

Carbon Monoxide/Hydrogen Titration Studies on Ru:Mn/Alumina Supported Bimetallic System for the Determination of Metal Surface Area

S. TAJAMMUL HUSSAIN

Dr. A. Q. Khan Research Laboratories, P. O. Box. No. 502, Rawalpindi, Pakistan

(Received 23rd July, 1992, revised 22nd August, 1993)

Summary: The CO/H₂ titration method was used to determine the metal surface area on Ru:Mn/Al₂O₃ supported system. This method was based on the assumption that CO is selectively adsorbed to form a monolayer on metal surface but is not adsorbed on the support surface and that all the adsorbed CO is hydrogenated to form CH₄ selectively. The data indicate that Mn covers the surface of Ru and hence the no of active sites responsible for the production of CH₄ is blocked by the addition of Mn. A continuous decrease in the dispersion of the active metal is discussed in terms of ensemble affect generated by the presence of Mn on the surface of Ru.

Introduction

Determination of metal surface area or the dispersion is essential for understanding the properties of supported metal catalyst. Studies have been performed by X-ray diffraction (XRD), Transmission

Electron Microscopy (TEM) and Selective Chemisorption [1,3,4] to determine the metal dispersion. The conventional XRD method gives the average size of the metal crystallize, but its application is limited to

the catalysts with relatively high metal contents and relatively large metal particles. The TEM method which gives the distribution of crystalline size directly can be applied to the catalysts with lower metal content and smaller metal crystallites than those determined by XRD. However TEM cannot be applied to highly dispersed metals i.e. very small metal crystallites. The selective chemisorption method is the most sensitive and is applicable to any highly dispersed metal crystallites.

The selective chemisorption method seems useless for determining very small metal surface areas because small differences in the amounts of adsorbed gas between the beginning and end of adsorption must be detected. The CO/H₂ titration method was used to determine the metal surface area [5]. In this method the amount of CH₄ formed is measured with the Flame Ionisation Detector (FID).

Verification of the method

The present method is based on the assumption that CO is selectively adsorbed to form a monolayer on metal surface but is not adsorbed on support surfaces and that all the adsorbed CO is hydrogenated to form CH₄ selectively. A blank experiment on the support was performed and no CO adsorption on the support was detected. To satisfy the other conditions of the experiment described in Figures 1-4 an experiment on the Ru/Al₂O₃ catalyst with different CO pulse size was performed and as shown in Figure 1, the pulse size did not have any affect in the range 0.5 to 2.5 cm³. Thus it has been shown that the requirement of the method is satisfied. Another experiment with the same catalyst to study the effect of purging time on the formation of CH₄ and to confirm that only adsorbed CO is hydrogenated was performed. Figure 3 shows that the purging time did not have any affect on the formation of CH₄, hence the condition of purging for the experiment to 15 minutes was chosen. The reaction temperature for the experiment was selected by performing an experiment on the catalyst at different reaction temperatures. Figure 4 presents the result of the experiment and it is noted that above 260°C the amount of CH₄ formed starts to fall perhaps due to sintering [2], or the reaction becomes diffusion controlled above the this temperature, hence the reaction temperature for the experiment was set at 260°C. Figure 2 presents the affect of reaction time. At 260°C the amount of CH₄ did not depend upon the reaction time in the range of 10 to

20 minutes. It was confirmed by using T.C.D. (Thermal Conductivity Detector) in place of FID (Flame Ionisation Detector) that under the experimental conditions used no CO was released from the catalyst bed without being hydrogenated.

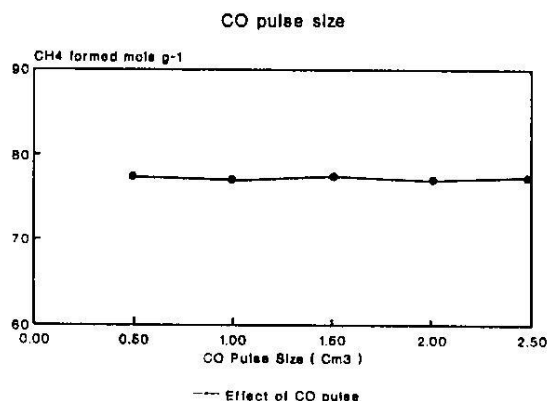


Fig. 1: Effect of CO pulse size on the amount of methane formed on Ru/Al₂O₃ catalyst at 260°C.

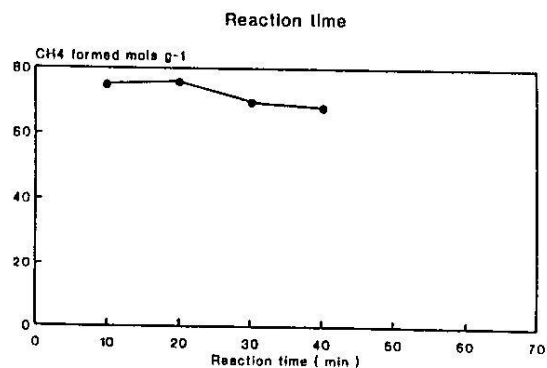


Fig. 2: Effect of reaction time on the amount of methane formed at 260°C on Ru/Al₂O₃ catalyst.

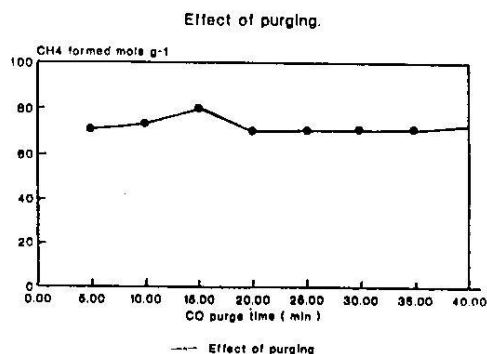


Fig. 3: Effect of purging time on the amount of methane formed on the Ru/Al₂O₃ catalyst at 260°C.

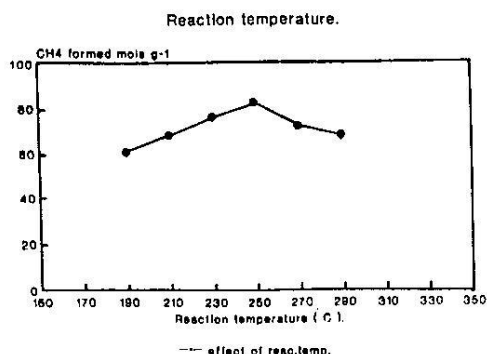


Fig. 4: Effect of reaction temperature on the amount of methane formed on Ru/Al₂O₃ catalyst.

Catalysts preparation

The ruthenium-manganese series of catalysts supported on alumina were prepared by the procedure described in reference [6] using co-impregnation method. Ruthenium trichloride trihydrate and Manganese Chloride (Analar Grade) were used for catalyst preparation. Five catalyst samples were prepared. One catalyst sample contains only ruthenium, four catalysts contained ruthenium and manganese in the atomic ratios 0.02, 0.05, 0.10 and 0.20. To ensure high metallic dispersion loading of only 1% w/w of ruthenium was used. The atomic ratios of each catalyst was checked by Atomic Adsorption Spectroscopy. The B.E.T. surface area of each catalyst was measured and the results are summarized in Table 1.

Table 1: Measured characteristics of the catalyst samples.

Catalyst samples	Surface area m ² g ⁻¹	Ru loadings % (W/W)	Mn loadings % (W/W)	Mn/Ru atomic (%)	100 Ru (Ru+Mn) ^a
100:00	134	1.02	0.00	0.00	100
100:02	141	0.98	0.019	1.93	98.09
100:05	143	0.91	0.051	5.60	94.69
100:10	148	0.96	0.094	9.76	91.10
100:20	152	0.90	0.192	21.33	93.50

a = Atomic adsorption

Results and Discussion

Table 2 presents the metal dispersion (Ru) calculated from the amount of methane produced on the assumption that CH₄/Ru_(s) = 1. Studying Table 2 it could be concluded that the addition of Mn blocks the active metal sites responsible for the production of CH₄. This is suggested from the study that perhaps

the addition of Mn produces ensemble effect which suppresses the production of CH₄, but possibly generates new surface sites like Ru:Mn responsible for the production of higher hydrocarbons [7].

Table 2: Dispersion of the catalyst system calculated from CO/H₂ titration experiment.

Catalyst samples	CH ₄ formed (mol/g)	Dispersion (%)
100:00	7.5 [*] 10 ⁻⁵	30.6
100:02	7.1 [*] 10 ⁻⁵	28.9
100:05	6.2 [*] 10 ⁻⁵	25.3
100:10	5.1 [*] 10 ⁻⁵	20.8
100:20	4.09 [*] 10 ⁻⁵	16.7

Experimental

Figure 5 presents a schematic diagram of the experimental apparatus. 0.5 g of catalyst packed in pyrex glass tubing was reduced in hydrogen at 450°C for one hour and then purged with helium at the same temperature of 1/2 hour. The catalyst was then cooled to room temperature in flowing helium. A 0.5 cm³ pulse of CO was injected onto the catalyst through hydrogen carrier gas so that the whole metal surface area could be covered by adsorbed CO. After the purge of excess CO with flowing hydrogen, three way valves were adjusted so as to trap the adsorbed CO together with gaseous hydrogen. The catalyst was then heated with a preheated furnace to hydrogenate the adsorbed CO to form CH₄. After the reaction had proceeded for 30 minutes, the CH₄ formed was released by adjusting the three way valve to allow detection by Flame Ionisation Detector. High purity CO was used. H₂ and He were purified by passing through a silica gel trap at liquid nitrogen temperature.

1. Three way valve.
2. Silica gel trap.
3. Liquid nitrogen trap.
4. Pulse inlet.
5. Catalyst.
6. Furnace.
7. Molecular sieve column.

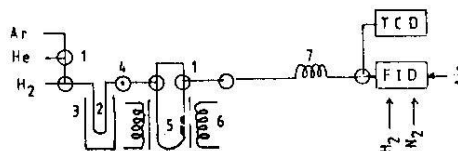


Fig. 5: Schematic diagram of apparatus for CO-H₂ titration experiment.

Experimental Conditions

The standard experimental conditions were as follows:

1. The amount of catalyst used was 0.5 g.
2. The flow rate of gases was 35 cm³/min.
3. The pulse size was 0.5 cm³.
4. The time for purging excess CO was 15 minutes.
5. The reaction temperature and the time for hydrogenated of preadsorbed CO was 260°C for 30 minutes respectively.

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