

The Effect of Alloying on Selectivity and Activity for Carbon Monoxide Hydrogenation Over Ru-Mn/SiO₂ Supported System

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Summary: The Ru:Mn/SiO₂ supported system with various level of Mn was prepared by co-impregnation method dispersed on high surface area SiO₂ support. The system was investigated for CO hydrogenation reaction. The catalytic activity and product selectivities data reveals electronic and ensemble effect produced by the addition of Mn to Ru/SiO₂ system. It is suggested that addition of Mn produces new surface sites Ru:Mn bimetallics which modify the catalytic behaviour electronically and geometrically.

Introduction

The catalytic synthesis of hydrocarbons from mixture of CO and H₂ is a well studied reaction and have been the subject of numerous investigations. Depending upon the support and the reaction conditions, a variety of products may be formed. All important parameters which may modify the catalyst activity and product selectivities is the addition of a metal promoter [1-6]. The use of supported Ru is well documented [7,8]. Supported Ru is reported to have higher Fischer-Tropsch (FT) activity and to be more selective towards the production of higher hydrocarbons [9]. The addition of Mn was seen to enhance back-donation of metal electrons to the 2π* orbital of the CO bond [10]. Another effect that added metal species might have is geometric, in that the adsorbed metal may serve to dilute the main metal surface and can therefore exert an ensemble effect.

The studies reported here have been undertaken to investigate the catalytic behaviour of a series of Ru/SiO₂ catalysts promoted with different levels of manganese in the CO hydrogenation reaction.

Results and Discussion

Arrhenius plots for the catalyst 100:20 investigated in the CO hydrogenation reaction are shown in Figure 1 (a-c) for total hydrocarbons, methane and higher hydrocarbons production.

Table-1 summarizes the apparent activation energies for the production of methane, higher hydrocarbons and total hydrocarbons.

Table-1: Activation energies in kJ/mol for the product in CO hydrogenation reaction.

Catalyst Ru-Mn(Mn%)	Methane E _a kJ/mol	Hydrocarbon E _a kJ/mol	Total hydrocarbons E _a kJ/mol
100:00	139 ± 6	127 ± 8	129 ± 5
100:02	126 ± 7	120 ± 6	122 ± 3
100:05	118 ± 5	129 ± 4	110 ± 10
100:10	91 ± 3	145 ± 7	97 ± 5
100:20	90 ± 2	139 ± 8	110 ± 12

Table-2: presents the kinetics study of the reaction.

Table-2: Table of measured order of reaction for the CO/H₂ reaction.

Catalyst samples	order of reaction	
	w.r.t CO(-ve)	w.r.t H ₂ (+ve)
100:00	0.21	2.14
100:02	0.27	1.56
100:05	0.31	1.23
100:10	0.36	0.79
100:20	0.39	0.60

The major product was methane on the system. The other hydrocarbons of various chain lengths were also formed. When the reaction was studied from its induction period through to steady state, it was observed that at 573 K methane peak appeared initially and after a short time higher hydrocarbons of different chain length appeared. Addition of Mn to the system has a very clear effect; even at higher temperature on Mn doped catalysts small amounts of olefinic products appeared along with alkanes. Similar results were obtained by Sachtler *et al.* and Berns *et al.* [11,12] on their supported systems.

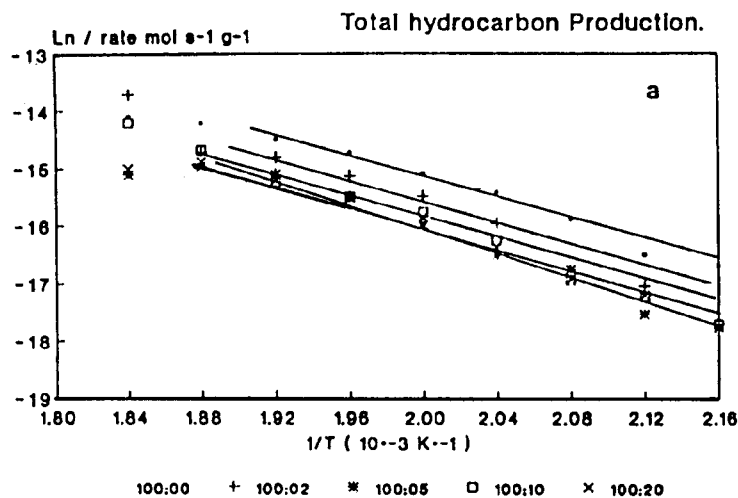


Fig. 1(a): The Arrhenius plots for total hydrocarbons production for CO-hydrogenation reaction over Ru:Mn/SiO₂ catalysts.

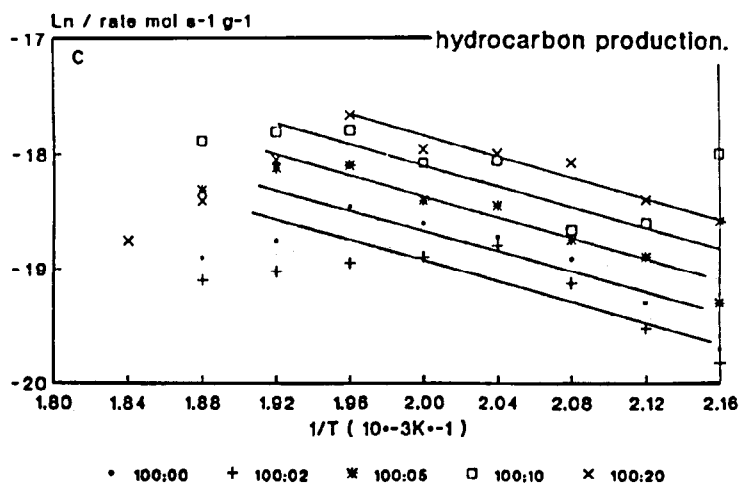
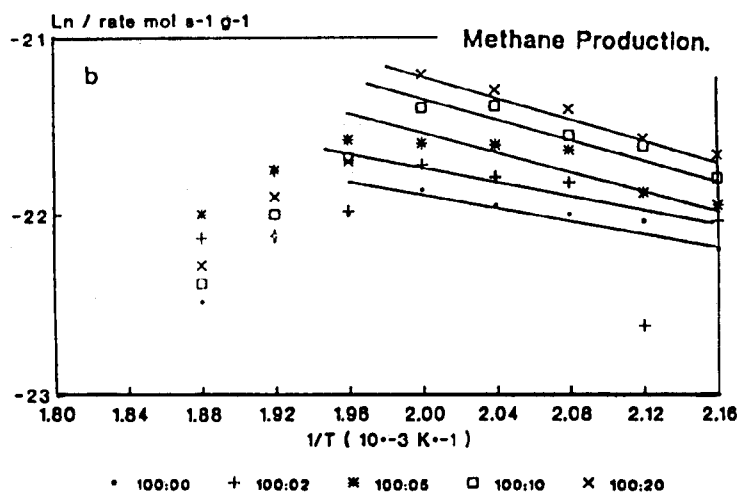


Fig. 1(b,c) The Arrhenius plots for methane and hydrocarbons production for the CO/H₂ reaction over the Ru:Mn/SiO₂ system

The Arrhenius plots for the formation of different hydrocarbons are presented in Fig. 1(a,c). While the plot of methane production is linear throughout the temperature range, those for the higher hydrocarbons deviate from linearity at higher temperature. This deviation is not so pronounced as compared to the studies made on other systems [13,14], it is proposed that addition of Mn (i) favours the production of higher hydrocarbons (ii) produces sites which stabilizes the system at higher temperature. The data in Table 1 and 2 suggest that the presence of Mn on the surface enhances CO dissociation but it does also seem to resist the conversion of carbidic carbon to graphitic carbon. The support to this suggestion came from the plot of TON (Turn Over Number) VS. CO conversion (Figure 2). It is strongly believed that at higher CO conversion the carbidic carbon is converted to graphitic carbon consequently decreasing the TON. On this system no such effect is observed.

Table 3 presents the activity of the system calculated from the CO/H₂ data.

Table-3: TON (activity) calculated from the CO-H₂ reaction.

Catalyst Samples	Meth. TON	H/HCs TON.	Total TON.
100:00	0.012	0.0006	0.0016
100:02	0.0093	0.0007	0.0013
100:05	0.0062	0.0016	0.0019
100:10	0.0082	0.0023	0.0023
100:20	0.0070	0.0035	0.0028

Table 4 presents the selectivity data calculated from the reaction.

Table-4: Selectivity for the reaction products calculated for the CO/H₂ reaction.

Catalyst % Sample Conv.	Products Selectivities							
	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	
100:00	6.0	96.2	0.033	1.35	0.15	1.35	0.044	0.76
100:02	5.8	92.2	0.067	2.50	0.27	3.75	0.046	1.07
100:05	6.3	88.07	0.131	3.74	0.57	5.13	0.068	2.27
100:10	5.4	76.2	0.115	14.0	0.82	5.89	0.10	2.84
100:20	5.9	65.3	0.125	22.9	0.76	7.96	0.12	2.01

C₁, C₂, C₃, C₄ in Table 4 presents unsaturated hydrocarbons.

The extent of the Mn effect on the catalytic behaviour depends upon many parameters such as the support used, preparation method, metal

PLOT OF TON VS. CO CONVERSION.

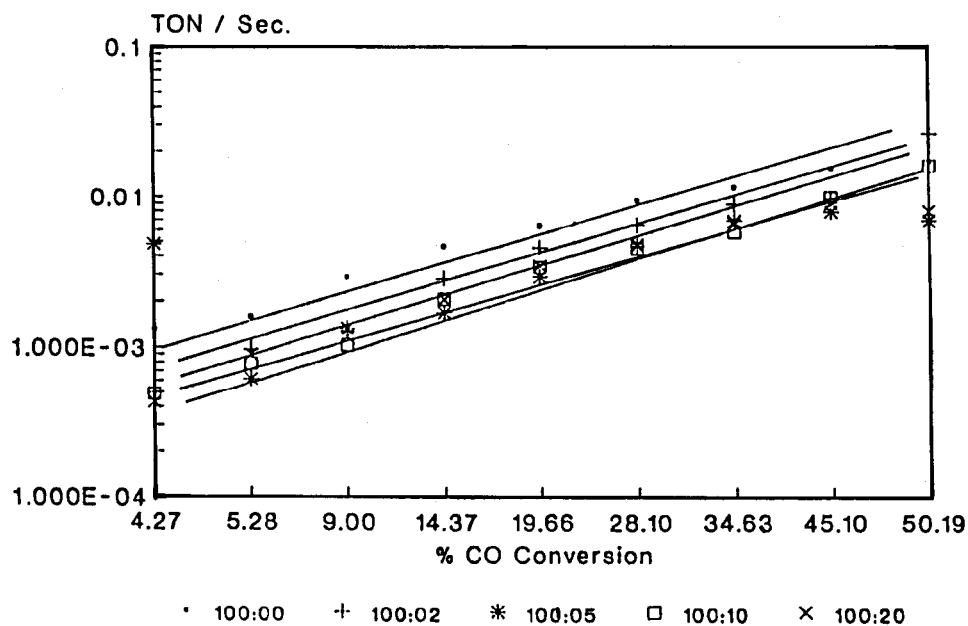


Fig. 2: Plot of TON (activity) VS CO conversion.

precursor, metal loadings. These parameters determine the extent of interaction between the Mn and Ru among other things.

The change in activation energies and the pattern of activity and selectivity changes reported in Tables 1,3,4 reveals two possibilities.

1. The presence of Mn blocks the surface sites geometrically responsible for the products of CH_4 .
2. The new surface sites (Ru:Mn) are generated. These sites produces an electronic interaction between Ru and Mn which in turn increases the product selectivity towards higher hydrocarbons.

The increase in surface area with the addition of Mn and the change in particle size, particle shape give further support to the argument that both electronic and geometric effect are operating on the system [15,16].

Studying Table 4 it could be concluded that although the comparison is made at nearly similar conversion levels, the extent of changes occurring in the product selectivities support the argument that anelectronic interaction between Ru and Mn is responsible for the observed effect.

Experimental

Catalyst preparation

The Ru/SiO₂ catalyst was prepared by impregnating a high surface area silica support (105 m²g⁻¹) with an aqueous solution of RuCl₃ to give a Ru loading of 1% w/w. The resulting solution was shaken for nearly half an hour to ensure uniformity. After impregnation, the catalysts were dried at 323 K for about 15 hours and then reduced in flowing hydrogen at 723 K overnight. The manganese promoted Ru/SiO₂ were prepared by adding the correct amount of aqueous manganese chloride solution to reduced, unused Ru/SiO₂ samples. The resulting mixture were dried, and the dried powders were calcined at 723 K in a flow of hydrogen overnight.

Five catalyst samples were prepared containing ruthenium and manganese in the atomic

ratios 0.00, 0.02, 0.05, 0.10 and 0.20. The samples were designated as RM/x:y where x:y is the ruthenium manganese ratio in the sample.

Catalytic studies

The catalytic experiment was carried out using a conventional flow system at atmospheric pressure. The reactor was constructed from Pyrex glass tubing of 12 mm internal diameter. The catalyst was held in place by means of quartz wool. The reactor was externally heated using a furnace connected to a temperature controller. For the experiment 1g of the catalyst was employed.

Before each experiment, the catalyst was pretreated in situ with a hydrogen flow at 723 K for nearly 16 hrs, then cooled to the reaction temperature before switching from pure hydrogen to the reactant feed. The reactant feed consists of premixed mixture of H₂:CO:Ar, with a composition of 42: 10: 48 by volume, supplied by B.O.C. Specialist Gases Ltd. U.K. The total gas flow rate over the catalyst was ca. 40 ml/min. Constant activity levels were obtained after nearly 25-30 minutes on stream. The reaction was performed in the temperature range of 493-598 K.

Exit gases were analysed using a Pye Unicam 104 programmable on-line chromatograph equipped with a flame ionization detector. A Poropak Q column of 1.5 m length and 80-100 mesh size was used to separate hydrocarbons formed. The main products including CH₄, C₂H₄, C₃H₆, C₃H₈, C₄H₈ and C₄H₁₀ were adequately analyzed by operating the gas chromatograph in a temperature programmed mode between 40° and 165°C. Methane was eluted at a column temperature of 40°C, the column temperature was then manually raised to 60°C for the elution of ethene and ethane, after which the temperature was raised to 165°C at a heating rate of 12°C/min. in order to analyze for propene, propane, butene and butane. Calibration of the detector response was carreid out by injecting a gas mixture of known composition supplied by Phase Separation Ltd. U.K.

Calculations involved in this study were carried out as follows. Activity for the production of product A expressed in moles/sec. was calculated by the following equation:

Activity = Mole fraction * molar flow rate

$$\% \text{ Conversion} = \frac{\sum_{n=1}^{n=4} n(C_n H_{2n+2}) + \sum_{m=1}^{m=4} m(C_m H_{2m})}{\text{CO fed in mol/sec.}} * 100$$

$$\text{Olefin Selectivity} = \frac{\sum_{m=2}^{m=4} m(C_m H_{2m})}{\sum_{n=1}^{n=4} n(C_n H_{2n+2}) + \sum_{m=2}^{m=4} m(C_m H_{2m})}$$

$$\text{Hydrocarbon Selectivity} = \frac{\sum_{m=2}^{m=4} m(C_m H_{2m}) + \sum_{n=2}^{n=4} n(C_n H_{2n+2})}{\sum_{n=1}^{n=4} n(C_n H_{2n+2}) + \sum_{m=2}^{m=4} m(C_m H_{2m})}$$

Conclusions

The following important conclusions emerge from this study:

1. The presence of Mn at the surface produce a surface geometry which although increase CO dissociation but prevents the conversion of carbidic carbon to graphitic carbon.
2. The new surface site Ru:Mn increase the olefinic production.
3. The increase in surface area and the production of methane and higher hydrocarbons on Mn doped samples suggest the presence of geometric and electronic effects.

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