JOURNAL OF CATALYSIS 145, 402–408 (1994)

Stable Nickel-Containing Catalysts for the Oxidative Coupling of Methane

Kerry M. Dooley,*† Shang-Yang Chen,* and J. R. H. Ross‡,[1]

*Department of Chemical Engineering, Louisiana State University, Baton Rouge, Louisiana 70803; and †Department of Chemical Technology, University of Twente, 7500AE Enschede, The Netherlands

Received July 9, 1993

A new catalyst based on the K/Ca/Ni oxide system has been developed for the oxidative coupling of methane at <700°C. It is capable of up to 70% selectivity to C_{2+} hydrocarbons at complete O_2 conversion (CH_4/O_2 ratio = 2.5) if 35% water is present in the feed. Unlike previous materials of this type, the present catalyst is stable at the conditions of its maximum yield to C_{2+} products and is not poisoned by CO_2. On the contrary, it appears as if CO_2 promotes formation of a selective hydroxycarbonate phase which develops under reaction conditions. © 1994 Academic Press, Inc.

INTRODUCTION

The oxidative coupling of methane (OCM) has been intensively studied for the past 10 years. Numerous catalysts have been tested and developed for this reaction, including alkali/alkaline earth oxide mixtures, rare earth oxides, and mixtures of alkaline earth oxides with post-transition metal oxides. Most of these require a reaction temperature well above 700°C in order to produce C_{2+} hydrocarbons at high selectivity (1, 2). However, doping alkali/alkaline earth oxide mixtures with certain transition or post-transition metals can reduce the temperatures of usage significantly, although selectivity may be sacrificed (3). In these catalysts the metal is apparently present as interstital cations rather than as part of a well-characterized metal oxide phase. This can be inferred from XRD studies and also from the comparatively poor catalytic properties of well-characterized alkali transition-metal oxides (4–6).

Water is necessary in the OCM feed mixture as more metal is added to an alkali/alkaline earth oxide mixture. As a minimum, the water is necessary to prevent rapid coking as in the case of methane steam reforming catalysts, where water/carbon ratios of 0.3–0.4 are absolutely necessary, and higher ratios are in fact used (7). Furthermore, water either in the feed (8, 9) or preadsorbed on the catalyst (10) promotes ethane formation. For example, Heinemann and co-workers (8, 9) tested a $Ca_3NiK_{0.1}$ oxide catalyst for OCM at temperatures below 600°C with 65 mol% water in the feed, and obtained >90% selectivities to C_{2+} hydrocarbons at low space velocities (methane WHSV ~0.016) and short times on stream. However, further work revealed that these high selectivities were relatively short-lived for this material and catalysts of similar composition (11). We made similar observations while testing a variety of K/Ca/Ni (Ca/Ni = 0.8–11) oxides at WHSV ~0.4 and water contents from 0–65 mol% (10, 12). Using a combination of kinetics, XRD, TGA, DSC, and Raman spectroscopy experiments, we found that these materials were multiphasic. One phase was a K/Ca oxide of high initial coupling activity, but it underwent rapid deactivation concurrent with its conversion to a mixed carbonate. At least one of the other phases, which contained Ni in valences of +2 and higher, also exhibited some coupling activity. We found maximum steady-state C_{2+} hydrocarbon selectivities in the range 30–40%, the values increasing with an increase in the partial pressure of water and decreasing with an increase in the C_1/O_2 ratio. However, we found an opposite trend in selectivity as a function of C_1/O_2 ratio for undoped K/Ca oxides (10), as did Heinemann and co-workers (11) for their materials at short times on stream. This supports our hypothesis that the very active and selective phase at short times on stream is an undoped K/Ca oxide.

Based on these results, we further suggested that the selective phase at long times on stream was a hydrous K/Ca/Ni oxide with some Ni in valence higher than +2, while NiO was a nonselective phase. Potassium ions promote the formation of higher valent Ni, especially in hydrous oxides (13–15). One reason for the higher steady-state selectivities observed in our work was probably the higher K/Ni ratios in some of our catalysts (e.g., K/Ni = 0.6), in contrast to the materials of Heinemann and co-workers (typically K/Ni = 0.1). If a K/Ca/Ni oxide of high K/Ni could be prepared containing no sepa-

---

[1] Present address: Dept. of Industrial Chemistry and Chemical Engineering, Univ. of Limerick, Plassey Park, Limerick, Ireland.

0021-9517/94 $6.00

rate NiO phase, it is conceivable that this K/Ca/Ni catalyst should be highly selective in the presence of water, even at long times on stream. Here we show that it is possible to prepare such a catalyst; its performance is highly sensitive to composition, as determined by microreactor experiments using a number of similar catalysts where Ba was substituted for Ca or Co for Ni.

METHODS

A number of ternary and quaternary oxides were prepared and studied, with cations K/Ca/Ni, K/Ca/Co, K/Ba/Ni, and K/Ca/Ba/Ni. A typical sample is given the shorthand designation *x*K/*y*(Ca or Ba)/*z*(Ni or Co), where *x*, *y*, and *z* are the atomic ratios used in the synthesis. Catalyst preparation involved two steps. In the first step, the mixed oxides CaO/NiO, CaO/CoO, and BaO/NiO were prepared by calcining the mixtures $Ca(NO_3)_2$ + $Ni(NO_3)_2$, $Ca(NO_3)_2$ + $Co(NO_3)_2$, and BaO + NiO, respectively, in static air; the calcination temperature was raised from ambient temperature to 1200°C over a period of 6 h, and then kept at 1200°C overnight. At this temperature the solubility of Ni in CaO is roughly 1.8 at% (16). A ternary Ca/Ba/Ni oxide was also prepared by calcining the CaO/NiO material with BaO, following the same temperature program. In the second step, K_2CO_3 was added to the calcined binary or ternary oxides by dry mixing and these samples were calcined in flowing O_2 (3–4 cm^3/min); the temperature was raised from ambient to 700°C at 5°C/min, and then maintained at 700°C for 18 h.

A Li-based catalyst (0.21Li/Mg/0.01Sn) catalyst was examined for comparison purposes. This was the same material as was used in a previous study of this relatively active and selective OCM catalyst (17).

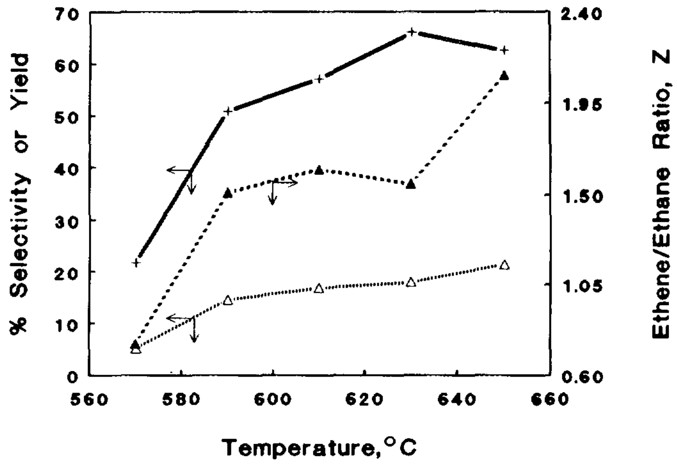

FIG. 1. Behavior of 0.1K/Ca/0.012Ni catalyst after 100 h time on stream. Feed composition: 36.6% CH_4, 14.5% O_2, 39.8% H_2O, balance He. Symbols: +, % C_{2+} selectivity; △, % C_{2+} yield; ▲, ethene/ethane product ratio.

Kinetics measurements were carried out in a conventional microreactor flow system with on line GC analysis. The reactor was quartz, 12.5 mm i.d. by 100 mm heated length, with thermocouples in three locations along the heated length; the temperature measured at the central thermocouple location, in the middle of the catalyst bed, is the one reported here. The entry and exit zones consisted of 8 mm quartz tubing held at slightly less than 400°C just above and below the bed and less than 200°C elsewhere. The C_1/O_2 ratio was 2.5, the methane WHSV 0.4 h^{-1}, and the pressure roughly 1 atm. Water was introduced by a syringe pump through a heated evaporator packed with glass beads. Except where otherwise noted, the feed composition consisted of 30 mol% CH_4, 12% O_2, 16% H_2O, with the balance He. Product analysis showed that the entire system had come to steady state after 3 h of operation.

TABLE 1

Catalyst Performance at Point of Maximum Yield

Sample composition	Temperature (°C)	% CH_4 conversion	% C_{2+} selectivity	Ethene/ethane ratio
0.1K/Ca/0.012Ni	630	37.0	54.2	1.52
0.1K/Ca/0.012Ni[a]	630	34.7	60.9	1.67
0.1K/Ca/0.012Ni[b]	630	37.3	55.1	1.60
0.1K/Ca/0.024Ni	650	35.1	53.3	1.50
0.024K/Ca/0.012Ni	630	34.0	55.5	1.49
0.1K/Ca/0.012Co	750	34.1	53.4	1.73
0.1K/Ca/0.012Ba/0.012Ni	710	35.8	54.9	1.66
0.1K/Ba/0.012Ni	780	29.6	34.3	1.25
0.21Li/Mg/0.01Sn	650	21.7	37.0	0.58

[a] After 24 h time on stream.

[b] 36 h final calcination.

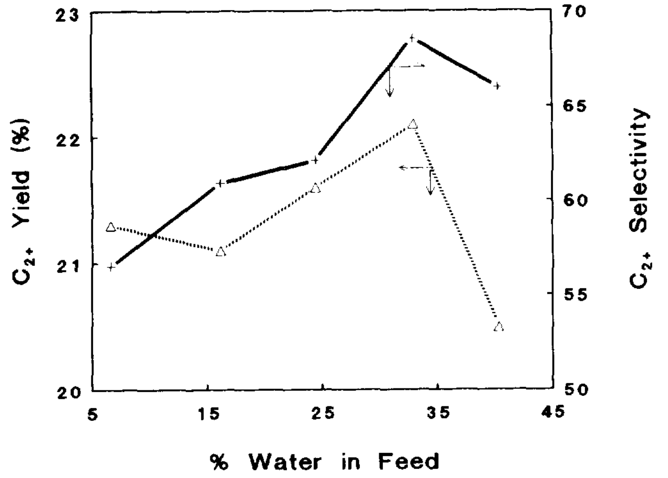

FIG. 2. Effect of varying water content in feed on 0.1K/Ca/0.012Ni catalyst at 630°C, 100% O_2 conversion, CH_4 partial pressure = 0.30 bar, C_1/O_2 feed ratio = 2.5. Symbols same as in Fig. 1.

Thermogravimetric analysis was performed using a Perkin-Elmer TGA 7. A 0.1K/Ca/0.012Ni catalyst was used in all TGA experiments. "Fresh" catalyst denotes a fully calcined material not yet used in a reaction experiment. Experiments were performed by passing mixtures of 95% air + 5% CO_2, water-saturated 95% air + 5% CO_2, water-saturated air, or undiluted air over the samples. In those cases where a water saturator was used, it was maintained at ambient temperature so that the water content did not exceed 3%. The temperature of the TGA furnace was increased from 30 to 630°C at 200°C/min and then maintained at 630°C for 2 h; this was sufficiently long to bring the samples to constant weight.

XRD measurements at ambient conditions were made on a Scintag PAD-V powder diffractometer using Cu-$K\alpha$ radiation. The JCPDS powder diffraction file was used to identify the crystalline phases present. The surface area measurements were made with N_2 using an automated BET apparatus (Omicron Omnisorb-360). SEM micrographs were taken using an Electroscan Model E-3. Samples were mounted with epoxy and gold coated.

RESULTS AND DISCUSSION

Figure 1 shows typical results for product distribution, C_{2+} selectivity, and C_{2+} yield as a function of temperature for a 0.1K/Ca/0.012Ni catalyst with roughly 40% water in the feed at a C_1/O_2 ratio of 2.5. In this work, the selectivity (S_i) is defined as

$$S_i = \frac{(\text{mol } i \text{ product})\,(\text{mol carbon/mol } i)}{\sum_j (\text{mols } j \text{ product})\,(\text{mol carbon/mol } j)} \qquad [1]$$

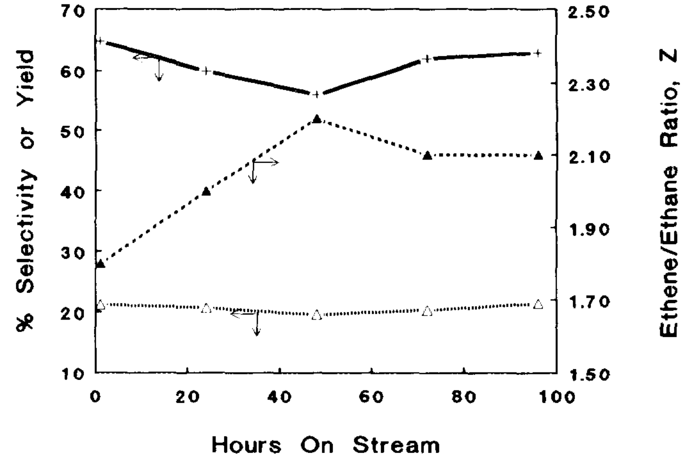

FIG. 3. Behavior of 0.1K/Ca/0.012Ni catalyst with time onstream at 650°C. Same feed composition and symbols as in Fig. 1.

and the methane conversion (X_{C_1}) was computed as

$$X_{C_1} = \frac{\sum_j (\text{mol } j \text{ product})\,(\text{mol carbon/mol } j)}{(\text{mol } C_1 \text{ out}) + \sum_j (\text{mol } j \text{ product})\,(\text{mol carbon/ mol } j)}. \qquad [2]$$

The yield is defined as the product of methane conversion and selectivity. The carbon balances were 100 ± 3%. The products included C_{2+} hydrocarbons, CO, and CO_2. The C_2/C_3 ratio was at least 15, and only traces of C_{4+} hydrocarbons were observed.

The results in Fig. 1 on C_{2+} selectivity and yield were obtained after the catalyst had already been onstream for 100 h at 630°C. The results show that a Ni-containing catalyst can be active for OCM even below 600°C, and that the coupling activity may be long-lived. The selectivity to C_{2+} appears to be maximum around 630°C. This last result is consistent with our previous results on catalysts of higher Ni-content (10, 12).

The results obtained for the various catalysts when

TABLE 2

Bulk Phases Identified by XRD

Catalyst	Major phases	Minor phases
0.1K/Ca/0.012Ni, fresh	CaO	None
0.1K/Ca/0.012Ni, used	$CaCO_3$, $Ca(OH)_2$	CaO
0.05K/Ca, fresh	CaO, $Ca(OH)_2$	$CaCO_3$
0.05K/Ca, used	$Ca(OH)_2$	$CaCO_3$

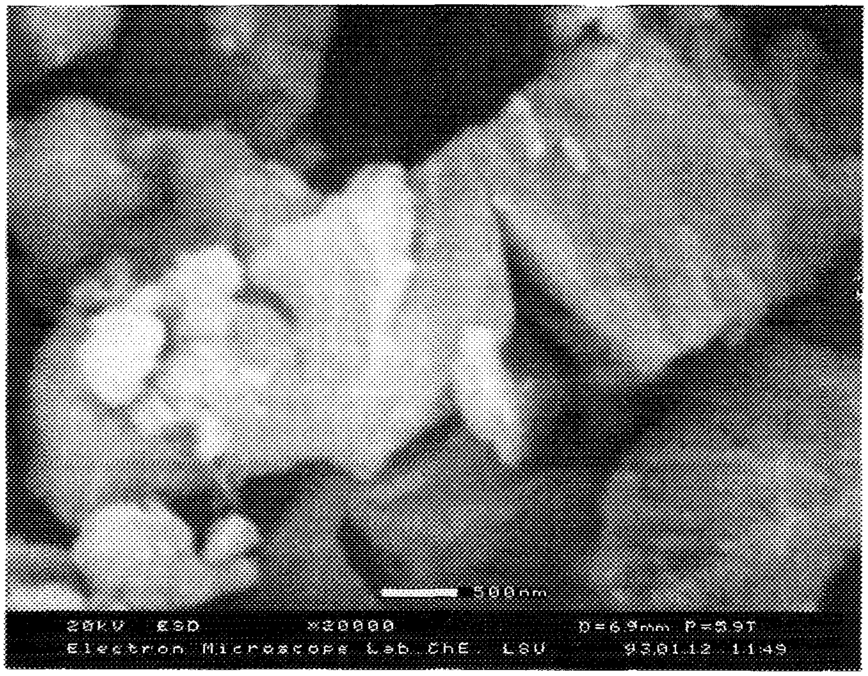

FIG. 4. SEM micrographs (×20,000) of fresh (a) and used (b, c) 0.1K/Ca/0.012Ni.

using the standard feed composition are compared in Table 1. The data given were those obtained at the point of highest yield, which in all cases occurred at a temperature associated with 100% O_2 conversion. The catalyst 0.1K/Ca/0.012Ni was the most active one tested, also giving the highest C_{2+} yield: 20–21% at 630°C. With a conventional OCM catalyst, temperatures higher than 700°C are necessary to give such high yields (2).

The first two entries in the table are for the same 0.1K/Ca/0.012Ni sample; this sample showed only slight changes in catalytic performance in 24 h time on stream, and constant yield. The third entry is for a different sample of the same starting composition, but calcined for 36 h rather than 18 h. Again, the yield was unchanged, suggesting that the normal calcination procedure was adequate. In the fourth and fifth entries of the table (0.1K/Ca/0.024Ni and 0.024K/Ca/0.012Ni, respectively), it is shown that perturbing the potassium or nickel contents did not affect the behavior of this catalyst. However, note that the K/Ni ratios were never less than 2/1.

Catalytic behavior was sensitive to the particular transition metal or alkaline earth used; the replacement of Ni by Co (sixth entry in the table) or the addition of even small amounts of Ba (seventh entry) resulted in far less active, but in other respects similar, catalysts. The complete replacement of Ca by Ba in the 0.1K/Ba/0.012Ni sample (eighth entry) decreased the selectivity as well as the conversion, reflecting the influence of gas-phase combustion reactions at the temperatures required to use this catalyst. Extensive blank experiments with $C_1/C_2/O_2/H_2O$ feeds have shown that at <700°C, taking into account C_{2+} hydrocarbon combustion, the C_{2+} selectivity could be as high as 80% for the case of no combustion reactions occurring on the catalyst (10). However, at >700°C the rates of gas-phase C_{2+} combustion in these blank experiments increased substantially, and therefore all data taken above this temperature may have been affected by combustion of the C_{2+} products. These results on C_{2+} combustion are in rough agreement with previous work on rare-earth (18) and Li/MgO (19) catalysts.

A Li/Mg/Sn catalyst is the most active Li-based material which still exhibits high C_{2+} selectivity (3, 20). The significantly poorer performance of 0.21Li/Mg/0.01Sn (last entry in Table 1) under the present conditions confirms the specificity of the Ni-containing catlaysts at temperatures <700°C. But it should be noted that at roughly 700°C Li/Sn/MgO is also capable of yields as high as 20%, without water addition to the feed (20).

The effects of the amount of water in the feed mixture on catalyst behavior were investigated. These experiments were performed at constant partial pressures of CH_4 and O_2; helium was used to keep the total gas flow rate constant. The results shown in Fig. 2 demonstrate an increasing C_{2+} selectivity as the partial pressure of water was increased, up to about 35% water. These results are in qualitative agreement with our previous results (10, 12) for catalysts with much lower Ca/Ni and K/Ni ratios; however, the 0.1K/Ca/0.012Ni catalyst used here requires far less water to attain maximum selectivity. It was noted that the present material was stable in the presence of 16% water, but it was transformed over a period of about 12 h in the presence of 6.7% water, the lowest feed

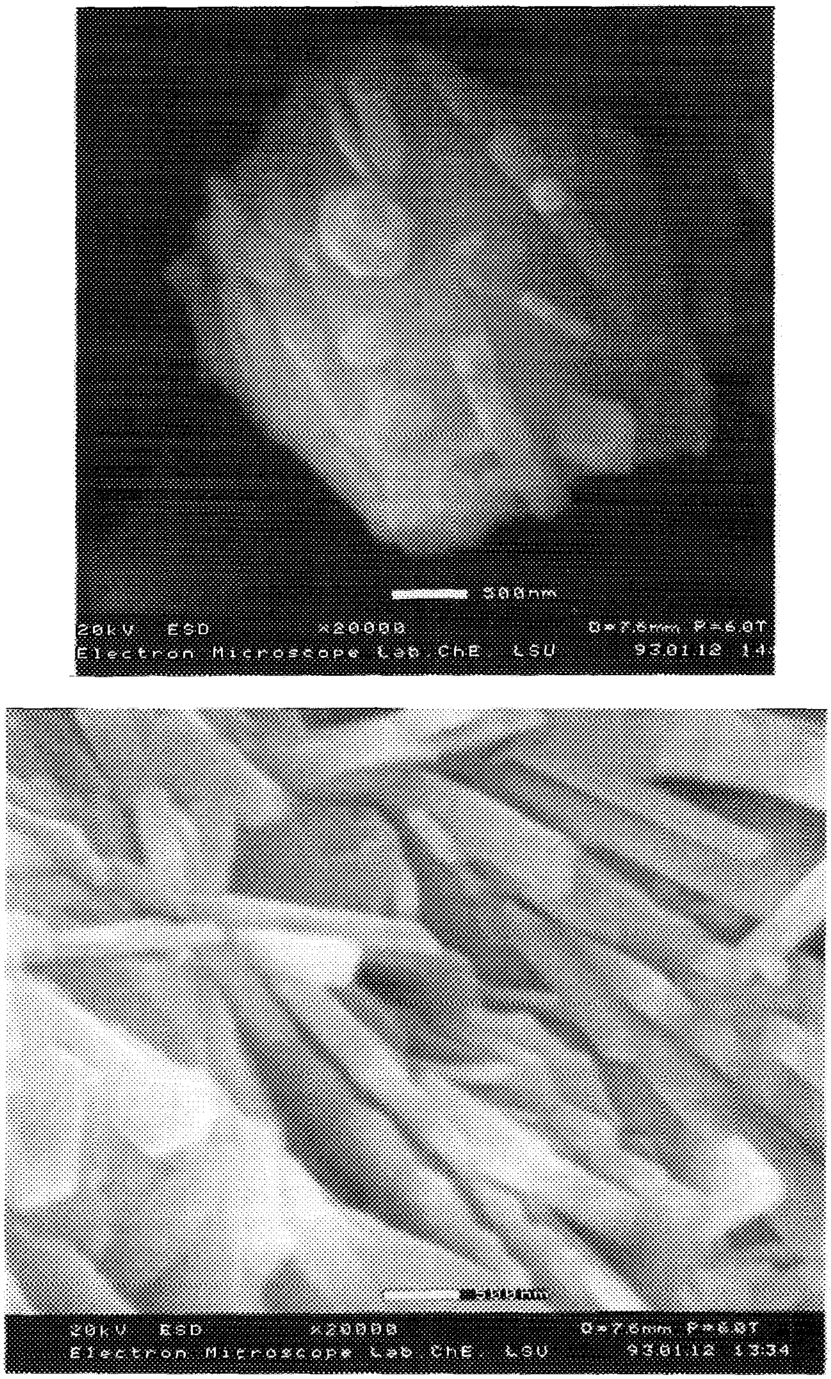

FIG. 4—*Continued*

content examined. Evidence for the transformation was extensive carbon deposition as indicated by carbon balances <90%, a complete loss of C_{2+} selectivity, and dramatic increases in the amounts of CO and H_2 produced. Such reforming behavior was previously observed under similar conditions for catalysts of higher Ni-content (12).

The 0.1K/Ca/0.012Ni catalyst was tested for 100 h using a feed of composition $CH_4/O_2/H_2O/He$ = 36.6%/14.5%/39.8%/9.1%; the C_1/O_2 ratio here was also 2.5. The C_{2+} hydrocarbon selectivity and yield showed no significant changes over this period (Fig. 3); however, the alkene/alkane ratio of the products increased somewhat during the experiment. These data are in marked contrast to recent results of Heinemann and co-workers (11), who tested a 0.1K/3Ca/Ni catalyst at 600°C and methane WHSV = 0.016 h^{-1} and observed steadily decreasing hydrocarbon selectivities from 90+% to less than 30% over a period of 15 h. It is clear that 0.1K/Ca/0.012Ni and similar catalysts differ substantially not only from the materials studied by Heinemann and co-workers but also from the several low Ca/Ni ratio materials which we have previously examined (10, 12).

The crystalline phases of the 0.1K/Ca/0.012Ni catalyst were determined by XRD; the results are listed in Table 2. Upon use, phase transformations from oxides to carbonates and hydroxides were observed, and the XRD signal intensity was greatly reduced; these changes are typical of K/Ca mixed oxides, as also indicated in Table 2. No crystalline NiO or higher oxides of Ni were detected. These phase transformations were accompanied by an increase in BET surface area of ~7 to ~17 m^2/g, a result typical of hydrous oxide formation. SEM measurements showed the development of a smoother shape and more regular habit as shown by the micrographs pictured in Fig. 4. The predominant particle shapes changed from rough chunks (a) to smoother-shaped but still irregular particles (b) and rod-like particles (c). Even the large particle in (b) contains rod-like matter on its surface. The differences in the catalytic behavior of the present catalyst from pure K/Ca oxide can therefore be attributed to a Ni-containing K/Ca mixed hydrous oxide or hydroxycarbonate, at least on the surface.

The surface and bulk chemistry of the 0.1K/Ca/0.012Ni catalysts were further explored through a series of TGA experiments at 630°C using carrier gases of differing composition. The philosophy behind these was as follows. Saturating the carrier gas with water should result in insignificant weight loss from a sample at 630°C if the hydrated form was stable. For a material of high carbonate/oxide ratio, treatment with a CO_2-containing carrier gas should also result in an insignificant weight loss if the carbonate was stable at 630°C. However, treatment with air only at 630°C should result in a large weight loss on the basis of previous work with wet and dry calcite (21–23) and mixed K/Ca oxides (10). Moreover, the fresh catalyst was oxidic and so TGA experiments with CO_2- and/or H_2O-containing carrier gases should provide information on the development of the working catalyst at short times on stream.

The results of the TGA experiments are summarized in Table 3. The slight loss of weight for the fresh catalyst in dry air was probably due to loss of residual water picked up in sample handling. The fresh catalyst lost the same percentage of weight in both wet and dry air; this indicates that there was minimal hydroxide formation at 630°C when CO_2 was absent. In the presence of CO_2, however, a substantial amount of water was incorporated in the fresh catalyst, as may be inferred upon comparing the first two table entries. This inference was confirmed by injecting gas samples from a subsequent desorption experiment (630°C, with air as carrier gas) into a GC; these samples contained both H_2O and CO_2. The water was desorbed rapidly at 630°C, the CO_2 slowly. This behavior is characteristic of hydroxycarbonates with molecular water inclusion between layers (24). Finally, an adsorption experiment using fresh catalyst at 630°C was performed using the microreactor apparatus and an air stream containing 5% CO_2 and 2% H_2O. The results are shown in Fig. 5, where it is seen that CO_2 is rapidly adsorbed, after which H_2O adsorption begins. About twice as much total CO_2 as H_2O was adsorbed during this experiment. All of these results are consistent with the XRD results showing both hydroxide and carbonate formation in used materials, and also suggest hydroxycarbonate formation at the surface. It can certainly be concluded that at 630°C, a carbonate-rich oxide is far more reactive toward water.

TABLE 3

TGA Experimental Results

0.1K/Ca/0.012Ni catalysts	Carrier gas	Weight change
Fresh	Air/CO_2[a]	+11%
Fresh	$Air/CO_2/H_2O$[b]	+23%
Fresh	Air	−2.3%
Fresh	Air/H_2O[b]	−2.3%
Used	Air/CO_2[a]	+1.6%
Used	$Air/CO_2/H_2O$[b]	+1.3%
Used	Air	−31%
Used	Air/H_2O[b]	−29%

[a] Gas mixture consisted of 95% air and 5% CO_2.

[b] The water saturator was at ambient temperature.

When either the air/CO_2 or the air/CO_2/H_2O mixtures were passed over the used catalyst, the weight increased slightly. However, the used catalyst lost roughly 30% of its weight when contacted with either the air or the air/H_2O mixtures. In other words, in the absence of gaseous CO_2 the catalyst could not retain water at 630°C, even in the presence of a water-saturated carrier gas stream.

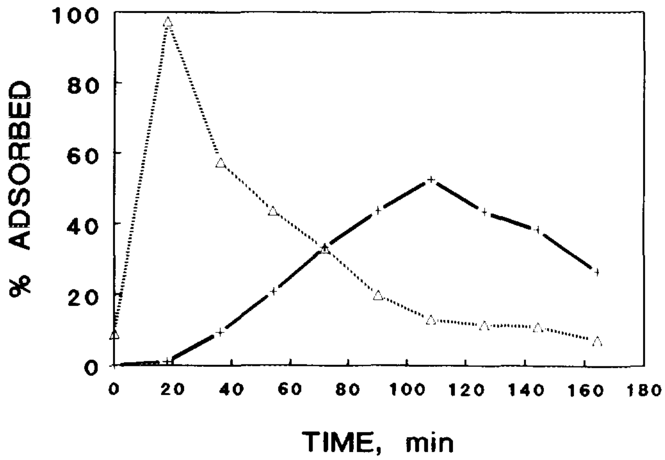

FIG. 5. Adsorption at 630°C (percentage adsorbed of the entering composition) onto fresh 0.1K/Ca/0.012Ni from a stream of air containing 5 vol% CO_2 and 2% H_2O. Total flow rate = 50 cm^3/min. Symbols: +, H_2O; △, CO_2.

Again, the presence of a hydroxycarbonate phase at the surface could account for this behavior.

All previous results for these catalysts, and the results in Fig. 2, suggest that the active phase of these catalysts must be a Ni-containing hydrated phase. From the TGA results, we conclude that water does not prevent carbonate formation in these materials, but rather carbonate formation enhances formation of an active Ni-containing hydroxycarbonate at the surface. Further work is required to determine if the hydroxycarbonate is of a layer-type structure similar to hydrotalcite minerals such as takovite, $Ni_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$, a steam reforming catalyst precursor (24, 25). Takovite consists of brucite-type layers with octahedral sites containing both divalent and trivalent cations, separated by disordered interlayers of water molecules and carbonate anions. A similar material containing Ca^{2+}, Ni^{2+}, and Ni^{3+} could be envisioned, but the role of K^+ would still be unclear. However, our previous Raman spectroscopy experiments showing the presence of Ni^{3+} only in the more selective K/Ca/Ni oxides lends plausibility to the speculation.

Finally, these new results help explain our previous findings (12) that calcination of K/Ca/Ni oxide catalysts with a mixture of O_2 and CO_2 resulted in a superior catalyst at short times on stream when compared to calcination with O_2 alone. They are also consistent with our initial microreactor experiments with 0.1K/Ca/0.012Ni, where we observed that the activity for C_{2+} formation developed more slowly and erratically when KNO_3 rather than K_2CO_3 was used as the potassium source in the preparation.

ACKNOWLEDGMENTS

KD gratefully acknowledges receipt of a fellowship from the Netherlands–America (Fulbright) Commission for Educational Exchange. This work was supported by the EC Joule Project and by the Louisiana Educational Quality Support Fund under Contract RD-B-5.

REFERENCES

1. Lee, J. S., and Oyama, S. T., *Catal. Rev.-Sci. Eng.* **30,** 249 (1988).
2. Amenomiya, Y., Birss, V. I., Goledzinowski, M., Galuszka, J., and Sanger, A. R., *Catal. Rev.-Sci. Eng.* **32,** 163 (1990).
3. Korf, S. J., Roos, J. A., Veltman, L. J., van Ommen, J. G., and Ross, J. R. H., *Appl. Catal.* **56,** 119 (1989).
4. Ungar, R. K., Zhang, X., and Lambert, R. M., *Appl. Catal.* **42,** L1 (1988).
5. Miro, E. E., Santamaria, J. M., and Wolf, E. E., *J. Catal.* **124,** 451 (1990).
6. Moggridge, G. D., Rayment, T., and Lambert, R. M., *J. Catal.* **134,** 242 (1992).
7. Ridler, D. E., and Twigg, M. V., *in* "Catalyst Handbook" (M. V. Twigg, Ed.), p. 225. Wolfe, 1989.
8. Pereira, P., Lee, S. H., Somorjai, G. A., and Heinemann, H., *Catal. Lett.* **6,** 255 (1990).
9. Rasko, J., Pereira, P., Somorjai, G. A., and Heinemann, H., *Catal. Lett.* **9,** 395 (1991).
10. Dooley, K. M., and Ross, J. R. H., *Appl. Catal. A* **90,** 159 (1992).
11. Rasko, J., Somorjai, G. A., and Heinemann, H., *Appl. Catal. A* **84,** 57 (1992).
12. Dooley, K. M., and Ross, J. R. H., *Prepr. Am. Chem. Soc. Div. Pet. Chem.* **37,** 93 (1992).
13. Bode, H., Demhelt, K., and Witte, J., *Z. Anorg. Allg. Chem.* **366,** 1 (1969).
14. Levason, W., and McAuliffe, C. A., *Coord. Chem. Rev.* **12,** 151 (1974).
15. Bro, P., and Cogley, D., *J. Electrochem. Soc.* **113,** 521 (1966).
16. Smith, D. E., Tien, T. Y., and van Vlack, L. H., *J. Am. Ceram. Soc.* **52,** 460 (1969).
17. McNamara, D., Korf, S. J., Seshan, K., van Ommen, J. G., and Ross, J. R. H., *Can. J. Chem. Eng.* **69,** 883 (1991).
18. Eckstrom, A., Lapszewicz, J. A., and Campbell, I., *Appl. Catal.* **56,** L29 (1989).
19. Nelson, P. F., and Cant, N. W., *J. Phys. Chem.* **94,** 3756 (1990).
20. Korf, S. J., Roos, J. A., Vreeman, J. W. Derksen, J. W., van Ommen, J. G., and Ross, J. R. H., *Catal. Today* **6,** 417 (1990).
21. Juntgen, H., and van Heek, K. H., *in* "Proceedings of the 3rd International Conference on Thermal Analysis" (H. R. Oswald and E. Dubler, Eds.), p. 423. Birkhauser-Verlag, Basel, 1972.
22. Wist, A. O., *in* "Proceedings of the 2nd International Conference on Thermal Analysis" (R. F. Schwenker and P. D. Garn, Eds.), p. 1095. Academic Press, New York, 1969.
23. Haga, T., Ozaki, J.-I., Suzuki, K., and Nishiyama, Y., *J. Catal.* **134,** 107 (1992).
24. Kruissink, E. C., van Reijen, L. L., and Ross, J. R. H., *J. Chem. Soc. Faraday Trans. 1* **77,** 649 (1981).
25. Bish, D. L., and Brindley, G. W., *Am. Miner.* **62,** 458 (1977).