Study on the Mechanism of Heterogeneous Catalysis (2)

—The Relative Catalytic Activities of Fe, Co, Ni, Cu, Ag and SiO$_2$ in the Carbon Catalyzed Gasification Reaction

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Abstract

This is a validation article. The experimental results such as the relative catalytic activities of Fe, Co, Ni, Cu, Ag and SiO$_2$ poisoning in the carbothermic reduction iron oxide show that the Electron Cyclic Donate-Accept Catalytic Mechanism-ECDAM or Electron Obital Deformation-Recovery cycle Catalysis Mechanism-EODRM are credible, and the Chemical Reaction Model Catalytic Cyclic Mechanism-CRMM such as the Oxygen Transfer Mechanism-OTT that is long and wide spread in the literature is completely unreliable. Because the Fe, Co, Ni, Cu, Ag were unlikely to react cyclic oxidation—reduction reaction with the carbon in the carbon reduction reaction tank.

Keywords

Heterogeneous Catalysis, Mechanism, Reduction, ECDAM or EODRM

1. Introduction

As the packing carburizing of steel part surface, the carbothermic reduction in the sponge iron production is also an ancient method. They are all dependent on the carbon gasification reaction. The gasification reaction rate is strongly influenced by impurities in the carbonaceous solid. Most natural carbonaceous materials usually contain appreciable amounts of adventitious inorganic impurities that generally increase, but occasionally decrease the reactivity of carbon. The influence of these impurities is of a great practical significance. Many scholars have studied this subject. Unfortunately, the mechanism of catalysis or poison of impurities is still not understood as yet. The most popular interpretation in the literature is the CRMM [1] [2] [3] [4]. The CRMM is deeply rooted in the cata-

lytic academia. Because of the lack of a correct theoretical guidance, scientific research and production practice are more or less blind.

1963 [5], the author pointed out that the CRMM was not credible. 2000, 2008, 2012 [6] [7] [8], the author once again pointed out that the CRMM was not credible. Unfortunately, it didn't get noticed.

In 1970s, the Electron Cyclic Donate-Accept catalysis Mechanism-ECDAM was proposed by author [9] [10]. ECDAM is also called as EODRM (Electron Orbital Deformation-Recovery Cyclic Catalysis Mechanism). ECDAM has three main arguments:

1) There is a demarcation between the catalyst and the poison;

2) The relative activities or poison of catalyst or poison depend on their electronegativity value;

3) The activity of the catalyst depends on its chemical state.

In order to verify ECDAM or EODRM, we have done two experiments. This article is one of them.

2. Experiment

Figure 1 is a reaction box used in the experiment. The box was made of steel plate 4 mm thick. Its size is $65 \times 65 \times 100$ mm. The top on the reaction box has an 8 mm vent hole. A $\Phi 8$ mm stainless tube was fitted so that gaseous mixture produced during reduction process can be collected to determine the gaseous composition and to measure the flow rate.

Mill-scale ($-60 + 80$ mesh) and metallurgical coke powder (-4 mm $+ 40$ mesh) used in the sponge iron production were used as samples for this study. Coke powder was treated with aqueous solution of 50% hydrochloric acid for about 10 hours to avoid the interference of alkali compounds in the coke. Then washed with distill water, finally dried.

The ash amounts and ash components of the coke were not analyzed in detail, because they could be offset against each other in the comparative test.

Mill-scale powder (250 grams) and coke powder (150 grams), both the powder was filled separately into the box in sequence. The mill-scale powder was arranged in the middle of the coke powder. A refractory sieve (200 mesh) was placed between the mill-scale powder and coke powder to avoid the iron oxide powder falling into the coke powder layer.

The different catalysts were separately added to the coke powder. Except the addition of different catalysts, the samples are all the same. After the samples were filled into the iron box, whole thing was sealed by welding. At the top of the box, there is a 8 mm vent hole, and a 8 mm stainless tube was fitted.
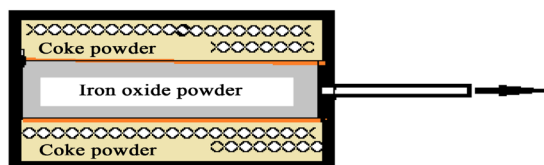

Figure 1. Reduction reaction box.

To compare the relative activities of two catalysts, a couple of boxes were used at each time, for example: Fe-none, Cu-none, Fe-Cu, Fe-Ni, Co-Ni,SiO$_2$-none etc. The boxes in which it contains different catalysts enter into the furnace at the same time and heated zone. The distance between two boxes is about 10 mm.The end of thermocouple was seated between both boxes.

The stainless tube was joined with gas flow meter, from which the flow rate of the gas produced by reduction reaction was measured and the gaseous composition was determined by gaseous analyser.

When reduction process has finished, both boxes were taken out from furnace at the same time, and quickly cooled with water, then the box was cut and sponge iron ingot was taken out for chemical analysis.

3. Results and Discussion

The composition and the flow rate of the produced mixture gas were given in Figures 2-10 for Fe-none, Cu-none, Fe-Cu, Fe-Ni, Cu-Ni, Ag-cu, Co-Ni and SiO$_2$-none of the couple experiments. In addition, there are two lines drawn in each picture. One is the gasification reaction equilibrium composition line (CO$_2$-CO-C). Another is the reduction reaction equilibrium composition line (FeO-Fe-CO$_2$-CO).
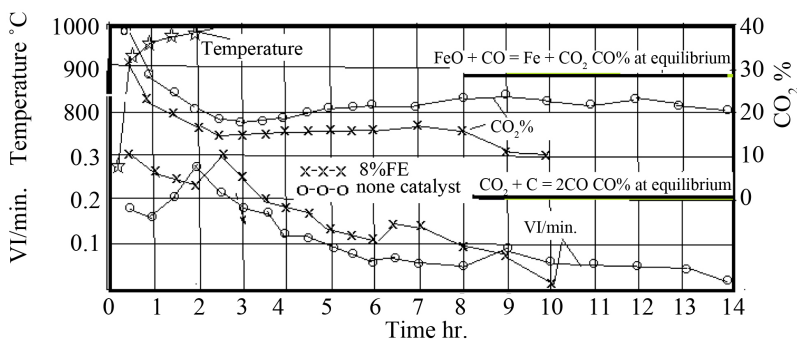
Figure 2. Catalytic activity of iron in the reduction process with coke.
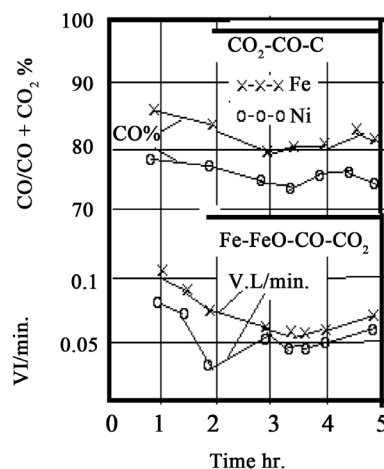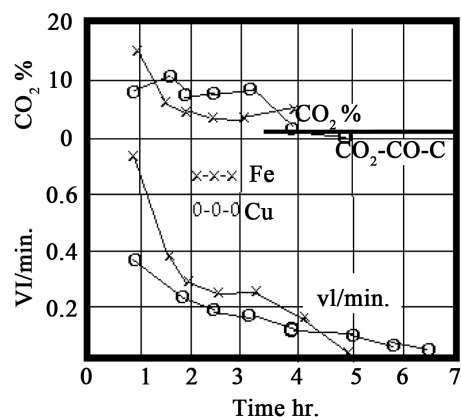

Figure 3. Catalytic activity of Fe. Ni. 900°C.
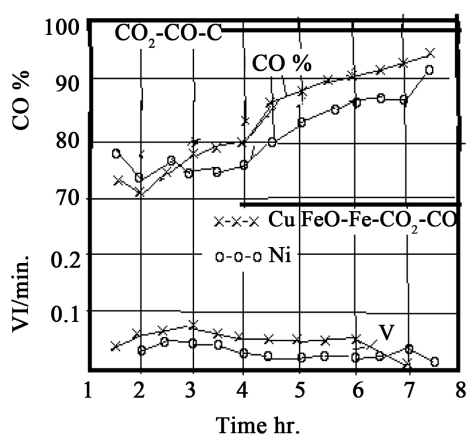
Figure 4. Catalytic activity of Fe. Cu. 980°C.

Figure 5. Catalytic activity of Cu. Ni. 900°C.

Figure 6. Catalytic activity of Cu. Ni. 950°C.

The compositions of gases evolved from reaction box and Gas composition of $FeO + CO = Fe + CO_2$, $CuO + CO = Cu + CO_2$, $CO_2 + CO = 2CO$ equilibrium reaction were given in **Table 1**. The contents of sponge ingot for Fe-none, Cu-none, Fe-Cu couple experiment were given in **Table 2**.

When the residual nitrogen and moisture in the reaction box are completely exhausted at the beginning, the gas in the reaction box consists entirely of CO_2

Figure 7. Catalytic activity of Cu. 900°C.

Figure 8. Catalytic activity of Ag. Cu. 1000°C.

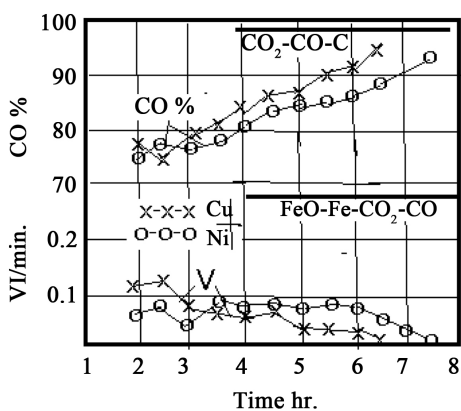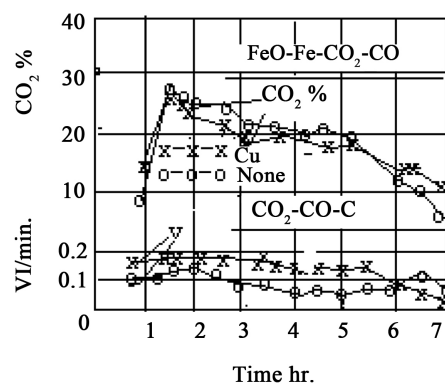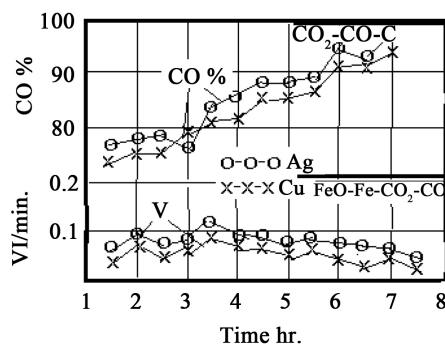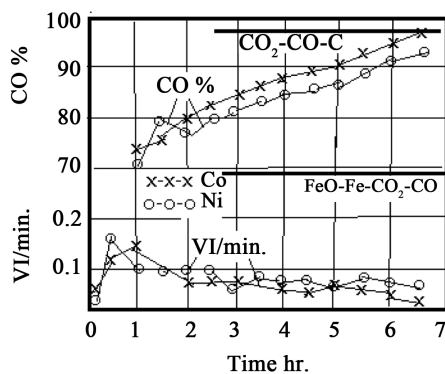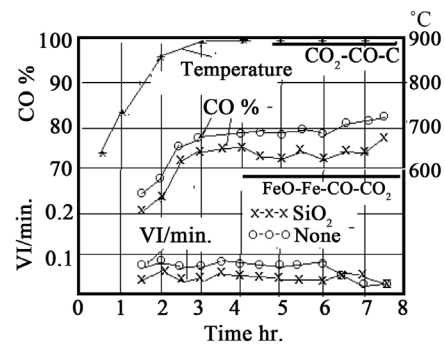**Figure 9.** Catalytic activity of Co. Ni. 900°C.

Figure 10. Catalytic activity of SiO_2 900°C.

Table 1. The composition of gas evolved from box and gas phase equilibrium composition of RO + CO = R* + CO_2 reaction, 1000°C.
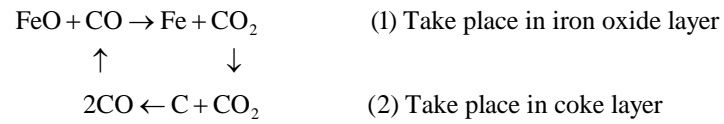
Additive or equilibrium reaction	Gas phase composition	
	CO%	CO_2%
None catalyst	80	20
Fe catalyst, 8%	85	15
Cu catalyst, 10%	82.5	17.5
FeO + CO = Fe + CO_2 at equilibrium	74	26
CuO + CO = Cu + CO_2 at equilibrium	~10^{-7}	~100
CO_2 + C = 2CO	~100	~0

R*-Fe or Cu.

Table 2. The carbon content of sponge iron ingot.

Sample couple	Fe-None		Cu-None		Fe-Cu	
Temperature, °C	1000		900		990	
Time, Hr.	14		7		6.5	
Additive catalyst	None	Fe	None	Cu	Fe	Cu
Carbon content of sponge iron. %	0.35 0.32	0.59 0.52	0.35	0.41	0.51	0.34

and CO. During the reduction stage, there are only two reactions in the reduction box, namely, reduction reaction and carbon gasification reaction, it is as follows:

$$FeO + CO \rightarrow Fe + CO_2 \qquad \text{(1) Take place in iron oxide layer}$$
$$\uparrow \qquad \downarrow$$
$$2CO \leftarrow C + CO_2 \qquad \text{(2) Take place in coke layer}$$

The cyclic reaction (1)→(2)→(1) goes on until the end of the reduction process, and the iron oxide phase disappears completely, and then the gas phase is converted to a carburizing atmosphere.

During the carburizing stage, there are three reactions, namely;

$CO_2 + C \rightarrow 2CO$ Take place in coke layer

$2CO \rightarrow CO_2 + [C]$ Take place in surface of steel part. (3)

$3[C] + Fe \rightarrow Fe_3C$ Carburizing reaction. (4)
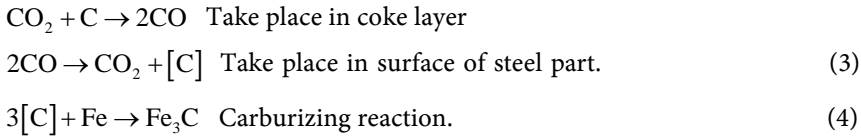
The differences between the reducing stage and the carburizing stage are that the concentration of CO in the carburizing stage is much higher than the reducing stage, such as, at 1000°C, the content of CO is about 30% for the reducing stage, and 100% for the carburizing stage. When the carbon content in iron has been saturated by carbon, the chemical reaction in the reaction box is only the carbon gasification reaction, while the gas phase composition in the reaction box is completely determined by the gasification reaction (2).

$$CO_2\% + CO\% = 100\% .$$

In the nine figures (from Figures 2-10), of which Figure 2 is a typical figure.

Observing Figure 2, the change curve of CO_2% content on none catalyst Fe is always close to the equilibrium gas phase composition of Reaction (1), and far away from the carbon gasification reaction equilibrium composition. After adding the iron catalyst, the CO% content in the gas phase goes up, but still close to reaction (1), and away from the carbon gasification reaction equilibrium (2). Therefore, It can be claimed that the velocity V_1 of the reduction reaction (1) occurring in the iron oxide layer is always greater than the rate of gasification reaction V_2 occurring in the carbon layer, namely, $V_1 > V_2$. Therefore, it is claimed that the carbon gasification reaction (2) is the rate-controlling step of whole reduction process. In fact, the carbon gasification reaction is also the rate-controlling step at carburizing stage. Because after adding the catalyst, the carburizing rate is accelerated.

The higher CO concentration in the gas phase, the higher gas flow rate, and the higher carbon content in sponge iron indicate that the rate of carbon gasification reaction is faster and the catalyst is active. Conversely, it is poison.

From Figures 2-10, Table 1, Table 2, these experiment results confidently indicated that:

1) Fe, Co, Ni, Cu, Ag all appear catalytic activity on the carbonthermic reduction of iron oxide. But the SiO_2 appears a poison;

2) The relative catalytic activity of these metallic elements are as follow:

Fe > Cu, Fe > Ni, Cu > Ni, Ag > Cu, Co > Ni. The Fe active is the most.

The two results above mentioned are almost in agreement with the ECDAM EODRM judgement.

ECDAM or EODRM has three main arguments, one of which is that the Electron Negativity Values (ENV) of any elements or compounds are less than carbon, or an element that is located in the right side of the carbon in the Element Periodic Table, such as Alkali and Alkaline metals, these elements or compounds can donate electrons towards carbon, they must have catalytic activity.

Figure 11 shows the relationship between ENV differences ($\Delta\chi$) and catalytic
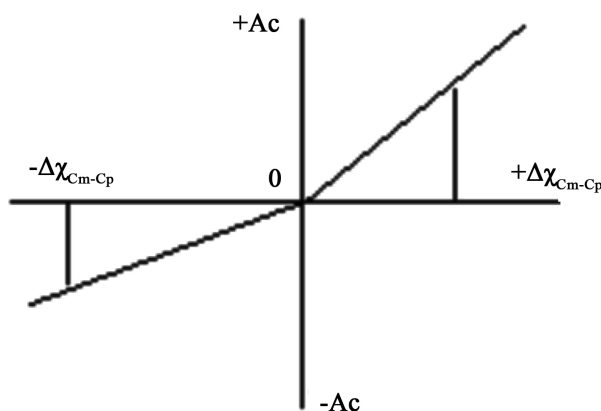
Figure 11. Relationship between electronegativity differences and catalytic activities.

activities (Ac) or poison. In the figure, the χ_{cm} shows the ENVs of carbon or metal catalyst; the χ_{cp} shows the ENVs of catalyst, promoter, or poison. The $\Delta\chi_{cm\text{-}cp}$ shows the difference between carbon, metallic catalyst and poison or promoter. The $+\Delta\chi_{cm\text{-}cp}$ greater, the greater the catalytic activity is. On the contrary, the $-\Delta\chi_{cm\text{-}cp}$ greater, the greater the poison is.

For example:

On the carbon gasification with Fe, Pt, or S as catalyst or poison;

On the Fe catalyst: $\Delta\chi_{Cm-Cp} = \chi_C - \chi_{Fe} = 2.55 - 1.83 = +0.72$, Fe is active catalyst.

On the Pt catalyst: $\Delta\chi_{cm-cp} = \chi_C - \chi_{Pt} = 2.55 - 2.28 = +0.27$, Pt is also active catalyst, but the activity is less than Fe catalyst.

On the sulphur, $\Delta\chi_{Cm-Cp} = \chi_C - \chi_S = 2.55 - 2.58 = -0.03$, the sulphur is poison.

On the Chlorine, $\Delta\chi_{Cm-Cp} = \chi_C - \chi_{Cl} = 2.55 - 3.16 = -0.61$, it is a poison. It's poison is higher than the sulphur.

According to ECDAM, the ENVs of Fe, Co, Ni, Cu, Ag are all less than the carbon. Therefore, they all have catalytic activity for carbon gasification reaction. Their ENVs size are Fe(1.83) < Co(1.88) < Cu(1.90) < Ni(1.91) < Ag(1.93). Their activities size should be Fe > Co > Cu > Ni > Ag.

As for Ag > Cu (Figure 8), due to $\chi_{CU}(1.9) < \chi_{Ag}(1.93)$, this result is completely different from the ECDAM judgment. The reason for this result may be multifaceted. The catalytic phenomenon is very complex, because the chemical and physical properties of the catalyst act simultaneously in the catalytic process. Sometimes, the beneficial side of physical properties has concealed the negative side of chemical properties, such as specific surface area. It is causing to be dazzled and not know how to behave. Although the electronegativity is an useful physical quantity, but its mark value has not yet fully unified. The main reason for this result, in the author's opinion, may be the silver melt down at 1000˚C, Cu melting point: 1083˚C, Ag melting point: 960˚C. It increases the catalytic activity of silver by increasing the contact area with carbon.

The comparison between the gas phase compositions measured from Figures 2-10 and the equilibrium gas phase compositions of $FeO + CO = Fe + CO_2$ and $CO_2 + C = 2CO$ reaction can prove that:

1) The gas phase compositions measured all falls between the two equilibrium gas phase compositions of the reduction and gasification reaction;

2) Samples that contain catalysts Fe, Cu etc., the concentration of CO in the evolved gas has increased. But on the SiO_2, the concentration of CO has decreased.

Standard free energy of formation of metal oxides clearly indicates that the oxides of Fe Co, Ni, Cu, Ag are very easy to be reduced by carbon at common metallurgy temperature. From Table 3, the content of CO in the gaseous phase of equilibrium reaction $CuO + CO = Cu + CO_2$ is only 10^{-7} at 1000˚C. It is very clear that copper oxide is easily reduced by carbon, but it is difficult to oxidize it.

Table 3. Shows the ENVs of elements (Pauling value).

H	u	Na	K	Rb	Cs	Fr	Be	Mg	Ca	Sr	Ra	Fe
2.2	0.98	0.93	0.82	0.82	0.79	0.7	1.57	1.31	1.00	0.95	0.9	1.83
Co	Ni	Cu	Zn	B	C	N	O	F	Al	Si	P	
1.88	1.91	1.90	1.86	0.24	2.55	3.04	3.44	3.98	1.61	1.90	2.19	
S	Cl	Mo	W	Os	Ir	Pt	Au	Ag	Ru	Rh	Pd	
2.58	3.16	2.16	2.36	2.2	2.20	2.28	2.54	1.93	2.2	2.28	2.2	
La-Ce												
1.1-1.3												

As for the Ag, Au, Pt etc. noble metals catalysts which their chemical stable is higher than Cu, the CO concentration at equilibrium is more lower, so the Fe, Ni, Co, Cu, Ag as a catalyst appears only to be in a metallic state, and cannot form the oxide, carbide or carbonate at the reaction condition.

This question of chemical state is very relevant to the mechanism. One of the three arguments in ECDAM is that different chemical states have different ENVs and different catalytic activities. The above argument completely obeys the basic principles of thermodynamics. Unfortunately, the CRMM and OTM which is completely contrary to the basic principle of thermodynamics, is widely popular for long time, and it is incredible. Some investigators even think that it is not claimed that the thermodynamic data can provide a clear-out answer, because they refer to bulk phases, while surface phases which are responsible for catalysis may have different stabilities. Thus it can be seen that the idea of catalysis academic circles is so chaotic. Under the guidance of this confused idea, catalysis of academic research and production is bound to chaos.

This result strongly proved again that the oxidation-reduction cyclic catalyzing reaction on the active catalysts Fe, Co, Ni, Cu, Ag could not occur, and therefore the widely popular CRMM was simply not credible.

From Figures 2-9, the relative activities of Fe > Cu, Fe > Ni are doubtless Figure 3 and Figure 4). From Figure 5 and Figure 6, Cu > Ni, if according to the mark value of ENVs, $\chi_{Cu} > \chi_{Ni}$ ($\chi_{Cu} = 1.90$, $\chi_{Ni} = 1.91$), it is exactly the same as ECDAM's judgment, while the Cu is located on left of Ni in the periodic table.

From Figure 10, it is unsuspected that the SiO_2 is a poison on the carbon gasification. It is consistent from the ECDAM judgment. Due to the molecular ENV of SiO_2 (according to ENV homogenization principle, estimate the $\chi_{SiO_2} = 2.83$) is more than the carbon. It can be expected that those oxides that cannot be reduced by carbon and the molecule's ENVs are more than carbon, such as Al_2O_3, B_2O_3, TiO_2, which must be poison to carbon gasification. Similarly, when the temperature is below about 650˚C, the Fe_2O_3 cannot be reduced by carbon, the Fe_2O_3, Fe_3O_4 that there are greater ENVs than carbon, so that those Fe_2O_3, Fe_3O_4 must be also a poison to the carbon gasification.

4. Conclusions

1) According to the standart free energies of formation of metals oxides and the measured gas phase composition released from the reduction reaction box, it is shown that the catalysts Fe, Co, Ni, Cu, Ag in the carbon layer appear only in the metallic state, and they cannot form oxides, carbides or carbonates. The oxidation-reduction cyclic reaction of CRMM is less likely to occur. For the same reason, Silicon oxide can only appear in the form of SiO_2, and it cannot be reduced.

2) The experimental results show that Fe, Co, Ni, Cu, Ag appear catalytic activity, and SiO_2 is poison.

Because Fe, Co, Ni, Cu, Ag are less electronegative than carbon, they can provide electrons to the carbon. On the contrary, the electronegativity of the SiO_2 is greater than that of carbon, and it further captures the carbon matrix electron, making the carbon molecular orbital deformation more severe. It's not conducive to the decomposition of ketones.

3) The relative catalytic actives are Fe > Cu, Fe > Ni, Cu > Ni, Ag > Cu, Co > Ni.

The iron has the greatest catalytic activity. This result is consistent with the judgment of ECDAM or EODRM.

4) The author believes that this experimental method is a good way. In the reduction stage, the gas phase composition in the reaction tank is always confined between the two reaction equilibrium atmospheres ($Feo + CO = Fe + CO_2$ $CO_2 + C = 2CO$. The two reactive equilibrium thermal chemical data are very reliable), so that, we can use the metallurgy thermo-chemical data to judge the chemical state of the catalyst in the carbon layer.

Due to limited knowledge, shortcomings, in the inevitable, please know the criticism of corrections.

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