Determination of Active Metal Surface Sites by Carbon Monoxide Chemisorption on Ru:Ag Bimetallic Supported Alloy System

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Summary: Supported Ruthenium: Silver bimetallic alloy system dispersed on a high surface area Alumina support prepared by co-impregnation method was studied using CO-chemisorption for the determination of active metal site/metal surface area. The data indicates the presence of Ag on the surface of Ru. With the increase of Ag loadings a decrease in the CO adsorption occurred indicating that presence of Ag masks the active sites responsible for CO-adsorption. The data has been interpreted in terms of geometric and electronic effect caused by the addition of Ag.

Introduction

Determination of the number of sites (metal surface area) on the supported catalyst has been one of the most important subjects of investigation in heterogeneous catalytic chemistry [1-13]. Selective chemisorption is widely used technique for this purpose [14]. The use of dynamic pulse method to measure the metal surface area of working catalysts is used in a large number of laboratories. The technique was pioneered by Gruber [15] and has been described in detail by Freel [17].

Catalysts Preparation

The catalyst was prepared from $RuCl_3$ and $AgCl_2$ by the co-impregnation method described previously [18]. All catalysts were reduced in flowing hydrogen at 723 K for ca. 15 h. Five samples were prepared containing ruthenium and silver in the atomic ratios 0.00, 0.02, 0.05, 0.10 and 0.20. Ruthenium loading was 1% (w/w). The final composition of the catalysts were determined by atomic absorption and B.E.T. surface area measurements and presented in Table 1. The catalysts are designated as RM/ x:y where x:y is the ruthenium:silver ratio in the sample.

Table 1: Measured characteristics of the catalyst system

Catalyst samples	Surface Area (m^2g^{-1})	Ru loadings %(w/w)[a]	Ag loadings %(w/w)[a]	Ag/Ru atomic ratios	Ru coverage
100:00	121	0.79	0.00	0.00	0.011
100:02	119	0.70	0.03	3.6	0.009
100:05	123	0.86	0.06	6.2	0.011
100:10	125	0.74	0.08	10.8	0.010
100:20	143	0.87	0.18	21.0	0.012

a = atomic absorption.

Results and Discussion

The quantities of gas uptake for each catalyst under the experimental condition used are shown in Table 2.

From the results of the adsorption experiment (Table 2), it could be concluded that quantity of CO uptake is highest on the sample

Table-2: CO-uptake on the supported catalysts system

Catalyst samples (x:y)	CO uptake (cm^3g^{-1}) -catalysts.	CO/Ru
100:00	0.209	0.298
100:02	0.172	0.245
100:05	0.178	0.206
100:10	0.143	0.193
100:20	0.151	0.173

without Mn and decreases with the increase in Ag doping. The decrease can be attributed to physical covering of Ru surface atoms by Ag atoms as suggested by Rouco *et al.* [19].

The CO-adsorption results may be taken as evidence of interaction between Ru and Ag and may be rationalised by assuming as increasing coverage of Ru crystallites by Ag atoms. It is worth noting that the argument that CO chemisorption decreases with increase in Ag contents only prevails if Ru:CO stoichiometry is less than a 1:1 ratio, which is indeed the case. A suppression of hydrogen chemisorption in the bimetallic catalysts was first observed by Freel [20] who suggested that this decrease is due to alloy formation, supporting evidences came from the other studies [21,22]. This is added here to these many findings that in the presnt system Ru:Ag bimetallic particles would be expected to have fewer contiguous Ru atoms than a normal Ru crystalline i.e. one would expect fewer Ru atoms in Ru:Ag bimetallic than in pure Ru. Ag does not chemisorb CO. Monometallic Ru does chemisorb CO which requires a free Ru atoms on the surface. The suppression of CO chemisorption is the further evidence of the reduction of number of Ru atoms necessary for CO chemisorption.

Poltorak and co-workers [24-26] developed a scheme which relates particle size of different surface atoms to the surface stoichiometry. They pointed out that the major modification in the relative number of various types of surface atoms occurs for particles less than 4 nm in size. This is the region where the majority of bimetallic particles exist in the system [27]. This give further support to the argument that Ag is forming bimetallics with Ru and covering the surface of active metal consequently decreasing CO-adsorption.

Different CO/Ru stoichiometries have been reported for CO chemisorption experiment in the literature. On Ru/SiO_2 samples Miura *et al.* have found a CO to Ru ratio of 0.14 [28]. Shirasaki *et al.* [29] studied CO-chemisorption on Ru metal and on Ru/SiO_2 supported catalysts at 150°C. They found that CO/Ru ratio was more than unity and suggested that this value was due to the presence of $Ru-(CO)_2$, $Ru(CO)_3$ species. It is suggested that CO/Ru value of less than unity on the system is an indication that CO is adsorbed molecularly and present as Ru-CO. Similar results were obtained by Low and Taylor [30], Guerra [31] and Mckee [32].

From the CO-chemisorption data the crystallite size, Ru atoms exposed on the surface and θ_{Ag} (silver coverage)was calculated [33,34], the results are given Table-3(a-b).

Table-3 (a-b) Crystallite size, θ_{Ag} and No. of Ru atoms exposed on the surface.

(a) Crystallite size (nm), θ_{Ag}

Catalyst sample (x.y)	Crystal size. (nm)	θ_{Ag}
100:00	4.9	
100:02	5.7	0.18
100:05	6.3	0.27
100:10	7.2	0.36
100:20	9.6	0.44

(b) Calculation of Ru atoms exposed per g at the surface of the catalyst.

Catalyst sample (x:y)	Ru exposed
100:00	$3.64*10^{14}$
100:02	$2.64*10^{14}$
100:05	$2.07*10^{14}$
100:10	$1.71*10^{14}$
100:20	$1.07*10^{14}$

All the calculations presented in Table 1-3 demonstrate either the covring of Ag on the surface of Ru or the formation of Ru:Ag bimetallic through electronic interaction.

Experimental

The experiment was performed in a reactor system which can be operated in a pulse flow method described previously [27]. The sample holder was made of 1/4 inch diameter pyrex glass tubing and the catalyst bed was held in place by plugs of glass wool. The flow rate of the gas is

controlled by needles valves. A gas chromatographic system with thermal conductivity detector was used for gas detection. The analysis column is a poropak N column. The helium and hydrogen gases were purified by passing through a liquid nitrogen cold trap. The CO was passed throgh the molecular sieve column to remove water vapours.

Before the experiment the detector was calibrated using sample loop of 0.16 cm^3 to 2.0 cm^3. The detector response was found to be linear within this range.

A blank experiment was performed on the alumina support and on the sample without Ag. No adsorption of CO on both was detected.

0.5 gm of the catalyst was held in the sample holder. The catalyst sample was reduced for 30 minutes at 723 K under hydrogen flow and then helium gas was passed at 723 K for 30 minutes to desorb hydrogen. The reactor was then cooled to 273 K and pulses of CO (0.16 cm^3) were passed over the catalyst sample until the volume of the gas emerging from the reactor was constant. The volume of the gas irreversibly adsorbed was measured from the difference between the total quantity of the gas injected into the reactor and the total quantity of gas eluted.

Conclusions

The following conclusions could be drawn from the study.

1. Ag covers the surface of Ru. This results a decrease in CO-Chemisorption.
2. CO adsorb on the surface molecularly.
3. The affect of particle size and the presence of Ru:Ag bimetallics affect the CO-adsorption stoichiometry.

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