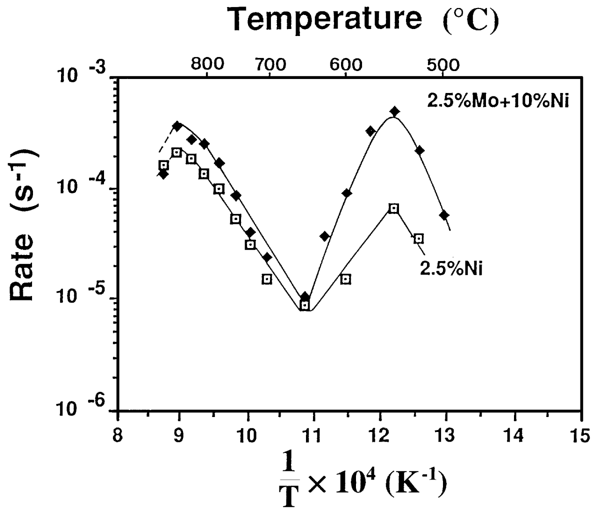


FIG. 5. Logarithmic plot of rate of gasification in hydrogen (P_{H_2} = 1 bar) for charcoal samples containing 2.5%Ni and 2.5%Mo + 10%Ni between 773 and 1123 K as a function of reciprocal temperature.

The apparent activation energy decreases from 209 ± 18 kJ mol^{-1} in noncatalytic gasification to 195 ± 2 kJ mol^{-1} with 2.5%Ni and 162 ± 6 kJ mol^{-1} with 2.5%Co catalyst. The order of reaction with respect to H_2 at 1073 K was in the range 0.8 to 1.

A large catalytic effect was observed for Ni and Co and a smaller effect for Mo. Cobalt appeared to be somewhat more active than nickel, as observed by Oh and Baker (14). The most active catalysts caused a substantial reduction in apparent activation energy for the reaction.

Figure 5 illustrates the effect of temperature in the Ni-catalyzed hydrogenation reaction over the range 773–1123 K. The decrease in rate at high temperature was due to the fact that the exothermic hydrogenation reaction became increasingly unfavorable with increasing temperature at the system approached equilibrium. The existence of two regions of activity was only observed for catalyst loadings above 2.5% Ni. Baker (15) has reported that, during the catalyzed reactions, both nickel and cobalt particles dig channels in carbon surfaces. The metal particles in the present work generally behaved like liquid droplets, as illustrated in the SEM micrographs in Fig. 6. Lobo *et al.*

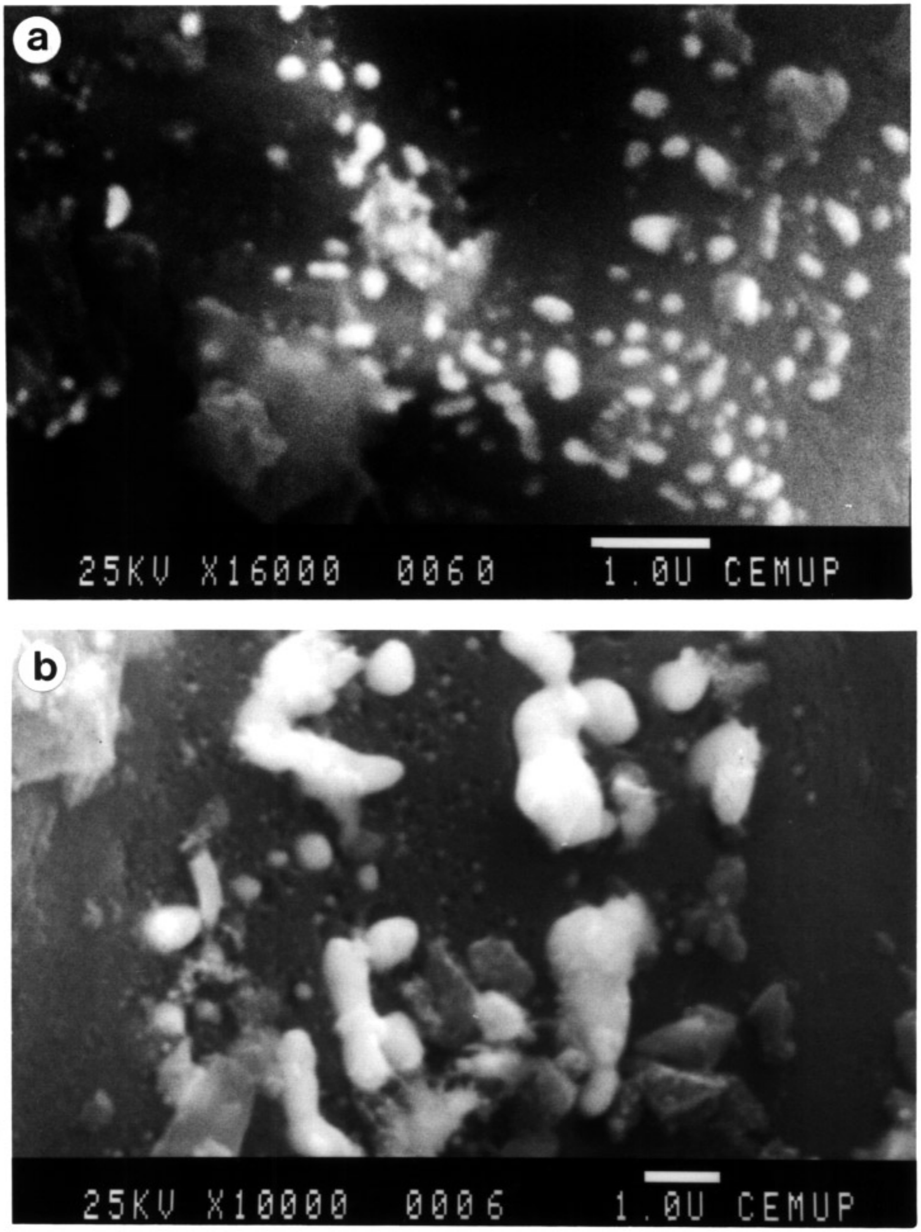


FIG. 6. Scanning electron micrographs of (a) Ni and (b) Co catalyst particles on charcoal during hydrogenation at 1023 K.

(17) and also Figueiredo and Trimm (18) have proposed a mechanism for the Ni-catalyzed hydrogenation process involving:

(i) chemisorption of hydrogen at the surface of the nickel particles,
(ii) reaction of adsorbed hydrogen atoms with carbon atoms at the surface, and
(iii) supply of carbon atoms to the surface by diffusion through the nickel particles.

Observed rates of the Ni-catalyzed gasification of carbon at high temperatures have been shown by these authors to be comparable to the calculated rates of diffusion of carbon through nickel at these temperatures. However, at temperatures in the range 773–823 K, a different mechanism appears to be operating. Perhaps in this case the nickel particles act as sites for H_2 dissociation with subsequent reaction at the carbon–metal interface between labile adsorbed hydrogen atoms and carbon, as proposed by Remick *et al.* (19).

The addition of Mo resulted in a small increase in catalytic activity in this low-temperature region (773–823 K) but the effect was minor compared with that observed in the $C{-}O_2$ reaction. When Mo was added to Co, no increase in the expected catalytic activity was observed, as illustrated in Fig. 7, and the bimodal behavior of Ni was not found in this case.

In order to investigate the effects of oxygenated surface groups on the carbon surface, experiments were carried out with Ni-catalyzed samples which had first been treated with nitrogen at 823 K before introduction of hydrogen. In this case the reactivity at low temperature was not observed. However, after exposure of the same samples to air for 30 min at room temperature, the hydrogenation reactivity at low temperatures was restored. This observation suggests that oxygenated groups on the carbon surface create active sites for the hydrogenation reaction. This behavior has been reported by other authors and it has also been found that interaction of nickel with surface groups results in increased catalyst dispersion, possibly as a result of the formation of Ni–O–C species (8). However, the hydrogenation of surface oxygenated groups would only be a temporary phenomenon and the effect should disappear when steady behavior is attained.

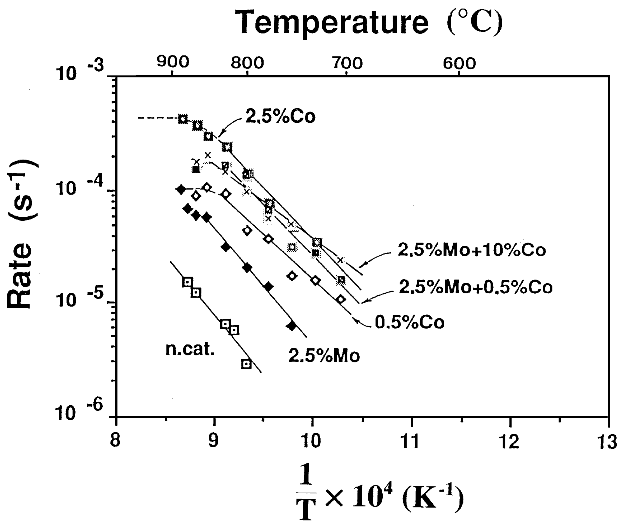


FIG. 7. Logarithmic plot of rate of gasification in hydrogen ($P_{H_2} =$ 1 bar) for charcoal samples containing Mo, Co, and Mo + Co between 973 and 1173 K as a function of reciprocal temperature.

Results of *in situ* XRD performed in hydrogen at different temperatures with the nickel, cobalt, and molybdenum catalysts are summarized in Fig. 8. In this environment, NiO was reduced to Ni, CoO was partially converted to metallic Co, and MoO_3 was reduced to MoO_2.

An interesting observation was the appearance of peaks of NiO in the *in situ* XRD spectra in the temperature range 848–873 K on heating the Ni–charcoal in hydrogen (Fig. 8a). It is possible that in this temperature range oxygenated groups on the charcoal surface were decomposing to form CO_2 and CO which reacted with the nickel particles to form NiO. This temperature range corresponded to a region of reduced catalytic activity. Above 923 K the catalytic activity was restored and the NiO peaks disappeared.

CONCLUSIONS

This study has indicated that kinetic measurements combined with X-ray diffraction are useful tools for interpreting catalyst behavior and dispersion and for identifying the phases present during catalyzed reactions. In the $C{-}O_2$ reaction, NiO was found to be a better catalyst than Co or Mo oxides and a redox mechanism could explain the behavior observed. The addition of Mo oxide increased the catalytic activity of nickel and cobalt oxides.

In the $C{-}H_2$ reaction, only nickel exhibited low-temperature activity, although both Co and Ni were active catalysts at high temperatures. Addition of Mo resulted in only a small enhancement of activity in this reaction. The catalyst particles remained in the metallic state throughout and a mechanism based on carbon dissolution and diffusion through the metal particles appeared most likely at the higher temperatures.

The catalytic activity of nickel below 873 K may result from a different process in which the metal particles act as sites for H_2 dissociation, followed by reaction of hydrogen atoms at the carbon-metal interface.

ACKNOWLEDGMENTS

The authors thank the Portuguese Secretary of State for Science and Technology (JNICT) for a research grant (Praxis XXI) to DWM. The authors are also undebted to Professor Brás Fernandes (CENIMAT) for helpful discussions and suggestions during the course of XRD experiments.

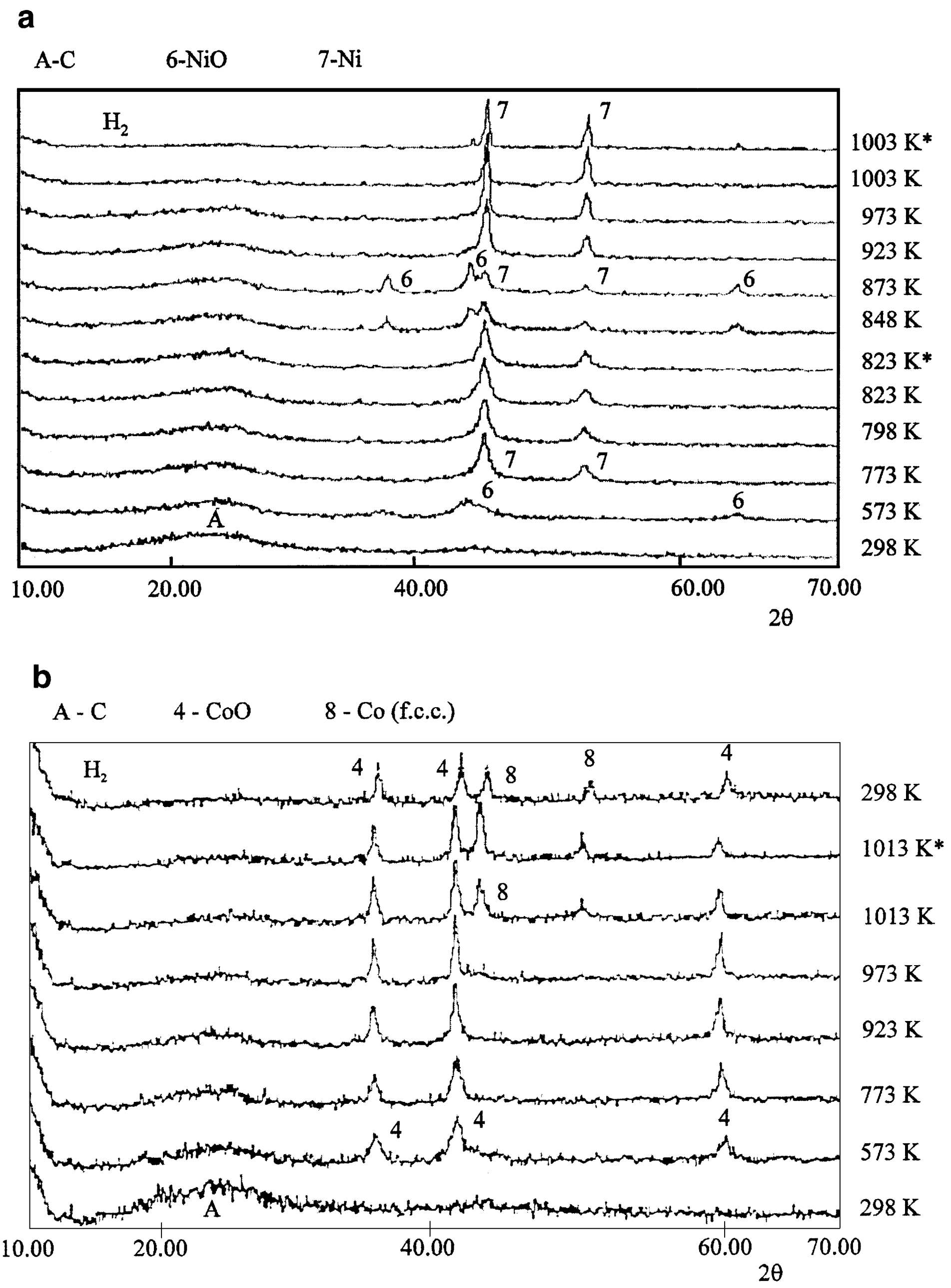


FIG. 8. *In situ* X-ray diffractograms obtained on heating (a) 5%Ni–charcoal, (b) 5% Co–charcoal, and (c) 5%Mo–charcoal samples in hydrogen at various temperatures. *The diffractogram was repeated after an additional time of 30 min.

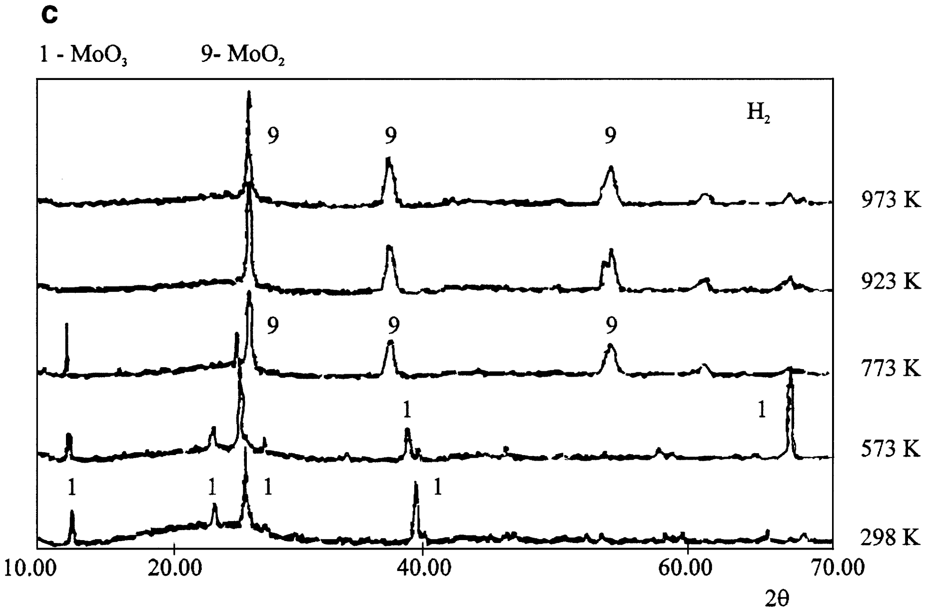


FIG. 8—*Continued*

REFERENCES

1. McKee, D. W., *in* "Chemistry and Physics of Carbon" (P. Walker, Ed.), Vol. 16, p. 1. Dekker, New York, 1981.
2. Keep, C. W., Terry, S., and Baker, R. T. K., *J. Catal.* **66**, 451 (1980).
3. Wigmans, T., van Doorn, Y. J., and Moulijn, J. A., *Surf. Sci.* **135**, 532 (1983).
4. Tomita, A., and Tamai, Y., *J. Catal.* **27**, 293 (1972).
5. Weber, J., and Bastick, M., *C. R. Acad. Sci.* **280**, 1177 (1975).
6. Weber, J., and Bastick, M., *High Temperature, High Pressure* **9**, 177 (1977).
7. Tomita, A., Sato, N., and Tamai, Y., *Carbon* **12**, 143 (1974).
8. Haga, T., Ozaki, J., Suzuki, K., and Nishiyama, Y., *J. Catal.* **134**, 197 (1992).
9. Haga, T., and Nishiyama, Y., *J. Catal.* **81**, 239 (1983).
10. McKee, D. W., *Carbon* **8**, 623 (1970).
11. Silva, I. F., and Lobo, L. S., *J. Catal.* **126**, 489 (1990).
12. Silva, I. F., Encinar, J., and Lobo, L. S., *Catal. Today* **7**, 239 (1990).
13. Baker, R. T. K., and Sherwood, R. D., *J. Catal.* **70**, 198 (1981).
14. Oh, S. G., and Baker, R. T. K., *J. Catal.* **128**, 137 (1991).
15. Baker, R. T. K., *in* "Carbon and Coal Gasification" (J. L. Figueiredo and J. A. Moulijn, Eds.), p. 231. NATO Series 105, Nijhoff, Dordrecht, 1986.
16. Castilla, C., Marin, F., and Utrilla, Y., *Fuel* **69**, 354 (1990).
17. Lobo, L. S., and Trimm, D. L., *J. Catal.* **29**, 15 (1973); Bernardo, C. A., and Lobo, L. S., *Carbon* **16**, 287 (1976).
18. Figueiredo, J. L., and Trimm, D. L., *J. Catal.* **40**, 154 (1975); Figueiredo, J. L., *Carbon* **19**, 146 (1981).
19. Remick, R. T., Wentrcek, P. R., and Wise, H., *Fuel* **53**, 274 (1974).
20. Kubaschewski, O., Evans, E., and Alcock, C., "Metallurgical Thermochemistry," 4th ed. Pergamon, Oxford, 1967.