

탄소원소들의 수증기 가스화반응에서 금속질산염들이 분해반
응기구와 이들의 촉매효과에 대한 연구

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**A study on the decomposition mechanism of metal nitrates
and the catalysis effects of these metals on steam gasification of
carbonaceous materials**

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Introductions

Useful chemicals (e.g. resources of C_1 chemistry, hydrocarbon gases, tar chemicals) can be obtained from coals, petroleum resids during pyrolysis at temperatures above 350°C.

Catalytic gasification of carbon solids is an old technology with patents dating back to at least 1954. But it is rising our interest for the gasification lately because it is important technology for which the carbon solid disposal is thereby reduced with the recovery of useable products.

The steam gasification reactivity is strongly dependent on the structure of the solid, which is very sensitive to the carbon source and the pyrolysis conditions

To gasify char coal, lignite or subbituminous coal, these materials were mixed with the hydroxides, carbonates or nitrates of alkali or alkaline earth metals. Considerably higher gasification rates or lower gasification temperatures were realized by these additives. Recent investigations have confirmed that some alkali metal compounds promote the char-steam, char-hydrogen, and char-carbondioxide reactions.

Knowledge of the initial state of the catalyst just prior to steam gasification of carbon samples is important information that permit development of better catalysts for this process.

With this in mind the decomposition of metal salts, in our case exclusively nitrates, used for depositing metal oxides on the carbon surface should be better understood so that information can be obtained on the ratio of oxygen and metals at the beginning of the gasification reaction

A TPR(Thermally Programmed Reaction) study of nitrate decomposition during the activation step prior to initiation of the steam gasification of graphite was performed.

In general catalysts, particularly alkali metal and binary oxides have been added to the carbon to improve its reactivity.

In this study, catalysts were prepared with potassium and calcium oxides and added transition metals for resistance of sulfur poisoning as a ternary catalyst.

Experiments

For TPR study of nitrate decomposition, a 1°C/min temperature program was used with 1cc/min He flowing continuously into the reactor to carry the products through a short line to the analytical system(G.C.). The frequency of analysis in most cases was between every 18 to 20 min, thus, at least one analysis for the products of decomposition was obtained for every 20°C. A small expansion volume(6ml) was provided between the reactor and the analytical system in order to ensure an integral analysis of the gases contained in the lines at every moment.

Secondly catalytic activity and selectivity have been tested to find better catalysts.

As a reactants chars were obtained by heating Argonne Premium coals(Illinois #6 high volatile bituminous) at 10°C/min to 640°C and holding for 2hr. And caustic-modified char were obtained by charring of the same coal in the presence of NaOH solution.

A K-Ca catalyst when used was added to the solid by impregnation with an equimolar solution of KNO₃ and Ca(NO₃)₂ · 4H₂O, followed by drying at 200°C for 10hr. In nearly all cases, catalyst loading was K:Ca:Ni:C=1:1:1:100 assuming 80wt% C in the solid.

Conventional flow reactor is used for the steam gasification apparatus Carbon solid (0.5g) is loaded into the reactor, which is then sealed, inlet nitrogen flow is kept at 2.0ml/min using a thermal mass flow controller, and the reactor is heated to the operating temperature (640°C) in a split tube furnace.

Water is pumped from a reservoir by a valveless piston pump at 0.055ml/min into a length of heated tubing(250°C) to generate steam which then flows with the nitrogen over the heated char, producing gaseous products. Unreacted water is removed from the product steam in a condenser(0°C) prior to gas analysis by GC/TCD.

Results and discussion

NO, CO₂, and O₂ are in that order the main products for all the decompositions studied. Only trace amounts of NO_x and hydrocarbons were found.

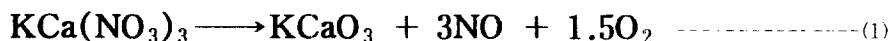
Their evolution as a function of temperature for a representative K-Ca/graphite system is shown in Fig. 1.

The integration of the total area for each compound and their ratios will give semi-quantitative information about the stoichiometry of the oxides left on the carbon surface .

In Table 1, the ratios are reported for each of the systems base on the compound having the smallest area.

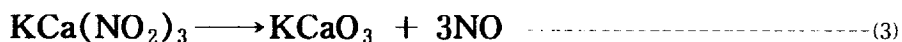
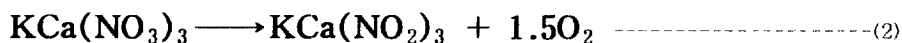
Based on these results, the oxidation state of the catalyst in each system can be arrived at by proposing chemical equations between nitrates and carbon that fit the proportions obtained for the released gases.

The system K-Ca/graphite shows a following reaction(1) with a small release of oxygen.



No evidence of oxygen spillover was found, and apparently the decomposition of the K-Ca system in the absence of carbon results in the same oxide as that obtained from the K-Ca/graphite system by the reaction(1).

According to the TPR pattern, this reaction is occurring in two steps.



Based on these results it appears that for a bimetallic system a higher valent oxide, relative to that obtained with the individual metals is present at the beginning of gasification.

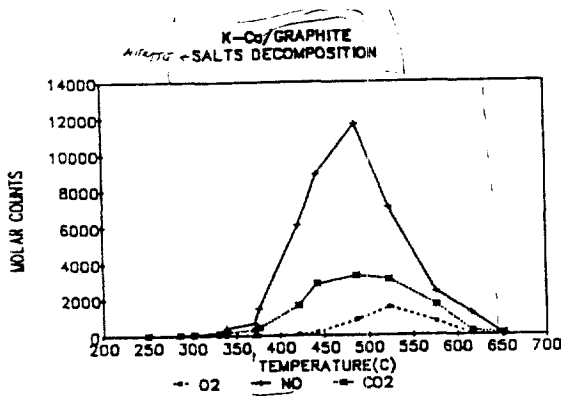
These results may suggest formation of an unstable carbonate or metal carboxylate species which decomposes cyclically into the lower oxide, which in turn is further oxidized by water (O₂ or CO₂). Thus, the oxidation of carbon keeps going on providing a possible mechanism for low temperature carbon gasification.

Secondly in the studies of catalytic performance, the results obtained using different catalysts are given in Table 2.

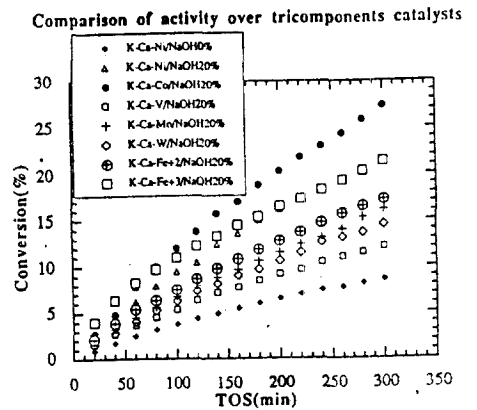
The presence of catalyst significantly enhanced the gasification of char, Ternary catalysts containing transition metals are more effective than binary K-Ca oxide catalysts.

With ternary catalysts containing transition metals, The order of catalyst activity is K-Ca-Co>K-Ca-N>K-Ca-Fe⁺³. The initial reaction rate of K-Ca-Fe⁺³ catalyst is faster than the others.

High selectivity to CO is undesirable because it means lower hydrogen production rates to achieve higher hydrogen production rate a water gas shift reaction has to be used. Addition of catalyst increase selectivity to CO₂ (80-90%). However even in the presence of transition metals selectivities to CO remained >10%. It seems that selectivity to CO is decrease in the case of increase H₂/CO_x ratio but it is revealed that selectivity of CO is higher though H₂/CO_x ratio is higher over the K-Ca-Ni catalyst.



▲ Fig.1



▲ Fig.2

System	NO	CO ₂	O ₂
K-Ni/graphite	1.9	1.0	*
K/graphite	2.4	1.6	1.0
Ni/graphite	1.9	1.6	*
K-Ca/graphite	9.5	3.8	1.0
Ca/graphite	4.0	1.0	*
K-Ca (no carbon)	1.9	---	1.0

*almost no oxygen released

◀ Table 1

Reference

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