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Fundamental Studies of the Mechanism of Catalytic Reactions with Catalysts Effective in the Gasification of Carbon Solids and the Oxidative Coupling of Methane

Quarterly Report

January 1–March 31, 1992

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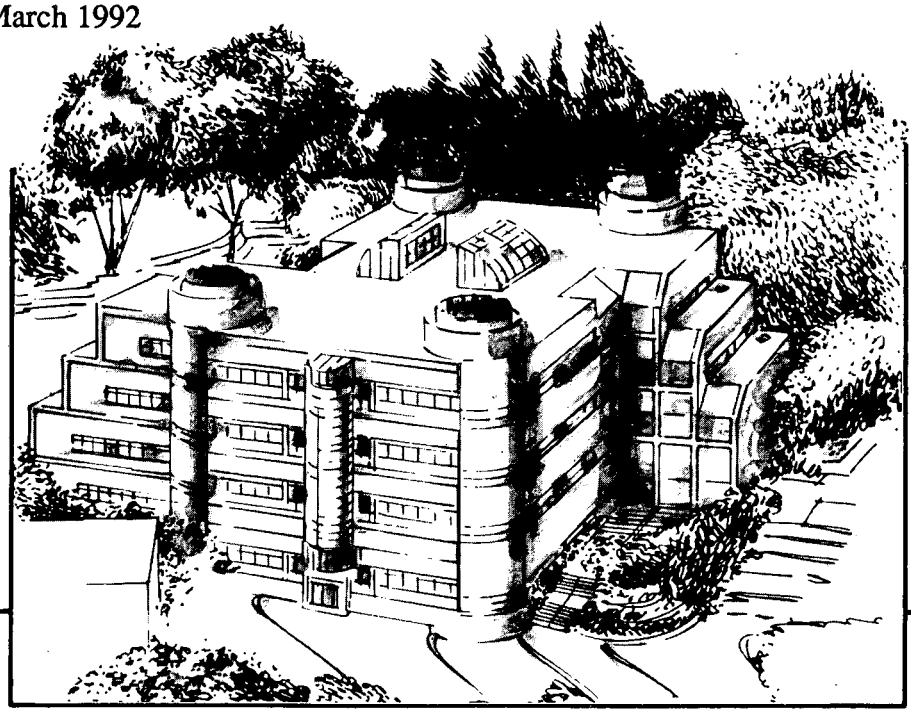

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QUARTERLY REPORT

January 1, 1992 - March 31, 1992

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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I. Task Description for FY 1992

Work will continue on the oxidative coupling reaction of methane over ternary oxide catalysts to produce C_2, C_3 and C_4 hydrocarbons and particularly olefins with high selectivity. The work which has shown that close to 100% selectivity can be obtained has received wide attention and has resulted in collaborative efforts with industry (CRADA) towards the development of a commercial process. An immediate purpose of additional work is to increase the conversion without diminishing the extremely high selectivity of the reaction and also to permit operation at higher space velocity to reduce equipment size. The mechanism of this reaction is not understood and much additional work is needed to explain the role of carbon formation and of water as intermediates in the reaction and to investigate whether carbon oxides are intermediates. It has been found that oxides other than calcium-nickel-potassium oxides can be useful catalysts for this reaction in the presence of steam and at relatively low temperatures and long contact times. Better definition of the class of binary metal oxides is required and better catalyst characterization is needed to ensure reproducibility of catalyst preparation and operational results. Pretreatment of the catalyst should be shortened and higher space velocities must be obtained. Close collaboration with Orion ACT is required to advance the project toward the pilot plant stage. In the area of coal and char catalytic steam gasification, the large volume of data obtained at atmospheric pressure will be extended to operations at higher pressures.

II. Introduction

At the request of the Morgantown Energy Technology Center, two previously separate projects (a) *Fundamental Studies of Gasification* and (b) *Synthesis and Characterization of Catalysts for Gasification of Carbonaceous Materials* were combined for funding purposes. This is the first quarterly report of the combined project. The principle investigators for part (a) remain Heinz Heinemann and Gabor A. Somorjai and for part (b) Dale L. Perry.

The potentially important discovery in the field of oxidative methane coupling, which was hinted at in the December 31, 1991, report is still under active investigation and through it had been hoped that it could be disclosed in the current report, the Patent Department has requested that disclosure be further delayed to

permit sufficient patent coverage. This will unfortunately shorten the content of the present report, since a good part of the present quarter's effort has been dedicated to the study of the newly discovered phenomenon.

Active collaboration with Orion ACT under the CRADA was started during the report quarter. Scientists from Orion visited LBL for two weeks to acquaint themselves with background and procedures and are now setting up experimental equipment in their own laboratories. The first phase of a joint research program was agreed upon and is under way.

III. Highlights

a) *Catalytic Steam Gasification of Coals and Cokes*

- Assembly of the new pressure unit is almost complete and it is about ready for testing.

- Addition of small amounts of spent caustic (e.g. from sulfur removal of gas and oil streams) to the petroleum coking process results in much higher non-catalytic gasification rates of the cokes. In some cases these rates are better than those obtained in the catalytic gasification of coke obtained in the absence of caustic. However, in all cases impregnation of the coke with K-Ca oxides leads to further rate improvement, even in the case of cokes obtained with added caustic.

b) *Oxidative Methane Coupling*

- The cooperative work with Orion ACT under the CRADA has been started.

- A much improved method for synthesizing active and selective Ca-Ni-K oxide catalysts has been developed.

- A number of rare earth oxide based catalysts have been prepared which have been described in the literature as active for methane oxidative coupling at conditions different from the standard conditions of the present project. These have been tested and while several exhibited activity, none have approached the high selectivity (90+%) to higher hydrocarbons obtained wit h Ca-Ni-K oxide.

- Additional work was performed on a novel discovery which cannot be described in this report because it is the subject of as yet unfiled patent applications.

c) Synthesis and Characterization of Catalysts

- Magneto-chemical techniques are being used to monitor chemical and electronic alterations of nickel in calcium-nickel-potassium oxide catalysts.

IV. Progress of Studies

a) Catalytic Steam Gasification of Coals and Cokes

Figure 1 shows a conversion vs. time plot for the steam gasification of a Maya coke prepared in different ways. Normal coking of heavy Maya resid resulted in a coke that could not be gasified at 600°C. When this coke was impregnated with 1% Ca-K-O_x catalyst by our standard procedure, gasification proceeded at a relatively slow rate (Figure 1 ❑). Coking the resid in the presence of 1% caustic resulted in a coke that gasified reasonable well (■) even in the absence of Ca-K-O_x catalyst. This particular coke was then impregnated with Ca-K-O_x catalyst and exhibited excellent gasification rates (✻). In another experiment the resid was coked in the presence of 5% water (no caustic) and the coke was then impregnated with K-Ca-O_x. This material gasified very well (+) and better than the catalyst containing normal coke (❑), but not as well as the coke prepared with caustic and then impregnated with catalyst (*).

In order to determine whether the above finding was generic, two other resids (Staffjord Bottoms and Torrance Honda) were coked both in the absence and presence of caustic and the resulting cokes were gasified after impregnation with K–Ca-O_x catalyst. Figure 2 demonstrates that essentially the same behavior was obtained as with Maya coke, although complete gasification was not achieved. Figure 3 presents the results for a Torrance Honda coke and again shows the superiority of the coking procedure in the presence of caustic.

On the basis of these results, it is concluded that coking in the presence of some caustic leads to easier to gasify cokes in all cases. A patent application has been filed. An obvious extension of this work will be the exploration of the gasification of chars which have been prepared from coals in the presence of some caustic.

b) Oxidative Methane Coupling

It has recently been found that a good Ca-Ni-K oxide catalyst can be prepared by carefully grinding together the right proportions of calcium and nickel oxides and either mixing or impregnating them with KNO_3. The catalyst is not calcined but only dried and heated to 400°C, then introduced into the unit for activation in O_2 at 680°C, followed by operation at 600°C. Three separate preparations were tested and gave identical results. This appears to be a much simpler catalyst preparation method than the one described earlier.

Table 1
Reaction of Methane with Oxygen Over $Ca_3NiK_{0.1}$ Catalyst

Catalyst	CH_4 cm^3/min	O_2 cm^3/min	$H_2O(g)$ cm^3/min	Reaction Temp. °C	Methane Conv.%	Oxygen Conv.%	Sel. to HC%	Sel. to CO_x%	CO/CO_2 ratio
	1.5	0.5	3.2	600	6	45	91	9	0
A	1.5	0.5	0	600	32	80	0	100	2.5
	1.5	0.5	3.2	600	7	50	90	10	0
B	1.5	0.5	3.2	600	8	56	90	10	0
C	1.5	0.5	3.2	600	9	70	91	9	0

Catalysts A and B: (physical mixture of CaO, NiO and KNO_3): 1.0g
Catalyst C: (impregnation of CaO and NiO with KNO_3 solution): 1.0g

Table 1 presents results obtained with the three preparations (A and B are dry mixed; C is impregnated with KNO_3) and also again demonstrates the need for the presence of steam; in the absence of which steam reforming prevails (CO/CO_2 ratio = 2.5 rather than 0).

A number of new catalyst preparations were made and tested to determine whether catalysts described in the literature for oxidative methane coupling at higher temperatures and high space velocities in the absence of steam would give high selectivities under our standard conditions. The catalysts tested so far were:

gallium oxide
samarium oxide
samarium-potassium oxide
dysprosium oxide

Table 2
Reaction of Methane with Oxygen Over Ga_2O_3 Catalyst [a]

CH_4 cm^3/min	O_2 cm^3/min	$H_2O(g)$ cm^3/min	Reaction Temp. °C	Methane Conv.%	Oxygen Conv.%	Sel. to HC%	Sel. to CO_x%	CO/CO_2 ratio
1.5	0.5	3.2	600	28	65	3	97	0.04
1.5	0.5	3.2	550	26	57	1	99	0.15
1.5	0.5	0	550	48	50	0	100	0.15

[a] catalyst: 1.0g

Results are shown in Tables 2, 3, 4 and 5. The gallium oxide catalyst (Table 2) was essentially inactive for the production of higher hydrocarbons. The samarium oxide catalyst (Table 3) showed relatively high conversion at low hydrocarbon selectivity both in the absence and presence of steam. To obtain higher selectivities, it was necessary to increase both temperature (to 700°) and space velocity (by a factor of 20). Even then at 32% conversion the selectivity to C_{2+} was only 25% for a C_{2+} yield of 8% with high CO_2 selectivity. This compares to an 8 — 10% yield at zero CO_2 selectivity for Ca-Ni-K oxide.

Table 3
Reaction of Methane with Oxygen Over Sm_2O_3 Catalyst [a]

CH_4 cm^3/min	O_2 cm^3/min	$H_2O(g)$ cm^3/min	Reaction Temp. °C	Methane Conv.%	Oxygen Conv.%	Sel. to HC%	Sel. to CO_x%	CO/CO_2 ratio
1.5	0.5	3.2	600	23	70	12	88	0.02
1.5	0.5	0	600	24	72	13	87	0.03
1.5	0.5	0	700	23	75	12	88	0.02
30	10	0	550	29	97	9	91	
30	10	0	600	30	97	18	82	
30	10	0	700	32	98	25	75	

[a] catalyst: 1.0g

Table 4

Reaction of Methane with Oxygen Over K/Sm_2O_3 Catalyst [a]

CH_4 cm^3/min	O_2 cm^3/min	$H_2O(g)$ cm^3/min	Reaction Temp. °C	Methane Conv.%	Oxygen Conv.%	Sel. to HC%	Sel. to CO_x%	CO/CO_2 ratio
1.5	0.5	3.2	600	28	65	8	92	0.02
1.5	0.5	3.2	550	26	65	12	88	0.02
1.5	0.5	0	550	19	50	1	99	0

[a] catalyst: 1.0g; atomic ratio of K/Sm: 0.1/3

The addition of 33% potassium oxide to samarium oxide (Table 4) resulted in lower C_{2+} selectivities than shown for Sm_2O_3 alone. However, in this case the presence of steam was necessary to obtain any oxidative coupling at all.

Table 5

Reaction of Methane with Oxygen Over Dy_2O_3 Catalyst [a]

CH_4 cm^3/min	O_2 cm^3/min	$H_2O(g)$ cm^3/min	Reaction Temp. °C	Methane Conv.%	Oxygen Conv.%	Sel. to HC%	Sel. to CO_x%	CO/CO_2 ratio
1.5	0.5	3.2	600	25	80	12	88	0.03
1.5	0.5	0	600	25	76	12	88	0.05
30	10	3.2	600	24	98	22	78	0.13
30	10	0	600	27	98	24	76	0.13
90	30	0	600	28	98	35	65	0.24
90	30	0	550	27	95	27	83	0.27
90	30	0	500	28	95	32	68	0.25
90	30	0	450	25	86	31	69	0.35
90	30	0	400	24	80	32	68	0.40
90	30	0	350	0	0	0	0	—

[a] catalyst: 1.0g

The dysprosium oxide catalyst (Table 5) showed relatively high conversions at high space velocity and low temperature, but again the best C_{2+} yield was about 10% with a lot of CO_2 production. There was no apparent advantage to the use of steam with this catalyst.

Table 6
Dependence of Product Distribution on Contact Time of Reaction of Methane with Oxygen Over Dy_2O_3 Catalyst at 600°C

Contact Time (s)	Methane Conv %	Sel. to HC %	Sel. to CO_x %	CO/CO_2 Ratio	Olefin/Alkane
5.13	25	12	88	0.05	0.06
0.26	27	24	76	0.13	0.58
0.08	28	35	65	0.24	0.98

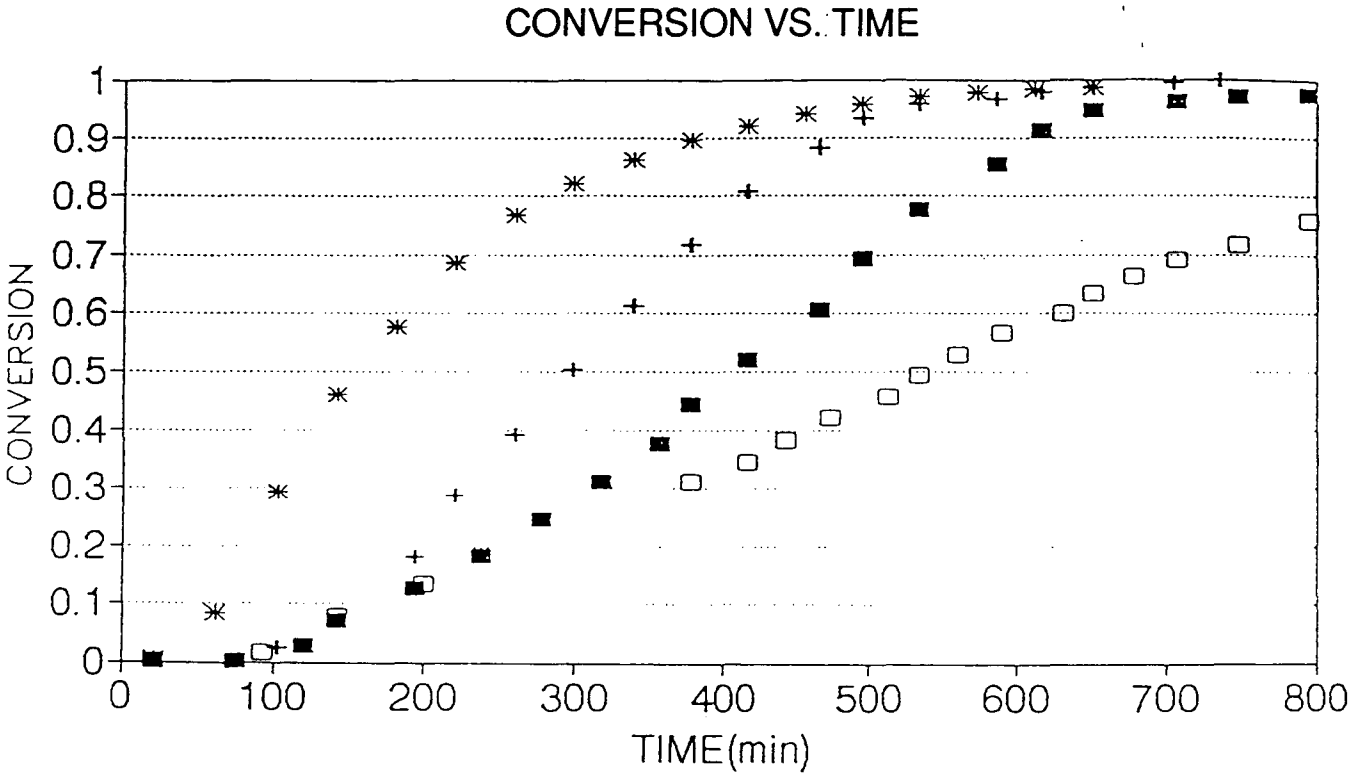
Table 6 clearly shows the importance of short contact times for operation over dysprosium oxide at 600°C. The high olefin/paraffin ratio obtained at short contact time is remarkable.

c) Synthesis and Characterization of Catalysts

During the last quarter, work has begun on using magnetochemical techniques to monitor chemical and electronic alterations of nickel in calcium-nickel-potassium oxide catalysts as a function of their synthesis routes and sample histories. The starting nickel materials used in the syntheses of the catalysts are always nickel(II) compounds, most commonly the nickel(II) oxide or hydrated nickel(II) nitrate. The formal electronic configuration of the nickel(II) is [Ar] $3d^8$; however, any alteration from the original starting material might effect changes in the magnetic moment of the nickel(II) species. Oxidation to nickel(III) from nickel(II), for example, would require a one electron loss process involving the central nickel sphere, resulting in an electronic state of [Ar] $3d^7$. This would markedly affect the effective magnetic moment of the nickel species, even if the nickel(III) exhibited a spin-only magnetic moment.

This magnetochemical approach might possibly be a more sensitive probe regarding the chemical state of the nickel ion in the catalyst, much more sensitive than vibrational techniques such as Raman or Fourier transform infrared spectroscopy. These approaches are more reflective of the structural aspects of the nickel species of interest, as is, of course, x-ray diffraction.

GASIFICATION OF MAYA COKE



■ Spent NaOH coke; no catalyst

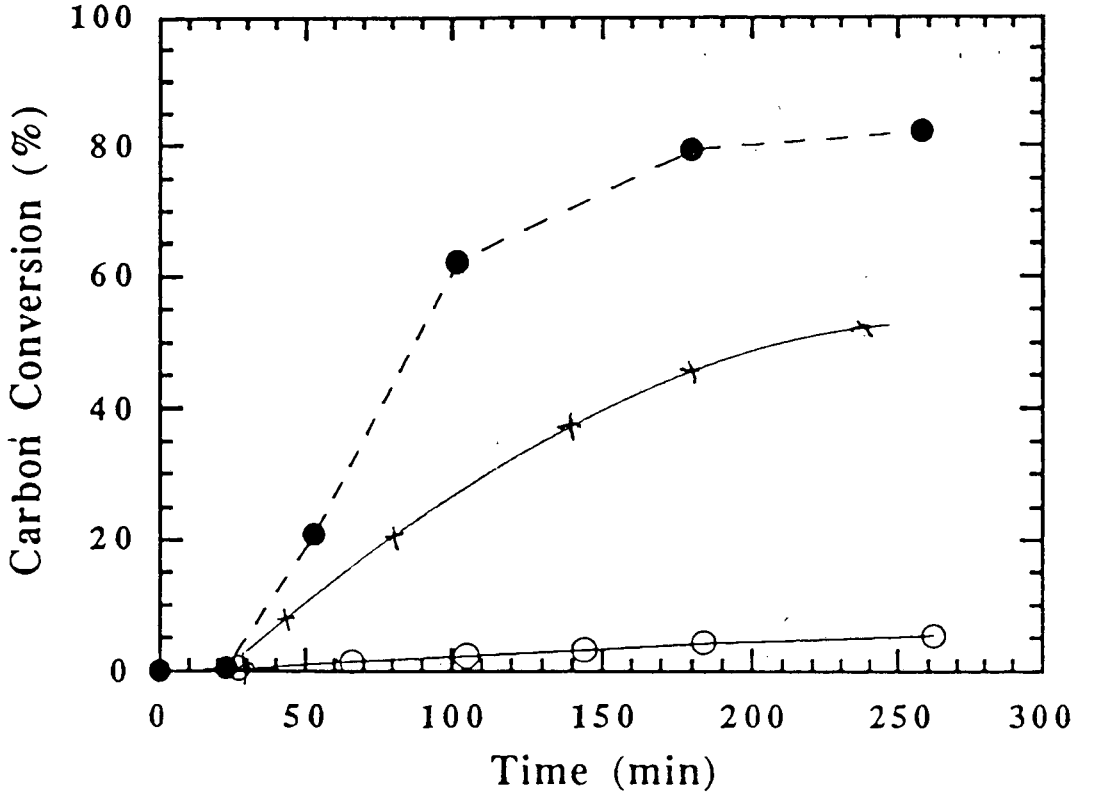
\+ Coke with water and catalyst

✳ Coke with NaOH and catalyst

❑ Maya coke with catalyst

Figure 1

STATFJORD BOTTOMS STEAM GASIFICATION



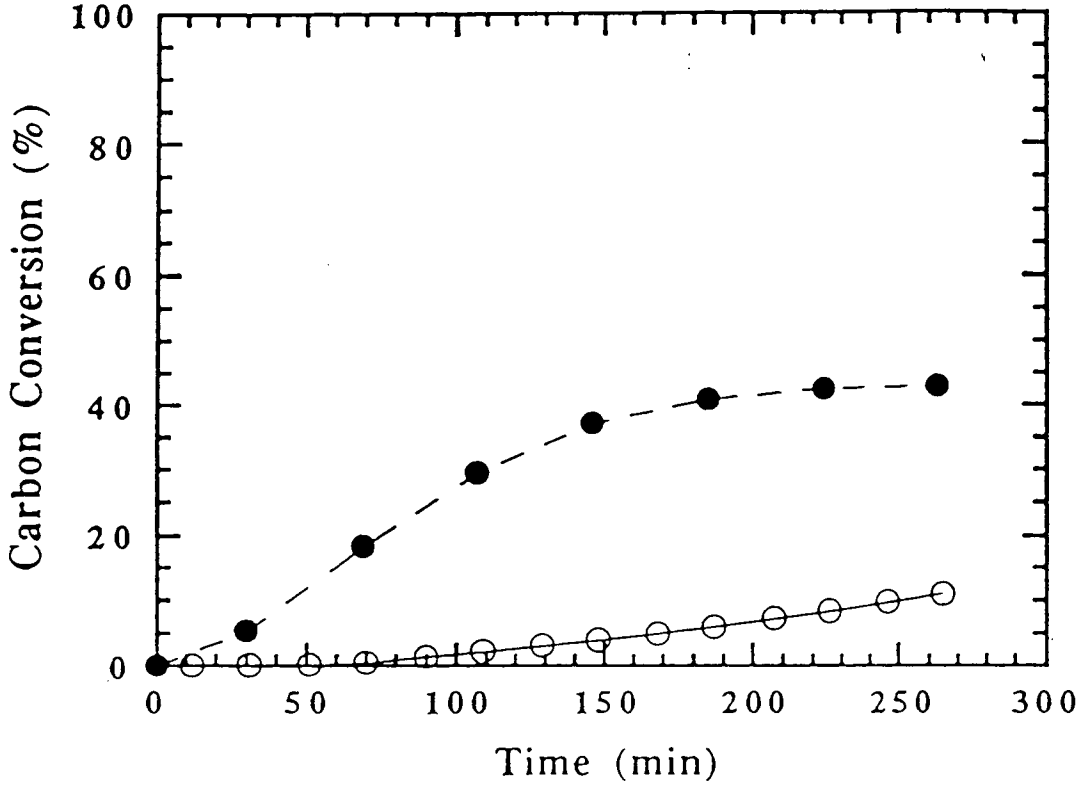
○ Normal coke plus Ca-K-O_x catalyst

● Coke prepared in presence of 1% caustic, then impregnated with Ca-K-O_x

\+ Coke prepared in presence of 1% caustic, not impregnated with Ca-K-O_x

Figure 2

TORRANCE HONDO
STEAM GASIFICATION



○ Normal coke plus Ca-K-O_x catalyst

● Coke prepared in presence of 1% caustic, then impregnated with Ca-K-O_x

Figure 3

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