ON THE PROMOTER ACTION IN THE CATALYTIC OXIDATION OF METHANE WITH STEAM.

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It has been recently reported by several authors⁽¹⁾ that the reduced nickel or reduced nickel promoted by thoria is a very suitable catalyst for causing the reactions,

$$CH_4 + 2H_2O \rightleftarrows CO_2 + 4H_2 \qquad (1)$$

$$CH_4 + H_2O \rightleftarrows CO + 3H_2 \qquad (2)$$

$$CO_2 + H_2 \rightleftarrows CO + H_2O \qquad (3)$$

to approach in equilibrium with rapidity. The present investigation, however, has been undertaken with the view of examining whether or not the products, which consist of mainly either CO_2+H_2 or $CO+H_2$, could be obtained by employing different promoters under different conditions, and moreover of inquiring into the mechanism of the promoter action.

When methane was allowed to pass over the catalyst, which consisted of reduced nickel promoted with a metallic oxide (such as Al_2O_3, ZrO_2, ThO_2, CaO, CdO, ZnO or MgO etc), with an excess of water vapor at 1000°, the product with the largest quantity of CO_2 was obtained by employing the catalyst promoted with Al_2O_3, whilst when the catalyst promoted with MgO was employed and water vapour was regulated, the product containing the largest quantity of CO was obtained as shown in the following table. The ratio $\frac{\text{Vol. of } CO_2}{\text{Vol. of CO}}$ at 1000° calculated from the results is represented in Table 1.

Table 1.

	Catalyst				$Ni_{(atom)} : Me_xO_{y(molecule)} = 1:0.02$												
Me_xO_y	Al_2O_3	ZrO_2	ThO_2	BeO	Cr_2O_3	Fe_2O_3	SiO_2	WO_3	MnO_2	CeO_2	SnO_2	CdO	CaO	MgO	CuO	Al_2O_3(poisoned with C_4H_4S)	ZnO
$\frac{CO_2}{CO}$	49.0	38.0	19.1	11.7	8.5	5.9	5.2	4.3	3.3	3.5	3.2	3.8	3.0	2.2	1.4	1.02	0.8

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(1) Neumann & Jacob, *Z. Elektrochem.*, **30** (1924), 557; Pease & Chesebro, *J. Am. Chem. Soc.*, **50** (1928), 1464.

$Ni_{(atom)}:Al_2O_3=1:0.2$	$Ni_{(atom)}:MgO=1:0.1$ (Water vapour regulated)
96.0	0.02

These results might possibly lead one to suppose that the reaction may be looked upon as taking place successively in the manner shown by the scheme below:

$$CH_4 \xrightarrow{H_2O} CO + 3H_2 \xrightarrow{H_2O} CO_2 + 4H_2,$$

and as the beneficial effect of promoters in these reactions is to transfer water molecules to the reaction centers of the catalyst where the action of water on methane is carried out, the product may be determined according to the adsorbing intensity of water molecules and the size of the promoter. Thus it seems to us that results we obtained are quite in good agreement with Balandin's "Multipletthypothese."(1)

According to his theory we may imagine, of course, a number of "Krystalkeimen (Multiplette)," of which the following is one:— $I_5(C{\scriptstyle CH_4},(H{\scriptstyle C}-H{\scriptstyle O})_3,O{\scriptstyle H_2O})$. In Fig. 1 A(Ni atom, radius=1.237Å)(2) denotes an adsorption center of methane molecule M(radius of C=0.77Å),(2) R_1R_2 and R_3 (Ni-atoms) reaction centers which attract hydrogen molecules, and P (metallic oxide for instance MgO, Mg=1.593Å)(2) an adsorption center of water molecule (w). Although this model is, naturally, quite hypothetical, it nevertheless serves to show that the yield of CO_2, as may be seen in the above table, increases successively in order of promoters, ThO_2, ZrO_2, Al_2O_3 (polyvalent metallic oxides) as the radius of the atom of promoter becomes smaller (Th=2.833Å, Zr=1.57 (1.61)Å,(2) Al=1.430Å), and also the yield of CO, in order of promoters CaO, CdO, MgO and ZnO (bivalent metallic oxides)(3) (Ca=1.97Å, Cd=1.714Å, Mg=1.597Å, Zn=1.329Å,)(2) for the distance (Δ) between H-atom in water molecule (w) and the reaction center (R) ($\Delta=f$(radius of P)) as shown by Balandin)(4) will be shorter according to the radius of promoter atom decreasing.

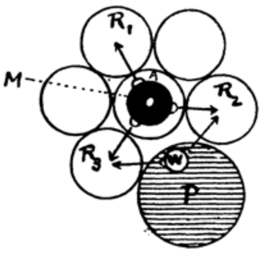

Fig. 1.

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(1) Balandin, *Z. physik. Chem.*, (B) **2** (1929), 289.

(2) W. P. Davey, "The Radii of Atoms and Ions," *Chem. Rev.*, **2** (1926), 356.

(3) BeO give an exception, because its radius is extraordinary small 1.106 Å and CuO is subjected somewhat to the reduction.

(4) Loc. cit.

Increasing the amount of promoter, for instance MgO, for a given amount of the catalyst, the rate of decomposition of methane rises up very rapidly which is represented graphically in Fig. 2.

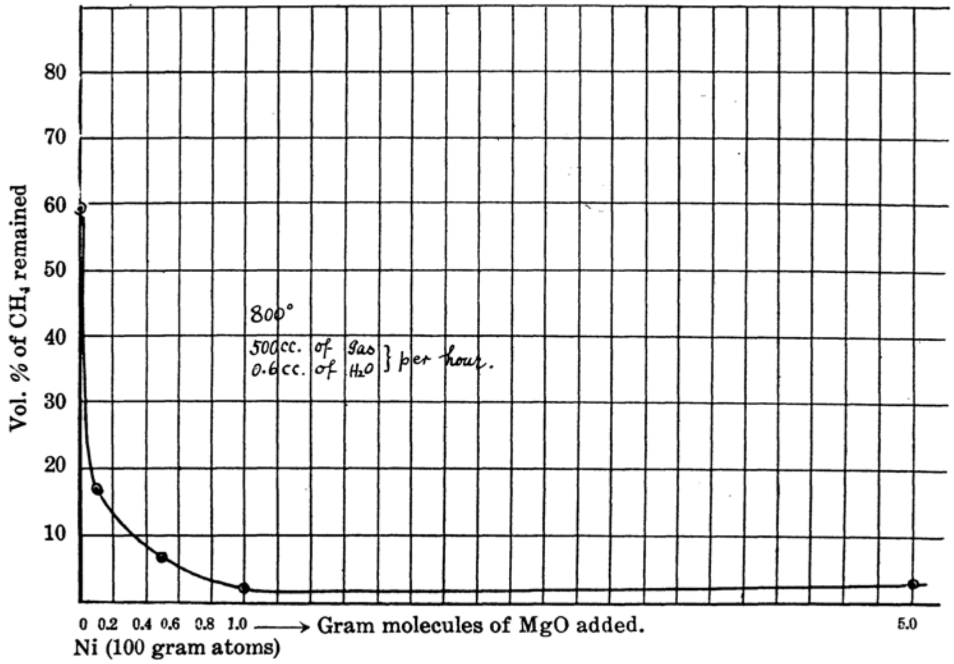
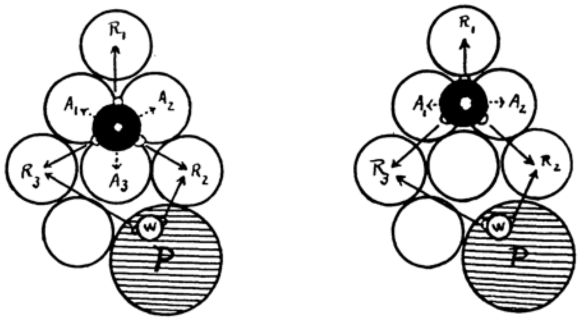


Fig. 2.

This fact may be explained clearly by the hypothesis in the following manner: The reduced nickel which composes the reaction centers and the adsorption centers for methane molecule, does not produce perfect multiplets for decomposing methane with water till it gets a supply of metallic oxide which composes the adsorption center for water molecule, and vice versa. Thus the minute quantity of MgO added to the comparatively large quantities of nickel may give rise to the rapid decomposition of methane.

There may exist, of course, multiplet and multiplet in addition to that shown in Fig. 1, and a sort of active centers giving rise to the hydrogenation of benzene nucleus, forms also a kind of very active multiplet with metallic oxide.

The fact that the nickel catalyst promoted with Al_2O_3 produces CO_2 and CO at 1000° in the ratio of $\frac{CO_2}{CO}=49.0$ (Table 1), but that it produces $\frac{CO_2}{CO}=1.02$ (Table 1) after it is subjected to the poisoning action of thio-



Before poisoning After poisoning

Fig. 3.

phene, shows us that the activity of this multiplet is weakened or is even lost by the poisoning action of thiophene by such a manner as shown in Fig. 3.

Experimental.

Catalysts were prepared by reducing with hydrogen at about 300° in the reaction tube the intimate mixture of nickel oxide and an other metallic oxide which is put on small grains of pumice. The intimate mixtures of metallic oxides were obtained by calcinating the fused mass of pure nickel nitrate and a calculated quantity of another metallic nitrate, for instance 29.1 gr. of $Ni(NO_3)_2.6H_2O$ and 3.75 gr. of $Al(NO_3)_3.9H_2O$ ($Ni:Al_2O_3=1$ atom : 0.01 mol), (in the case of CaO and MgO the acetates were used).

The natural gas obtained at the Kashiwazaki Province, compressed in bombs, consisting of 80.3% of CH_4, 15.8% of N_2, 3.6% of O_2, 0.2% of unsaturated hydrocarbon and 0.1% of CO_2, was allowed to pass over the catalyst (volume about 10 c.c.) in the velocity of 500 c.c. per hour with an excess (5–10 times for calculated quantity) of water vapour which was produced in a small flask in an oil bath heated at 125–150°, and was carried by the natural gas in form of bubbles.

The product was collected on mercury and was analysed.

Table 2.

Catalyst	Temperature	Products in %						
		CO_2	CO	H_2	CH_4	unsat. H. C.	O_2	N_2
Ni:Al_2O_3 1:0.02	800°	18.5	1.2	75.9	0.5	0.0	0.1	3.8
	900	19.4	0.6	76.6	0.0	0.0	0.1	3.3
	1000	19.6	0.4	76.8	0.0	0.0	0.1	3.2
Ni:Al_2O_3 1:0.05	800	19.2	2.1	75.3	0.0	0.0	0.1	3.3
	900	19.2	0.7	77.0	0.0	0.0	0.1	3.0
	1000	19.6	0.2	77.0	0.0	0.0	0.1	3.1
Ni:Al_2O_3 1:0.1	800	19.7	2.8	73.9	0.0	0.0	0.1	3.5
	900	20.0	0.4	76.4	0.0	0.0	0.1	3.1
	1000	19.2	0.2	77.4	0.0	0.0	0.1	3.1
Ni:Al_2O_3 1:0.2	800	19.6	0.7	76.4	0.0	0.0	0.1	3.2
	900	19.1	0.4	77.1	0.0	0.0	0.1	3.3
	1000	19.2	0.2	77.5	0.0	0.0	0.1	3.0
Ni:Al_2O_3 1:0.3	800	19.8	1.2	75.9	0.0	0.0	0.1	3.0
	900	19.0	0.5	77.3	0.0	0.0	0.1	3.1
	1000	19.0	0.3	77.6	0.0	0.0	0.1	3.0
Ni:Al_2O_3 0.1:1	800	1.8	3.3	21.5	66.4	0.0	0.3	6.7
	900	9.5	3.9	49.4	32.4	0.0	0.2	4.6
	1000	11.0	5.0	62.4	17.2	0.0	0.2	4.2
Ni:ZrO_2 1:0.02	800	18.1	1.2	76.5	0.0	0.0	0.1	4.1
	900	19.1	0.7	76.7	0.0	0.0	0.1	3.4
	1000	19.0	0.5	76.9	0.0	0.0	0.1	3.5
Ni:ThO_2 1:0.02	800	18.6	1.5	77.0	0.0	0.0	0.2	3.0
	900	19.3	1.0	76.4	0.0	0.0	0.2	3.1
	1000	19.1	1.0	76.5	0.0	0.0	0.1	3.3
Ni:BeO 1:0.02	800	18.7	0.8	74.2	0.0	0.0	0.1	6.2
	900	18.3	0.9	71.2	2.1	0.0	0.1	7.4
	1000	17.6	1.5	72.5	1.5	0.0	0.1	6.8

Table 2.—(*Continued*)

Catalyst	Temperature	Products in %						
		CO_2	CO	H_2	CH_4	unsat. H. C.	O_2	N_2
Ni:Cr_2O_3 1:0.02	800	19.0	1.7	74.7	0.5	0.0	0.1	3.5
	900	18.2	1.6	75.3	1.0	0.0	0.2	3.7
	1000	16.2	1.9	72.4	5.1	0.0	0.1	4.3
Ni:Fe_2O_3 1:0.02	800	13.2	1.8	48.6	30.2	0.0	0.2	6.0
	900	15.4	3.8	61.5	11.1	0.0	0.2	8.0
	1000	16.6	2.8	75.9	1.0	0.0	0.2	3.5
Ni:SiO_2 1:0.02	800	16.9	2.5	72.8	1.0	0.0	0.1	6.7
	900	15.6	2.3	75.9	1.1	0.0	0.1	5.1
	1000	15.6	3.0	71.4	3.1	0.0	0.1	6.8
Ni WO_3 1:0.02	800	14.1	3.9	69.8	6.8	0.0	0.1	5.3
	900	14.6	4.4	71.0	4.8	0.0	0.1	5.1
	1000	14.9	4.8	72.8	2.6	0.0	0.1	4.8
Ni:MnO_2 1:0.02	800	18.3	2.3	74.0	2.0	0.0	0.2	3.2
	900	16.5	3.6	71.6	4.0	0.0	0.2	4.1
	1000	15.7	4.7	74.2	1.5	0.0	0.2	3.7
Ni:CeO_2 1:0.02	800	17.8	1.6	75.8	0.0	0.0	0.1	4.7
	900	15.9	3.9	74.5	0.0	0.0	0.1	5.6
	1000	15.6	4.4	74.0	0.0	0.0	0.1	5.9
Ni:SnO_2 1:0.02	800	8.5	1.7	21.5	60.8	0.0	0.4	7.1
	900	10.0	3.2	46.8	33.7	0.0	0.2	6.1
	1000	17.4	5.5	67.8	4.6	0.0	0.1	4.6
Ni:CdO 1:0.02	800	10.6	3.1	41.0	41.0	0.0	0.2	4.1
	900	8.6	7.5	43.2	35.2	0.0	0.2	5.5
	1000	15.8	4.1	74.3	1.2	0.0	0.1	4.5
Ni:CaO 1:0.02	800	15.4	4.6	71.2	4.6	0.0	0.2	4.0
	900	12.3	9.5	73.5	0.6	0.0	0.2	3.9
	1000	16.0	5.2	74.8	0.5	0.0	0.2	3.3

Table 2.—(*Continued*)

Catalyst	Temperature	Products in %						
		CO_2	CO	H_2	CH_4	unsat. H. C.	O_2	N_2
Ni:MgO 1:0.02	800	14.0	5.9	75.8	0.5	0.0	0.1	3.7
	900	14.6	5.3	76.1	0.0	0.0	0.1	3.9
	1000	14.0	6.4	75.9	0.0	0.0	0.1	3.6
Ni:CaO 1:0.02	800	2.0	3.5	20.8	61.2	0.0	0.1	12.4
	900	7.6	5.0	45.5	32.2	0.0	0.1	9.6
	1000	13.8	5.5	62.2	9.9	0.0	0.1	8.5
Ni:ZnO 1:0.02	800	11.6	5.2	56.2	20.6	0.0	0.2	6.2
	900	13.0	3.9	77.4	1.1	0.0	0.2	4.4
	1000	10.0	12.4	73.2	0.0	0.0	0.2	4.4

Results with the natural gas ($CH_4 = 95.4\%$, $C_nH_{2n} = 0.1\%$, $CO_2 = 0.2\%$, $H_2 = 0.0\%$, $O_2 = 0.8\%$ & $N_2 = 3.5\%$) and regulated water vapour (0.8—0.6 c.c. H_2O per hour).

Ni:MgO 1:0.01	800	1.8	22.7	74.1	0.0	0.0	1.4	0.081
	900	1.2	23.1	74.4	0.0	0.0	1.3	0.052
	1000	0.5	24.0	74.4	0.0	0.0	1.1	0.021

The products obtained at 800° when Ni and MgO are present in various proportions are shown in the following table (Table 3), where the composition of the natural gas is 82.7% of CH_4, 16.3% of N_2, 0.7% of O_2, 0.2% of unsaturated hydrocarbons and heavy hydrocarbons, and 0.1% of CO_2; the velocity of methane gas is 500 c.c. per hour and the volume of the catalyst which is put on small grains of pumice is 10 c.c.

Table 3.

Catalyst Ni:MgO	Volume of H_2O used at 17°	Products in %						
		CO_2	CO	H_2	CH_4	O_2	N_2	Methane* remained
	c.c.							
100:0.0	6.0	8.7	2.2	43.0	36.1	0.1	10.9	76.8
	0.6	2.2	13.8	50.8	23.9	0.0	9.3	59.9
99.9:0.1	6.0	12.0	8.2	70.5	3.5	0.1	5.7	14.8
	0.6	0.8	18.8	68.5	4.0	0.0	7.9	16.9
99.5:0.5	6.0	14.8	3.5	73.0	1.0	0.1	7.6	5.2
	0.6	1.6	20.8	68.6	1.5	0.0	7.5	6.3
99.0:1.0	6.0	14.3	5.9	73.0	0.0	0.1	6.7	0.0
	0.6	1.8	22.0	69.2	0.5	0.0	7.5	2.1
95.0:5.0	6.0	12.4	5.4	74.2	0.3	0.1	7.6	1.6
	0.6	1.7	19.3	69.5	0.7	0.0	8.8	3.2
90:10	6.0	14.6	5.6	73.1	0.5	0.1	6.1	2.4
	0.6	2.5	20.4	68.1	0.9	0.0	8.1	3.8
80:20	6.0	16.3	3.3	73.5	1.0	0.1	5.9	4.9
	0.6	3.8	19.3	68.8	1.0	0.1	7.0	4.3
70:30	6.0	14.4	6.3	71.5	1.2	0.1	6.5	5.5
	0.6	1.2	18.8	69.0	1.5	0.0	9.5	6.9
60:40	6.0	15.1	3.8	70.9	1.5	0.1	8.6	7.6
	0.6	2.1	17.6	68.1	2.7	0.1	9.4	12.1
50:50	6.0	15.8	3.3	72.4	1.5	0.1	6.9	7.3
	0.6	2.5	15.9	68.9	4.2	0.1	8.4	18.6
40:60	6.0	15.3	2.8	73.2	2.8	0.1	7.1	7.7
	0.6	2.3	15.3	65.1	8.1	0.1	9.1	31.9
30:70	6.0	16.2	2.4	72.4	1.5	0.1	7.4	7.5
	0.6	2.2	14.7	62.1	10.6	0.0	10.4	38.5

Table 3.—(*Continued*)

Catalyst Ni:MgO	Volume of H_2O used at 17°	Products in %						
		CO_2	CO	H_2	CH_4	O_2	N_2	Methane* remained
	c.c.							
20:80	6.0	8.1	4.2	30.1	47.5	0.0	10.1	79.4
	0.6	1.0	12.4	41.2	12.8	0.0	12.6	48.8
10:90	6.0	3.8	3.6	25.2	53.2	0.0	14.2	87.8
	0.6	0.6	13.4	58.0	17.6	0.0	10.4	55.7
0:100	6.0	3.2	2.0	14.0	63.2	0.0	17.6	92.4
	0.6	2.6	3.1	20.3	59.4	0.0	14.6	91.2

$$* \text{ Percentage of methane} = \frac{[CH_4] \times 100}{[CO_2]+[CO]+[CH_4]} .$$

The data shown in Table 3 show that the most effective mixture of catalyst and promoter for CO formation is about 1.0 gram molecule of MgO

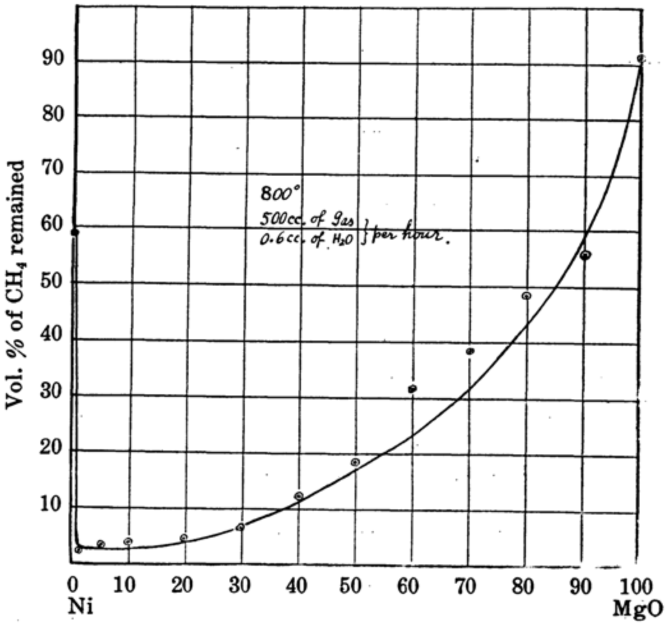


Fig. 4.

to 99.0 gram atom of Ni, and the volume percentage of methane which remained without changing, that is $\frac{[CH_4]\times 100}{[CO_2]+[CO]+[CH_4]}=2.1$, where bracket denotes the volume of the substance, are represented graphically in Fig. 4.

Summary.

In the catalytic oxidation of methane with steam in the presence of nickel, the promoter action of several metallic oxides were investigated.

It was found that the largest quantity of CO_2 was obtained by employing the catalyst promoted with Al_2O_3, whilst when water vapour was regulated the catalyst promoted with MgO gave the largest yield of CO.

These results might possively lead one to suppose that the reaction may be looked upon as taking place successively in the manner:

$$CH_4 \xrightarrow{H_2O} CO+3H_2 \xrightarrow{H_2O} CO_2+4H_2,$$

and as the beneficial effect of promoters in these reactions may be to transfer water molecules to the reaction centers of the catalyst where the action of water on methane is carried out, the products may be determined according to the adsorbing intensity of water molecules and the size of the promoter. Thus it seems to us that the results we obtained are quite in good agreement with Balandin's "Multipletthypothese."

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