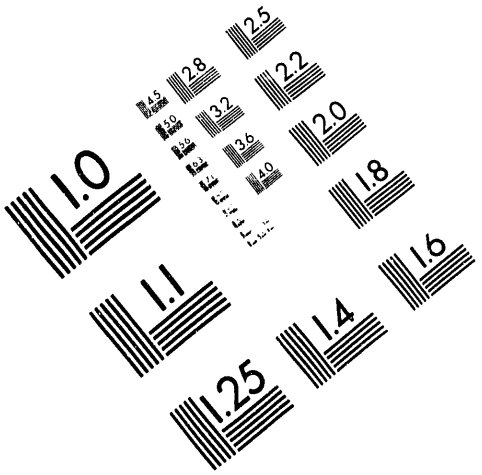

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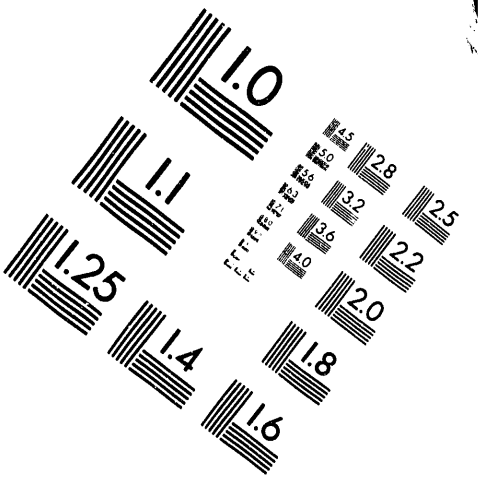

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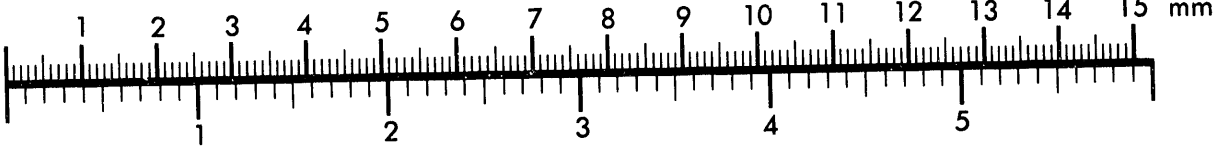

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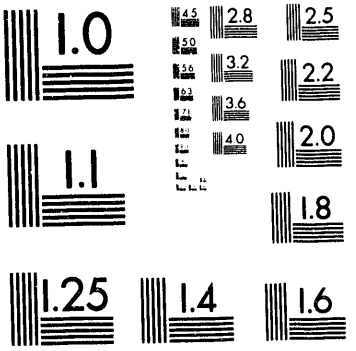

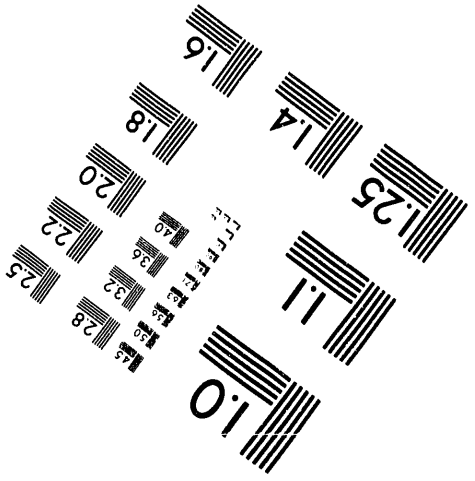

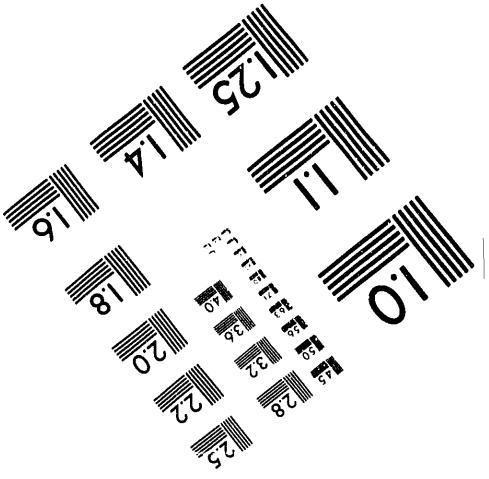

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QUARTERLY REPORT

January 1, 1993 - March 31, 1993

FUNDAMENTAL STUDIES OF THE MECHANISM OF CATALYTIC REACTIONS WITH CATALYSTS EFFECTIVE IN THE GASIFICATION OF CARBON SOLIDS AND THE OXIDATIVE COUPLING OF METHANE

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TABLE OF CONTENTS

		Page
I.	Task Description for FY 1993	3
II.	Highlights	3
	a) Catalytic Steam Gasification of Coals, Chars and Cokes	3
	b) Oxidative Methane Coupling and Partial Oxidation of Methane	4
	c) Synthesis and Characterization of Catalysts	4
III.	Progress of Studies	5
	a) Catalytic Steam Gasification of Coals, Chars and Cokes	5
	b) Oxidative Methane Coupling and Partial Oxidation of Methane	7
	c) Synthesis and Characterization of Catalysts	13
IV.	Appendix	
	PAPER: *A Temperature Programmed Isotope Exchange Study of Ca-Ni-K and Mi-Li Oxide Catalysts Used for Oxidative Coupling of Methane*	

I. Task Description for FY 1993

Task 1: Work on catalytic steam gasification with chars and coals will be extended from atmospheric to elevated pressures using the newly built pressure unit. The novel finding that coking of petroleum in the presence of small amounts of caustic greatly improves the gasification rates and characteristics of the coke will be extended to chars. The chars will be prepared by charing coals in the presence of minor amounts of caustic and the resulting chars will be steam gasified in the absence and presence of catalysts.

Task 2: In the oxidative coupling of methane over ternary catalysts, a large number of factors remain poorly understood and must be investigated to improve results and move them into the commercially interesting area. Emphasis will be placed on low temperature coupling and on the oxidative production of syngas from methane at low temperature. Work on the CRADA between LBL and Orion ACT will continue and will be expanded to include methane coupling to higher hydrocarbons in a membrane reactor. Isotope studies will be undertaken to better understand the nature of the active catalyst sites.

Task 3: Experimental work will continue on the synthesis of the mixed catalyst, and they will be characterized by a number of techniques, including elemental analyses, x-ray diffraction, and surface area determination. Scanning electron microscopy will be used to monitor the variations of the surface morphology as a function of the preparative route. X-ray photoelectron, Auger, Raman and infrared spectroscopy will be used to study chemical and bonding aspects of the catalysts.

II. Highlights

a) Catalytic Steam Gasification of Coals and Cokes

- Three component catalysts were tested for the gasification of Ill #6 char. They were Ni-Ca-K oxide and Co-Ca-K oxide.

- The three component catalysts were more active then the Ca-K oxide and Co-Ca-K oxide was more active than Ni-Ca-K oxide.

- Chars prepared in the presence of NaOH were more easily gasified than the base char even if the chars were washed to remove all residual free NaOH.

- Gasification rates increased with increasing amounts of caustic used in charring the coal.

- A combination of charring in the presence of NaOH and gasifying in the presence of a three component oxide gave the best gasification rate.

b) *Oxidative Methane Coupling*

- A membrane reactor has been built and temperature tested.

- Work in preparing an alumina supported yttrium oxide membrane is nearing completion.

- A paper on determination of active sites of coupling catalysts by isotope exchange has been written and submitted for journal publication.

- Cobalt-magnesium oxide catalysts are superior to cobalt-silica and cobalt-HSM-5 for the production of syngas from methane and oxygen at high inlet temperature (~ 700°C) and high space velocity. Conversion was ~ 60% and selectivity to $CO + 2H_2$ ~ 90%.

- The reaction temperature for the partial oxidation is hard to measure. An infra-red radiation thermometer gives it as ~ 1600°C.

- At this high temperature the reaction may be largely thermal through the different product distribution for three catalysts tested indicates that catalysis plays a role other than reaction initiation.

c) *Synthesis and Characterization of Catalysts*

- Magnetic properties studies of calcium-nickel-potassium oxide catalysts have continued.

- X-ray diffraction has been used to study the chemical state of cobalt in cobalt-magnesium oxide catalysts.

III. Progress of Studies

a) Catalytic Steam Gasification of Coals, Chars and Cokes

The previous report summarized results on steam gasification of chars prepared from Illinois #6 coal in the presence of sodium hydroxide. It has been shown that chars prepared in the presence of sodium hydroxide give a higher hydrogen production rate than chars prepared in the absence of sodium hydroxide. In the present report, results obtained in the presence of catalysts are presented. The catalysts studied include K-Ca, K-Ca-Ni, and K-Ca-Co. To reveal possible roles of residual sodium hydroxide in chars prepared in the presence of sodium hydroxide, gasification experiments were conducted with chars after being washed in hot water. The latter treatment was to remove potential residual sodium hydroxide in chars.

Char samples were prepared from Illinois #6 coal using the same procedure as previously used. The charring temperature was 640°C.

To remove residual sodium hydroxide, the chars were washed three times in hot water (under refluxing and constant stirring, 1 g of char in 200 g of distilled water). The washed chars were dried at 110°C before being used for gasification.

Samples containing catalyst were prepared by impregnating the char with an aqueous solution of the corresponding nitrates. The content of each metal component was kept the same: 0.01 g of metal per gram of char. The mixtures were dried at 200°C for 10 h before being used for gasification.

An amount of 0.5 g of sample (char and catalyst) was used for the steam gasification test. The sample was treated in nitrogen (4 $cm^3 \bullet min^{-1}$) from room temperature to 640°C at a heating rate of 20°C/min before steam was introduced. Steam feeding rate was 68 $cm^3 \bullet min^{-1}$ (STP) and nitrogen flow was 2 $cm^3 \bullet min^{-1}$. Nitrogen was used as an internal standard for GC quantification. A cold trap (at 0°C) and a $CaSO_4$ trap mounted in between the out-let of reactor and the sampling valve were used to prevent water from entering into the GC column.

Figure 1 presents data of carbon conversion of Illinois #6 coal chars prepared with different NaOH loadings. Washing of the chars after preparation resulted in lower gasification rates than using the unwashed char. However, the gasification rate of the washed char was still appreciably higher than that of char prepared in the absence of caustic.

Results obtained using different catalysts are given in Table 1. The presence of catalyst significantly enhanced the gasification of char. Catalysts containing transition metals are more effective than binary K-Ca catalyst. It seems that Co is more active than Ni.

Table 1 Effect of Catalyst on Illinois Char (20% NaOH)

Catalyst	Carbon Conversion % [a]
–	10.2
K-Ca	19.2
K-Ca-Ni	21.5
K-Ca-Co	27.5

a, conversion at time on stream of 300 min.

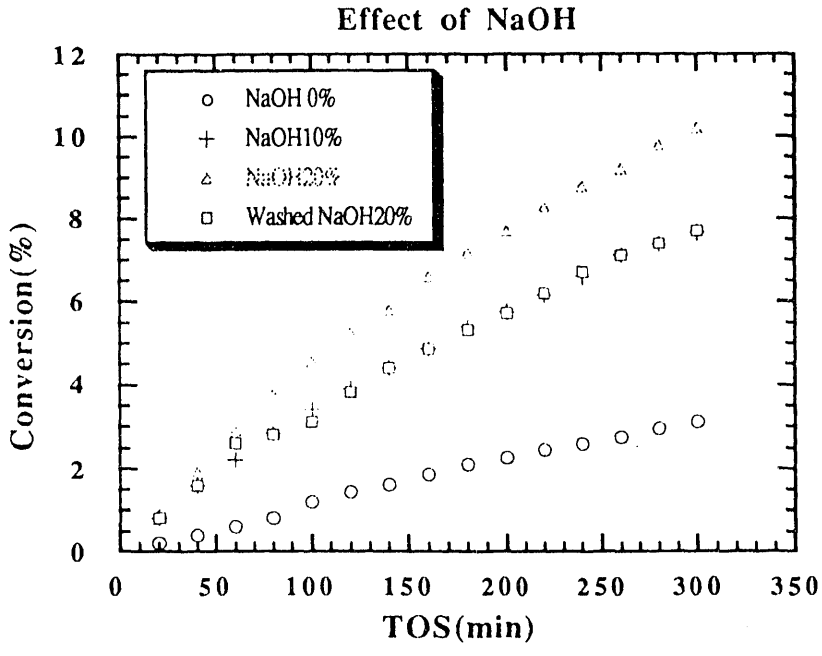
Table 2 compares the effectiveness of K-Ca-Ni catalyst on chars prepared with different NaOH concentrations. It appears that the catalyst is more effective for chars prepared with higher NaOH concentration.

Table 2 Effect of Catalyst K-Ca-Ni on Chars Prepared at Different NaOH Concentration

	Carbon Conversion % [b]	
Char sample/NaOH% [a]	No Catalyst	with K-Ca-Ni
0	3.2	8.5
20	10.2	21.5

a, amount of NaOH used in charring;
b, conversion at 640°C at TOS of 300 min.

Fig. 1



b) Oxidative Methane Coupling and Partial Oxidation of Methane

Results from an isotope study to determine active surface sites on oxide catalysts for the oxidative coupling of methane were mentioned in the previous quarterly report (LBL-33241). These have now been summarized in a paper which has ben submitted to the JOURNAL OF CATALYSIS and which is appended to this report as Appendix a.

Membrane Reactor

A membrane reactor for the reaction described in the last quarterly report (LB L-33241) has been constructed. A major problem has ben to achieve a seal between the reactor interior and surroundings in the area of the membrane. Using an alumina support for a membrane, a seal has now been established at temperatures up to 200°C.

Much work has been done learning to prepare a uniform membrane on a porous alumina disc. Materials used and a procedure are outlined below.

Raw Materials: Strontium Isopropoxide, $Sr(OC_3H_7)_2$
Calcium Methoxyethoxide, $Ca(OC_2H_4OCH_3)_2$
Zirconium Isopropoxide, $Zr(OC_3H_7)_4$

Cerium Isopropoxide, $Ce(OC_3H_7)_4$
Yttrium Isopropoxide, $Y(OC_3H_7)_3$
Indium Methoxyethoxide, $In(OC_2H_4OCH_3)_3$
Isopropanol (anhydrous), $(CH_3)_2CHOH$
Methoxyethanol, $CH_3OC_2H_4OH$
Diethanolamine, $HN(C_2H_4OH)$
Anotec® porous supports

Equipment:

In dry box:
- Volumetric flasks
- Balance
- Syringes

Spin coater
Furnace

Procedure: (Based on discussions with the ceramics group at LBL.)

1. In dry box, dissolve/dilute metal alkoxides to 0.4 M in the solvent. (Methoxyethanol is preferred over IPA). A small amount of DEA may be necessary to dissolve the yttrium.

2. Mix the solutions in the appropriate ratios for the following stoichiometries
   $SrCe_{0.95}Y_{0.05}$
   $SrCe_{0.9}Y_{0.1}$
   $SrZr_{0.95}Y_{0.05}$
   $SrZr_{0.9}Y_{0.1}$
   $CaZr_{0.9}In_{0.1}$
   Cap the flask and remove from dry box.

3. Affix Anotec disc to the spin coater. Place a few drops of the alkoxide solution in the center of the disc. Slowly accelerate to 2500 RPM and spin for a few minutes.

4. Remove disc from spin coater and place in furnace. Ramp at 0.3°C/min to 400°C and hold for 2 h.

5. Densification (can be done either in the furnace or after mounting in reactor). Heat to 600°C (or reaction temperature) and hold for 2 h.

Problems occurred in the dissolution of the yttrium isopropoxide. These problems were avoided by purchasing a solution of predissolved yttrium methoxyethoxide in methoxyethanol (Methyl Cellosolve®). Gel membranes have been prepared by spin coating a $SrZr_{0.9}Y_{0.1}$ mixed alkoxide solution (0.4 M total metal ions) in Methyl Cellosolve® on the Anotec® porous alumina discs. Visual inspection reveals that these membranes did not have uniform thickness over the

entire area. Adjusting the coating procedure will correct this deficiency. Once uniform thickness membranes are obtained, they will be fired and tested for reactivity.

Methane Partial Oxidation

Efforts have been made to achieve partial oxidation of methane to syngas over supported Group VIII transition-metal catalysts. Partial oxidation of methane to CO and H_2 over a Co/MgO catalyst was achieved at temperatures 500-830°C. At temperatures ≥ 700°C, conversion of methane was greater than 60%, and selectivities to hydrogen and CO were over 90%. The H_2/CO ratio of the product was very close to 2, a stoichiometric value for partial oxidation of methane to CO and hydrogen. Blank experiments were conducted to determine potential contribution from homogeneous reactions. It is found that the contribution of homogeneous reaction at temperatures < 810°C is negligible. The homogeneous reaction led to a low H_2/CO ratio.

The effect of space velocity on conversion of methane and selectivity to hydrogen and CO was studied. It seems high space velocity is essential to partial oxidation. Low space velocity results in formation of carbon dioxide and water.

High reaction temperature (≥700°C) is needed to achieve high selectivities (> 90%) to hydrogen and carbon monoxide though reactions at lower temperatures also led to formation of hydrogen and carbon monoxide.

Results from two blank experiments are given in Table 3 and Table 4. Table 5 and Table 6 present the results obtained at two different space velocities over a Co/MgO catalyst. The activation energies estimated for homogeneous and catalyzed reactions are given in Table 7. Table 8 and Table 9 give results obtained at various gas space velocity.

Table 3:
Results of Reaction of Methane with Oxygen in Empty Quartz Reactor [a,b]
1/18-19/93

Temp./°C	Conversion CH_4 mol.%	Selectivity CO mol.%	Selectivity CO_2 mol.%	H_2/CO molar ratio
702	0.2	~100	~0	– [c]
810	1.2	90	10	1.6
925	16.1	86	14	0.7

a, Quartz reactor, thermocouple contained in a quartz jacket;
b, CH_4: 125 $cm^3 \bullet min^{-1}$; O_2: 62.5 $cm^3 \bullet min^{-1}$;
c, data unavailable;

Table 4:
Results of Reaction of Methane with Oxygen in Empty Quartz Reactor [a,b]
1/18-19/93

Temp./°C	Conversion CH_4 mol.%	Selectivity CO mol.%	Selectivity CO_2 mol.%	H_2/CO molar ratio
700	0.8	52	48	– [c]
802	4	80	20	1.1
913	34	87	13	0.7

a, Quartz reactor, thermocouple contained in a quartz jacket;
b, CH_4: 31.2 $cm^3 \bullet min^{-1}$; O_2: 15.6 $cm^3 \bullet min^{-1}$;
c, data unavailable;

Table 5 :
Results of reaction of methane with oxygen over CoO/MgO [a]
1/20/93

Temp [b] /°C	Conversion mol.% CH_4	O_2	Selectivity mol.% H_2	CO	CO_2	H_2/CO mol. ratio	carbon balance %
821	73	93	96	96	4	2.00	109
720	62	94	88	89	11	1.98	109
614	50	94	80	81	19	1.99	108
540	46	94	77	75	25	1.99	106

a, CoO/MgO (Co/Mg=3/1) : 0.026 g; reduced in 20% H_2 (100 $cm^3 \bullet min^{-1}$;) at 500°C; CH_4: 125 $cm^3 \bullet min^{-1}$; O_2: 62.5 $cm^3 \bullet min^{-1}$;
b, data obtained acccording to the temperature sequence as listed in the table;

Table 6

Results of reaction of methane with oxygen over CoO/MgO [a]

1/21/93

Temp /°C	[b] Conversion mol.% CH_4	O_2	Selectivity mol.% H_2	CO	CO_2	H_2/CO mol. ratio	carbon balance %
733	56	94	89	82	18	2.16	109
710	58	94	92	83	17	2.21	108
690	47	94	83	74	26	2.24	106
650	34	94	72	61	39	2.36	107
510	19	63	55	47	53	2.35	111
433	14	50	43	38	62	2.23	114

a, CoO/MgO (Co/Mg=3/1) : 0.130 g; reduced in 20% H_2 (100 $cm^3 \bullet min^{-1}$;) at 500°C; CH_4: 125 $cm^3 \bullet min^{-1}$; O_2: 62.5 $cm^3 \bullet min^{-1}$;

b, data obtained acccording to the temperature sequence as listed in the table;

Table 7

Activation Energy of Catalyzed and Homogeneous Reaction of Methane with Oxygen

Catalyst	Flow Rate CH_4/O_2 ml/min	Temperature Range/°C	Ea $kJ \bullet mol^{-1}$
– [a]	125/62.5	700~925	221
– [a]	31.2/15.6	700~913	168
Co/MgO [b]	125/62.5	540~820	12.5
Co/MgO [b]	31.2/15.6	433~733	28

a,no catalyst;

b, Co/MgO: 0.026 g;

Table 8
Effect of Gas Space Velocity on the Reaction of Methane with Oxygen over Co/MgO at 700°C

GHSV	Conversion of		Selectivity to		
$cm^3 \bullet g^{-1} \bullet h^{-1}$	CH_4 mol.%	H_2 mol.%	CO mol.%	CO_2 mol.%	H_2/CO
0.4×10^5	22	0	0	100	–
1.6×10^5	55	88	82	18	2.16
6.4×10^5	62	88	89	11	1.98

Table 9
Effect of Gas Space Velocity on the Reaction of Methane with Oxygen over Co/MgO at 620°C

GHSV	Conversion of		Selectivity to		
$cm^3 \bullet g^{-1} \bullet h^{-1}$	CH_4 mol.%	H_2 mol.%	CO mol.%	CO_2 mol.%	H_2/CO
0.4×10^5	22	0	0	100	–
1.6×10^5	34	72	61	39	2.36
6.4×10^5	50	80	81	19	1.99

It was found that the thermocouple used had catalytic activity of its own and increased total combustion. With increasing space velocity, there was a shift from total oxidation to partial oxidation. Subsequently, it was discovered that the thermocouple , even if sheeted and located on top of a very small amount of catalyst, did not give the real reaction temperature. Using an infrared radiation thermometer, it was shown that the actual temperature could be as much as 1000°C

higher than that of the thermocouple. To use the infrared radiation thermometer, the furnace had to be opened, but the exothermicity of the reaction was such that the catalyst continued to glow and the reaction proceeded. At temperatures of 1200-1600°C it can be assumed that the reaction is a free radical rather than a catalytic one. At this high temperature thermodynamics predicts partial oxidation to synthesis gas rather than total combustion.

Experiments were carried out with three catalysts: Co-MgO (Co:Mg = 0.3:1); Co-HZSM-5 (Co:Mg = 0.3:1); Co-SiO_2 (Co:Mg = 0.24:1). The Co-MgO catalyst was the most active and produced approximately the stoichiometric 2:1 ratio of H_2/Co. The HZSM-5 produced little hydrogen and much CO, indicating that combustion of hydrogen occurred. The Co-SiO_2 catalyst gave relatively low conversion. Very high space velocities are requited to produce syn-gas rather than CO_2.

c) Synthesis and Characterization of Catalysts

Several samples of calcium-nickel-potassium oxide catalysts have been prepared under a variety of conditions and studied by SQUID magnetrometry for differences in magnetochemical states.

The most highly magnetic catalyst samples are essentially completely magnetized in fields of only a few tenths of a tesla (a few thousand gauss). In contrast the other samples show a magnetic moment which is roughly proportional to the applied magnetic field. For the highly magnetic samples, a second look at the x-ray diffraction data reveals a small peak at the location expected for elemental nickel. This peak is absent for the other samples. An estimate of the amount of elemental nickel may be obtained from the saturation magnetization; one gets 2.0% (percent of Ni atoms present as elemental Ni) for one sample and 3.7% for the other. These are estimates only, as the saturation magnetic moment of very small (nanometer-sized) particles is known to depend somewhat on particle size.

From the above information and from the x-ray data (which always shows strong NiO diffraction peaks), one expects the nickel to be present primarily in the form of NiO. Magnetic measurements directly on NiO show the expected behavior: nearly temperature independent susceptibility, and the magnetic moment is proportional to the field; the magnetic moment is about 0.47 emu per gm of NiO at 280 K and 4 tesla. The less magnetic samples approximate this behavior, but often have a smaller moment than 0.47 emu per gm of NiO. The least magnetic sample is less than 0.02; other values of this parameter are 0.06, 0.15, and 0.33. This lack of magnetism is not readily explained. Most nickel compounds are more magnetic than NiO. However, there are some reports in the literature of similar behavior. The explanations refer to a "dead" layer on the surfaces of small particles, presumably NiO particles are "passivated" by some sort of chemisorbed layer.

Finally, the samples are rather variable as to the environment of the calcium ions. All samples contain $Ca(OH)_2$, but some contain $CaCO_3$ as the majority phase and CaO as well.

Mixed cobalt-magnesium oxide catalysts have been studied by x-ray diffraction in order to determine the chemical state of the cobalt. Two phases were detected in the catalysts, with the cobalt and magnesium phases being found in different proportions to one another in the different catalysts. The only phase of magnesium found was MgO, while the only phase found for cobalt was Co_3O_4. Thus, the chemical oxidation state of the cobalt is mixed, consisting of both cobalt (2^+) and cobalt (3^+) species.

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