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The Effect Of Carbidic/Graphitic Carbon on the Surface Reactivity of the Alumina Supported nano Bimetallic Catalyst

*S.Tajammul Hussain, Asima Siddiq

National Centre for Physics, Quaid-i-Azam University, Islamabad

ABSTRACT

Ruthenium silver bimetallic catalyst was prepared using co-impregnation method supported on high surface area alumina oxide support. The supported alloy system was subjected to CO (carbon monoxide) disproportion and the hydrogenation of the deposited carbon to study the effect of carbidic and graphitic carbon on the surface reactivity of the system. The data indicates that the carbon deposited as carbidic carbon enhances the production of the higher hydrocarbons. The reduction of the system at higher temperature converts a part of carbidic carbon into the graphitic carbon which inhibits the catalytic reaction. The data has been discussed in terms of ensemble /geometric and particle size effect produced by the addition of inactive metal to the active metal.

Key Words: Disproportionation, hydrogenation, Hydrocarbons, CO dissociation, Carbidic carbon, graphitic carbon

INTRODUCTION

The disproportion of carbon monoxide and the hydrogenation of the deposited carbon to methane or higher hydrocarbons has been well known since 1902. When Sabatier first reported the synthesis of the methane over nickel catalyst [1-3]. The production of oil from synthesis gas was commercially developed during world war II in Germany again this reaction is being recognized as a potential method of producing clean energy from coal [4,5].

It is well known that the relatively small amounts of inactive metal or atoms may show a large effect if they are preferentially segregated to the surface [6]. Chin [7] suggested that metal on which CO adsorbed in the bridged form shows higher activity in methnation of adsorbed CO than metals on which CO is adsorbed in linear form. Osamu [8] reported that CO bond of

adsorbed CO on Ru/Al₂O₃ is weakened by Hydrogen and under real conditions the only active species on Ru is molecular CO. this study reports the effect of two types of carbon on the surface reactivity of bimetallic supported alloy system in the hydrogenation of adsorbed carbon.

MATERIALS AND METHODS

2.1 Samples Preparation:

The samples were prepared from RuCl₂ and AgCl₂ by the co-impregnation method described previously [1] on the high surface area alumina oxide support. All samples were reduced at 723K in flowing hydrogen for 15hr. Five samples were prepared containing ruthenium and silver in atomic ratios 0.00, 0.02, 0.05, 0.10, and 0.20. Ruthenium loading was 1% (w/w) was used. The final composition of the prepared samples was determined by atomic absorption spectroscopy. The samples are designated as RM/x:y where x:y is the ruthenium :manganese ration in the sample.

The disproportionation of CO and hydrogenation of deposited carbon was carried out in a single pass flow reactor at atmospheric pressure. Gas chromatographic of CH₄, CO and higher hydrocarbon was made by the same method described previously [1,4,9]. The reaction was carried out at 523K.

RESULTS

When CO was passed over the catalyst, CO adsorbed on the surface, after two or three pulses it become constant. On all the samples studied substantial quantities of “irreversible adsorbed” CO was observed. When hydrogen was passed over the catalyst mainly methane is formed but the production of methane was also detected. The quantity of the carbon removed by hydrogenation was taken as a measure of the capacity of the catalyst to adsorbed “active carbon”. The quantity of CO adsorbed on the surface, CO irreversibly taken up and hydrocarbons formed is shown in Table 1.

Table 1 Products of the disproportion reaction and hydrogenation of deposited carbon on the system

Catalyst Samples.	CO ₂ mol/g	CO*(ads) mol/g	CH ₄ mol/g	C ₂ H ₆ mol/g	C (ads)! mol/g
100:00	3.2 x 10 ⁻⁶	2.99 x 10 ⁻⁵	7.09 x 10 ⁻⁶	2.0 x 10 ⁻⁶	9.08 x 10 ⁻⁶
100:02	3.16 x 10 ⁻⁶	2.88 x 10 ⁻⁵	7.02 x 10 ⁻⁶	8.11 x 10 ⁻⁶	8.13 x 10 ⁻⁶
100:05	2.41 x 10 ⁻⁶	3.14 x 10 ⁻⁵	6.60 x 10 ⁻⁶	1.20 x 10 ⁻⁶	7.80 x 10 ⁻⁶
100:10	2.00 x 10 ⁻⁶	2.42 x 10 ⁻⁵	6.10 x 10 ⁻⁶	9.82 x 10 ⁻⁷	7.08 x 10 ⁻⁶
100:20	1.83 x 10 ⁻⁶	2.70 x 10 ⁻⁵	3.80 x 10 ⁻⁶	6.74 x 10 ⁻⁶	4.47 x 10 ⁻⁶

*Estimated from the quantity of CO taken up irreversibly.

!Estimated from the quantity of CO removed by hydrogenation.

Table 2. Average silver coverage and Ru dispersion calculated from the experimental data

Catalyst samples	Ru Disp. (%)	Silver coverage
100:00	29.8	0
100:02	24.5	0.075
100:05	20.6	0.162
100:10	19.2	0.276
100:20	17.3	0.630

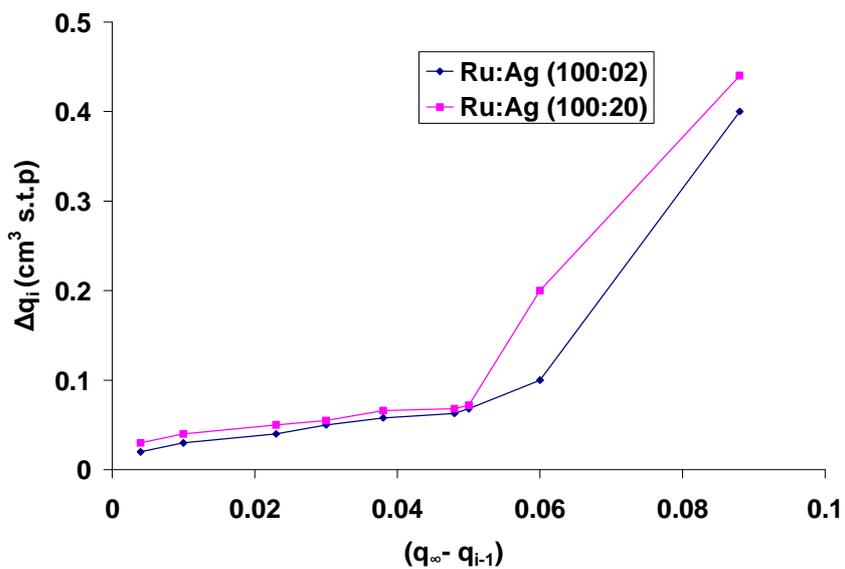


Figure 1(a). The kinetics of CO decomposition reaction on the catalyst system.

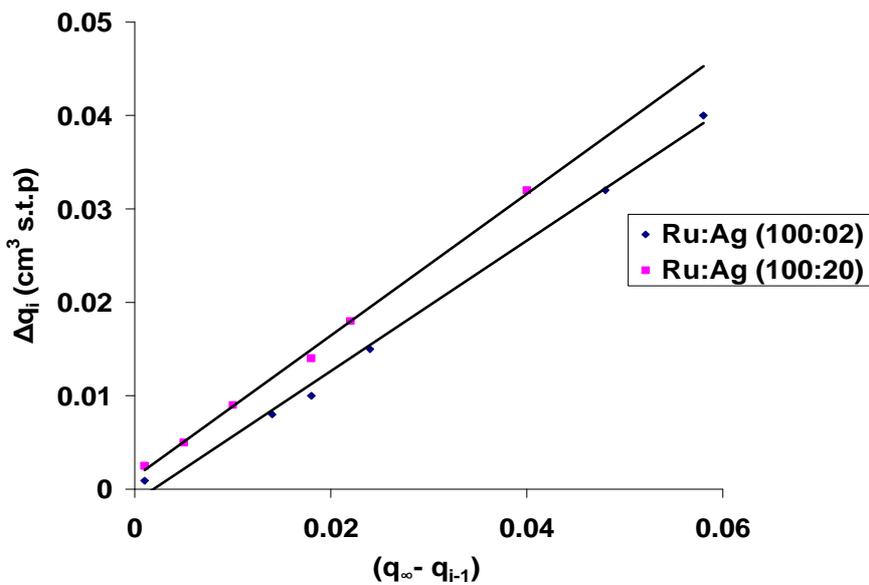


Figure 1(b). The kinetics of CO hydrogenation on the catalyst system

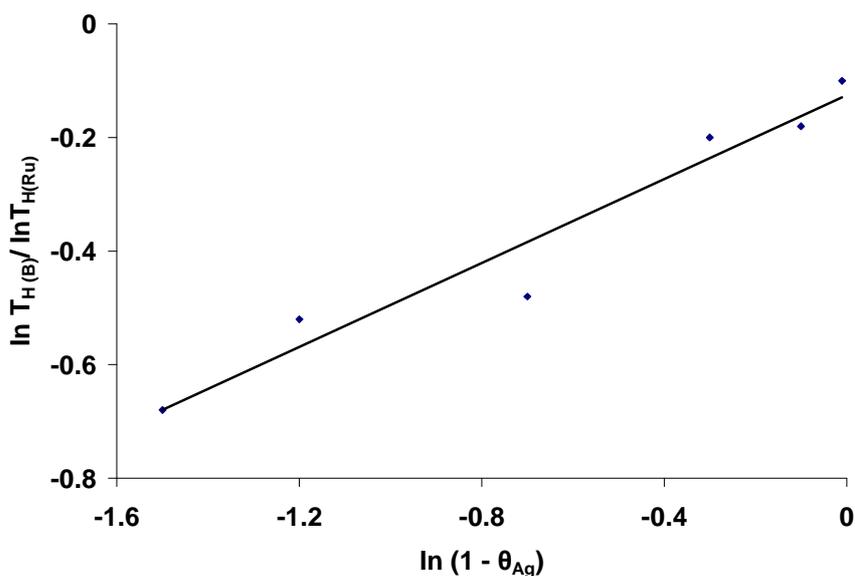


Figure 2(a). the relative activity of Ru :Ag bimetallic catalyst as a function of silver coverage for CO-hydrogenation

$T_{H(B)}$ = quantity of total hydrocarbon formation on bimetallic catalyst

$T_{H(Ru)}$ = quantity of total hydrocarbon formation on pure Ruthenium catalyst

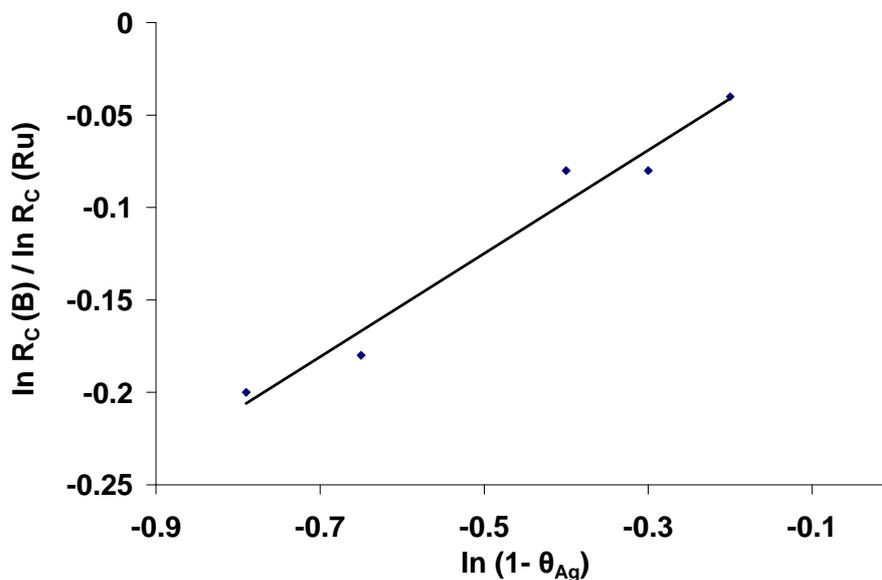


Figure 2(b). The relative activity of Ru :Ag bimetallic catalyst as a function of silver coverage for CO dissociation

$R_c(B)$ = quantity of reactive carbon adsorbed on bimetallic catalyst

$R_c(Ru)$ = quantity of reactive carbon adsorbed on pure Ruthenium catalyst

DISCUSSION

4.1 Kinetics of the Reaction

4.2 Disproportionation of CO

Disproportionation of CO takes place according to the following equation [10,11]



Where C_s stands for carbon deposited on the surface of the catalyst. The kinetics in case of CO dissociation can be expressed by the equation [12].

$$\text{CO}_{(i)} = \text{CO}_{2(\infty)} 1 - \exp^{-k_1 t} \quad (\text{i})$$

Where $\text{CO}_{(i)}$ representing the number of pulses of CO on the surface of the catalyst.

$\text{CO}_{2(\infty)}$ = total quantity of CO Produced after the i th pulse.

t = the constant time between CO and the catalyst.

k_1 = rate constant of the reaction.

Hydrogenation of the deposited carbon

The amount of carbon deposited C_s is equal to the number of CO_2 molecules in the gas phase. The number of all carbon atoms deposited on the surface can also be determined by quantitative hydrogenation of the deposited carbon. The amount of hydrocarbons formed from the deposited carbon again can be expressed by the empirical equation:

$$\text{H. C (t)} = \text{CO}_s = \text{CO}_{s(\infty)} 1 - \exp^{-k_1 t} \quad (\text{ii})$$

Where $\text{CO}_s(\infty)$ stands for the number of deposited carbons atoms. Junji [13] developed an arrangement using equation (i) and (ii) for both CO dissociation and C_s hydrogenation reaction represented by the equation (iii)

$$Dq_i = K\Delta t (q_\infty - q_{i-1}) \quad (\text{iii})$$

Where q_i = represents the quantity of CO_i and hydrocarbon produced after every pulse.

t = the contact time between CO and hydrogen pulse and the catalyst.

K_1 = reaction rate constant. CO_2 or hydrocarbons produced after ten pulses of CO or hydrogen.

q_∞ = Total quantity of CO_2 or hydrocarbons produced after ten pulses of CO or hydrogen

The data of the catalyst system using equation (iii) is plotted and presented in figure 1(a and b). Studying these figures it could be concluded that CO dissociation reaction does not follow the linear plot. In the case of C_s hydrogenation reaction removal of adsorbed carbon is followed with every hydrogen pulse with the formation of CH_4 and higher hydrocarbons. It is also observed that on this system ethane is detected at the reactor outlet when no more methane is coming out. This indicates the presence of two different sites at the surface, one for producing methane and the other for ethane and higher hydrocarbons. It is suggested here that site responsible for the production of higher hydrocarbons are the mixed Ru:Ag sites.

The effect of silver on the CO disproportionation and hydrogenation of the deposited carbon. Studying figure 1(b) reveals the behavior of highest loaded Ru:Ag sample with the other samples. From this figure it is also observed that the quantity of CO adsorbed on 100:20 sample

is less as compared to the other samples. It is suggested that this behavior could be due to the following reasons [13,14].

1. Since less CO is adsorbed on Ru:Ag (100:20) catalyst sample. Consequently less Cs is hydrogenated to hydrocarbons products.
2. At the reaction temperature the presence of silver enhances the conversion of carbidic carbon to less reactive graphitic carbon which inhibits the production rate.
3. It is also speculated that at the reaction temperature the presence of silver perhaps increases the deactivation of deposited carbon which resulted the change in behavior.

Since, apart from hydrogenation reaction, no further experiment to analyze the “carbon covered” surface was performed. The nature of carbonaceous species on different carbon loaded sample can only be speculated. The number of Cu atoms constituting an active ensemble for CO dissociation may be estimated by the method proposed by Yu et al [22] for Ni-Cu alloy system. They suggested that if inactive metal is randomly distributed on the surface of the metal crystallites and n adjacent Ru atoms form an active site, then the number of active sites and the surface coverage of inactive metal (i.m) is related by the equation [15]:

$$n_s \propto Q_{Ru}^n, \text{ (or } n_s (1q_{i,m})^n$$

By applying the same method the number of Ru atoms and the surface coverage of silver is calculated and presented in the table 2.

The log plot the quantity of reactive carbon formed and relative activity in the case of CO hydrogenation is plotted as a function silver coverage and presented in figure 2(a & b). From figure 2(a) the slope indicates that the no. of Ru atoms required for CO dissociation and the number of Ru atoms required for CO hydrogenation is 6 figure (2b).

Studying Ni-Cu bimetallic alloy system Martin [10,13] reveals that a 12 Ni metal atoms are required for CO hydrogenation reaction. It is proposed here that the difference in the ensemble size in the present study and the one reported in the literature is due to the following reasons [13-15]:

1. Ru and Ag forms mixed ensembles hence increasing the production of higher hydrocarbons.
2. Ag increases the conversion of carbidic carbon to graphitic carbon which inhibits not only the rate of reaction but also makes the no. of Ru atoms.
- 3.

CONCLUSION

The following conclusions could be drawn from the study:

1. At the reaction temperature the formation of unreactive carbon and deactivation affects the production rate of hydrocarbons.
2. The Ru:Ag mixed ensembles increases the CO dissociation and consequently increases the graphitic carbon on the surface.

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