Direct Determination of Oxygen in the Organic Compounds by the Hydrogenation. III. Reduction Mechanism on the Ni-Thoria Catalyst.

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In the previous paper the cracking mechanism on the Pt-silica gel catalyst was elucidated. We are going to examine the reducing reactions which occur on the Ni-thoria catalyst. Experimental details are found in the previous papers.

I. Reduction on the Ni-Thoria Catalyst. The CO and CO_2 which are produced in the cracking zone at 950°C are reduced on the Ni-thoria catalyst in the hydrogen stream of about 5 l/hr.

$$CO + 3H_2 = CH_4 + H_2O \quad \dots\dots\dots\dots\dots\dots \quad (1)$$

$$CO_2 + 4H_2 = CH_4 + 2H_2O \quad \dots\dots\dots\dots\dots\dots \quad (2)$$

$$2CO + 2H_2 = CO_2 + CH_4 \quad \dots\dots\dots\dots\dots\dots \quad (2')$$

The high partial pressure of water vapour may prefer the reaction (2′), but in our analytical condition the situation is opposite and, therefore, this reaction may be duly discarded.

(1) *Reaction Temperature and Equilibrium Constants.* The equilibrium constants of reaction (1) and (2) decrease as the reaction temperatures are raised; therefore, the higher the reduction temperatures on Ni-thoria catalyst, the less favourable the equilibrium condition and the temperature of 350°C was found best suited for our purpose.

(2) *Calculation of Unreacted Carbon Oxides.* The relations between the reaction temperatures and unreacted carbon oxides are shown in Fig. 12 for the various ratios of H_2 to CO or CO_2.

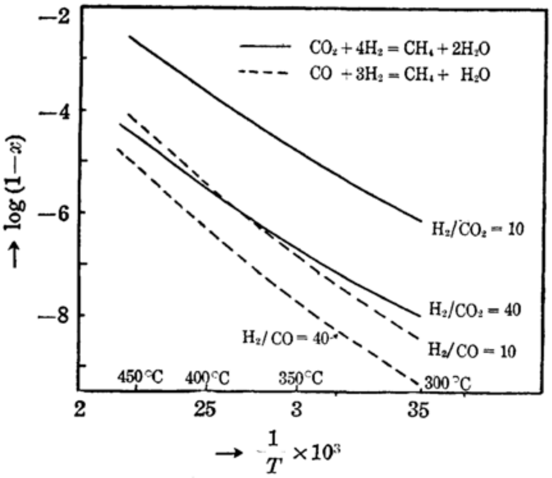

Fig. 12. Relation between Reaction Temperature and Rate of Reaction.

In our analytical conditions the ratio of H_2 to CO may be around 7.2–12.8 and that of H_2 to CO_2 14.4–25.6 as already been discussed in the previous paper. Fig. 12 definitely shows that above 400°C, even if the equilibrium state is nearly reached, the reduction of CO_2 may complete with difficulty.

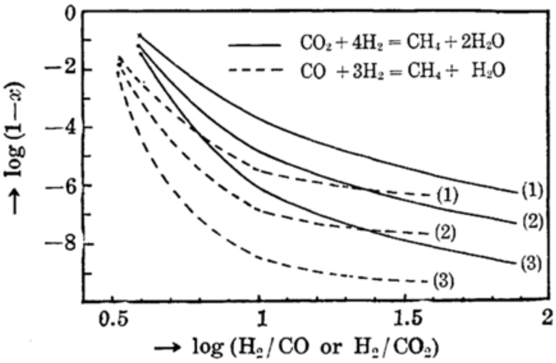

Fig. 13. Relation between reaction temperatures and ratio of concentration of reactants.

The relations between the logarithm of H_2/CO or H_2/CO_2 and the unreacted % of carbon oxides are plotted in Fig. 13.

Fig. 13 clearly shows that the decrease of hydrogen streaming velocity and consequently the decrease of hydrogen concentration or of H_2/CO and H_2/CO_2 inevitably increase the amount of unreduced carbon oxides. By the same reason the rapid cracking of sample results in the large partial pressures of carbon oxides and, therefore, brings the unsatisfactory results. The slow evaporation or decomposition of the sample is the key of success in this analysis.

(3) *Activity of Ni-Thoria Catalyst.* The Ni-catalyst was prepared after the method of H. S. Taylor and W. W. Russel⁽⁵⁾ and contained 2% of thoria. The activity of this catalyst was examined by reducing CO_2 which was evolved from $NaHCO_3$. The production of CO_2 exactly followed the reaction,

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2 .$$

The results of table 9 proved that the activity of Ni-catalyst was quite satisfactory.

Table 9. Reducing activity of Ni-Catalyst.

Sample pure $NaHCO_3$, Hydrogen streaming velocity 4 l/hr.
Calculated: residue 63.19%, H_2O 10.72%, CO_2 26.19% (as H_2O, 21.45%) Total H_2O 32.17%

Exp. No.	Catalyst temp. °C	Sample gr.	Found				cal-Expt. $\varDelta H_2O$
			H_2O	CO_2 (as H_2O)		Residue.	
			%	%	%	%	%
C−61	295	0.1962	31.96	0	0	63.20	−0.21
C−60	315	0.2669	32.22	0.11	0.09	63.58	+0.05
C−58	350	0.2393	32.05	0	0	63.23	−0.12
C−59	350	0.2166	31.90	0.28	0.23	63.02	−0.27
C−62	400	0.2227	31.61	—	—	63.45	−0.56
C−63	400	0.3035	31.66	0.33	0.27	63.13	−0.51

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(5) H. S. Taylor and W. W. Russel, *J. Phys. Chem.*, **29** (1925), 1325.

(4) *Hydrogenation Decomposition of Ethane and Ethylene.* The hydrocarbons higher than methane, i.e. ethane and ethylene, are easily and completely hydrogenated and decomposed to methane on the Ni-thoria catalyst(6) and, therefore, we are not concerned with the behaviour of these higher hydrocarbons which may be produced in the cracking reaction zone.

(5) *Effects of Water Vapour and Hydrogen Sulphide.* The oxidation of Ni-catalyst by the water vapour produced is impossible under the conditions employed.

$$Ni + H_2S = NiS + H_2$$

$$NiO + H_2S = NiS + H_2O$$

Poisoning effect of H_2S on Ni-catalyst is well known and, furthermore, water vapour produced in this reaction is the source of error in this analysis and, therefore, some device for the removal of H_2S prior to the reduction of carbon oxides is essential and will be discussed in the following paper.

II. Decomposition of Native High Molecular Compounds in the Hydrogen Stream.

Saccharose, cellulose, lignin and brown coal of Jarahinohl mine (Manchoukuo) are decomposed at several temperatures in the hydrogen stream and the % of oxygen evolved as the volatile oxygen compound is measured by the method developed above. The variation of heating time of the sample between 10–30 minutes changed the % of oxygen found very little. Fig. 14 shows that the higher the polymerisation degree of the sample the more difficult it is to expel the oxygen from the sample and needs the higher temperature.

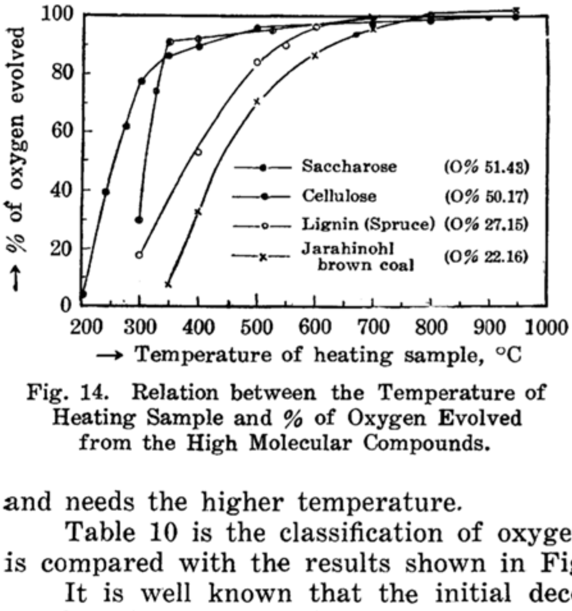

Fig. 14. Relation between the Temperature of Heating Sample and % of Oxygen Evolved from the High Molecular Compounds.

Table 10 is the classification of oxygen bonds in these samples and is compared with the results shown in Fig. 14.

It is well known that the initial decomposition of saccharose and cellulose is the liberation of water and, therefore, hydroxyl bond of alcoholic type is considered to be most unstable. Stabilities of pyran and furan rings or oxygen bonds of ether type placed between pyran and pyran or furan rings coming next; methoxyl bond and benzopyran or benzofuran ring seem to be most stable. Thus this analytical methods of oxygen in the organic compounds may be well employed for the study of thermal behaviour of high molecular compounds.

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(6) Kiyoshi Morikawa, W. S. Benedict and H. S. Taylor, *J. Am. Chem. Soc.*, **58** (1936), 1795; Kiyoshi Morikawa, N. R. Trenner, and H. S. Taylor, *ibid.*, **59** (1937), 1103.

Table 10. Classification of Oxygen Bonds.

Sample	O found %	Classification of Oxygen bonds.					
		Alcoholic OH %	Pyran or furan %	Etheric* %	Methoxy %	Benzopyran or Benzofuran %	Dimethylene Oxide %
Saccharose(7)	51.43	72.73	18.18	9.09	0	0	0
Cellulose(8)	50.17	60.00	20.00	20.00	0	0	0
Lignin(9) (spruce)	27.15	33.10	0	0	30.9	30.1	5.9
Brown coal (Jarahinohl)	22.16	—	—	—	—	—	—

* Oxygen bond placed between pyran and pyran or furan rings in cellulose or saccharose.

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(7) Tollens-Elsner, "Kurzes Handbuch der Kohlenhydrate", 4 Ed., 477, (1935).

(8) W. N. Haworth and H. Machemer, *J. Chem. Soc.*, **1932**, 2270.

(9) K. Freuderberg, M. Meister, and E. Flickinger, *Ber.*, **70** (1937), 500; K. Freudenberg, F. Sohns and A. Janson, *Ann.*, **518** (1935), 62.