Temperature Programmed Desorption (TPD) and Temperature Programmed Reduction (TPR) Studies of Alumina Supported Ploycrystalline Ru/Mn Bimetallic System

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Summary: TPR and TPD studies were carried out on alumina supported Ru:Mn system. From the experimental data it could be conluded that the addition of the Mn produces new sites which are responsible for the production of high molecular weight hydrocarbons. The data has been discussed in terms of the modification of surface electronically and geometrically by the addition Mn to the Ru/Al_2O_3 system.

Introduction

The temperature progammed reduction (TPR) and the temperature programmed desorption (TPD) techniques have been widely used for the characterisation of metal supported catalyst. The main feature of the TPR method is its capability of continuously monitoring the consecutive reaction of reducible species with increasing temperature, after adsorbing the adsorbate gas on the surface [1,2,19,20]. In many systems the presence of several desorption peaks revealed species with different adsorption strengths [3]. The temperature programmed reduction (TPR) in hydrogen flow of predesorbed CO on Ni/Al_2O_3 catalysts shows two reaction sites [4]. In a series of experiments in which heating was interrupted and the adsorption temperature was varied, communication between the two sites (called A and B) was observed [5-8].

There are complications in the application of this technique. For example impurities present on the surface of the catalyst may affect the TPD/TPR experiments. The results of Benninghoven [9] showed that during heat treatment, impurities could reach the surface by diffusion from within the catalyst. This aspect is very important and must always be kept in mind.

The application of TPD methods to catalytic problems has been reviewed earlier [10,13,18]. TPD and TPR studies has been conducted to investigate the interaction between the metals in the catalyst used and how this is reflected on its catalytic behaviour.

Results and Discussion

Figure 1-3 presents the TPD/TPR results of the catalyst system. During TPD (step 1) some but not all of the CO was desorbed, as measured by T.C.D. (Thermal Conductivity Detector). Small amounts of CO_2 were also produced on the 100:00 catalyst, which increase on 100:20 catalyst. Subsequent TPR (step 2) formed CH_4 only on the catalyst without Mn and methane, ethene and ethane on the sample doped with Mn. The shifting of the base line of the chart recorder connected to the G.C. indicates the formation of water as one of the products. The base line shift increases on the 100:20 sample. Similar results were obtained during TPR of adsorbed CO on the catalysts (step 3). The Mn/Al_2O_3 catalyst did not adsorb CO under the experimental conditions.

The evalution of CO occured at 350-450° K (TPD step 1) and this desorption of CO was observed on all catalyst except the pure Mn/Al_2O_3 catalyst. CO_2 evolution increases with the addition of Mn. Step 1 showed the most consistent CO_2 evolution.

The interaction of CO with Ru-Mn catalysts was investigated using TPD/TPR. The TPD of pre-adsorbed CO in helium (step 1) gave a peak of CO below 400° K and another at very high temperature at 500-550° K. The low temperature peak indicates weak associatively adsorbed CO, while the high temperature peak probably results from the mixture of CO and CO_2. The addition of Mn decreases the CO associatively adsorbed and increases the CO_2 and dissociative adsorption

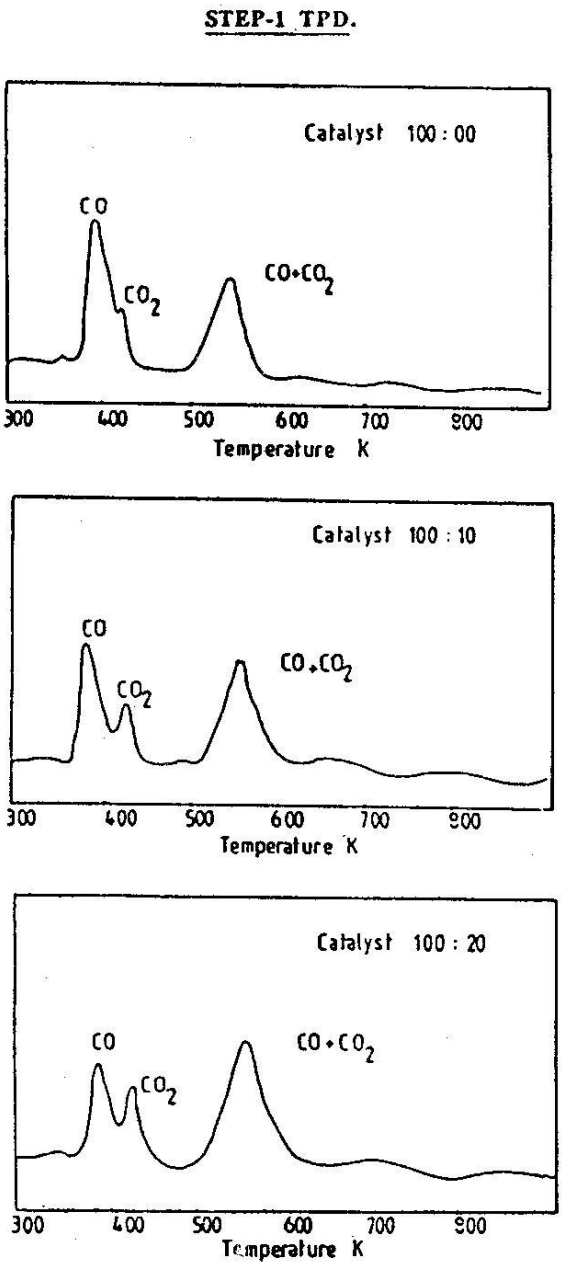

Fig. 1: The TPD of CO on the alumina suppored catalyst samples.

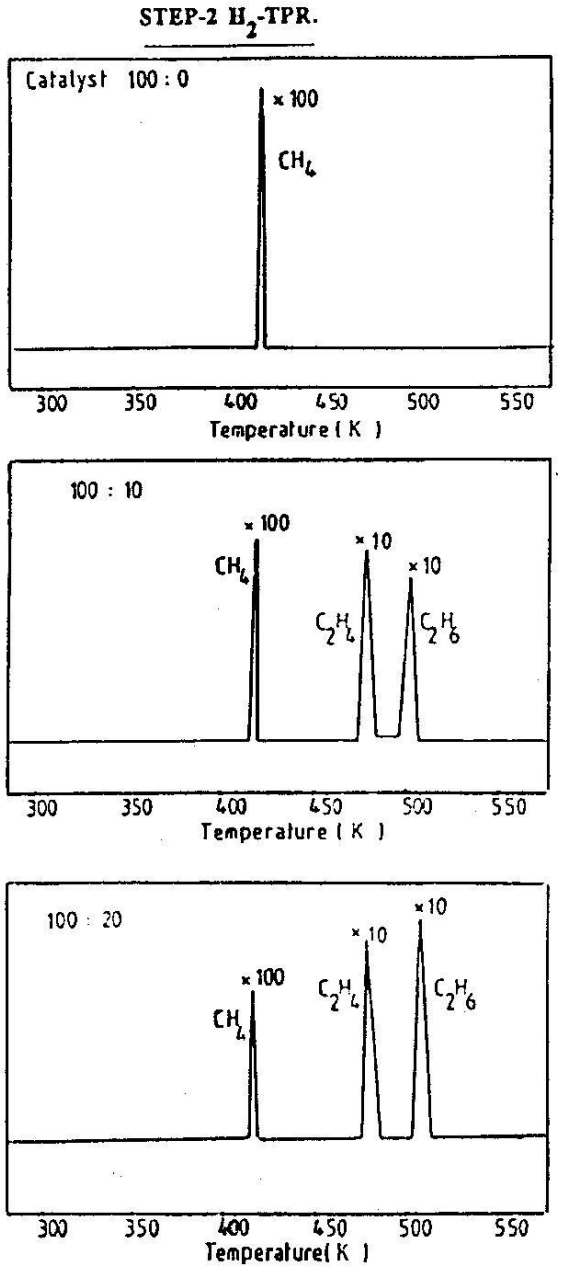

Fig.2: Hydrogen TPR on the alumina supported catalyst system.

of CO indicating that Mn increase CO dissociation under the conditions of the experiment. The presence of CO_2 suggests the disproportionation of adsorbed CO. This general behaviour is consistent with the CO TPD results observed by Amenomiya and Pleizier [14a], using an ammonia synthesis catalyst.

Both strongly adsorbed CO and residual carbon from CO disproportionation remain on the surface after TPD. The result of hydrogen TPR of the catalyst 100:00 (step 3) suggests that this is the case. The principle product on the 100:00 catalyst was CH_4. After helium TPD, any adsorbed CO would have been dissociated and the

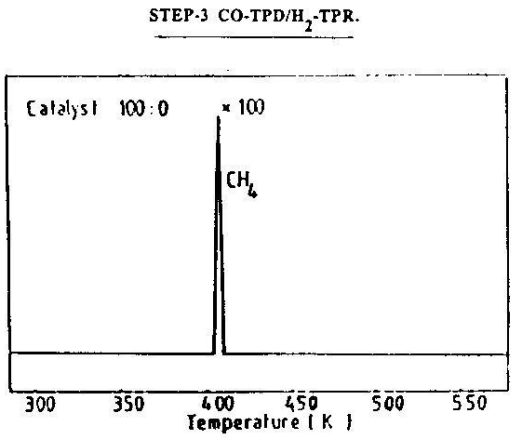

Fig.3: Hydrogen TPR on 100:00 catalyst sample.

formation of CH_4 after TPR (step 2) supports this view. On samples 100:10 and 100:20 the situation is different. In addition to CH_4, H_2 TPR also yields ethene and ethane and an increase in ethene and ethane peaks was observed with the increase in Mn loadings (step 2). These observations suggest that the Mn presence on the catalyst surface creates new sites for the formation of higher hydrocarbons. It is suggested in accordance with the TPR/TPD results that there are possibly two types of sites present on the Mn doped catalysts. Site "A" responsible for the production of methane and site "B" responsible for the production of higher hydrocarbons [21]. It is speculated that site A is affected sterically by the addition of Mn and site B is perhaps modified electronically with the addition of Mn.

The addition of Mn seems to promote the dissociative adsorption of CO. A possible explanation is based on the assumption that Mn in the presence of oxygen converts to MnO, which acts as an electron donor weakening the C-O bond resulting in the dissociation of CO [15]. Dry *et al.*, [16] argued that in the presence of a strong electron donor the carbon-oxygen bond is expected to be weakened resulting in CO dissociation. It is suggested here that in this case MnO performs this function.

The slight increase in temperature in the production of methane, ethane and ethene (step 2) in going from catalyst 100.00 to 100:10 and 100:20 suggests the presence of RuO and MnO. A similar argument is reported in the literature [18] for the TPR/TPD experiment. Here we would like to suggest that this increase in temperature could be due to conversion of carbidic carbon to graphitic carbon [14]. The idea was supported by comparing step 3 with step 2. Once CO is dissociatively adsorbed after step 1 when reacted with hydrogen in step 2 the oxygen and carbon leave the surface as hydrogen containing products. The formation of methane in step 3 at a slightly lower temperature suggests that dissociative adsorption of CO has already occured before the reaction. The decrease in CH_4 formation in step 2 when compared to that in step 3 indicates the possible conversion of part of the deposited carbon from carbidic to graphitic carbon. At this point it is difficult to decide which effect is responsible for the change in temperature in step 2 and 3, perhaps it is the combination of both effect which produces this change, this argument needs further experimental data.

Experimental

The catalysts samples were prepared by coimpregnation method described previously in reference [21]. Five catalyst samples were prepared, one contained only Ru dispersed on alumina, four catalysts contained Ru and Mn in the atomic ratios 0.02, 0.05, 0.10 and 0.20. Catalyst composition was measured by Atomic Absorption Spectroscopy.

TPD/TPR study was carried out in a flow reactor provided with a furance and a temperature programmer. The details of the apparatus used is described in reference [21]. 100 mg of catalyst sample was located in the reactor. The sample was reduced initially in hydrogen at 45°C for 4 hours, a constant rate of heating was maintained via feedback control monitored by a thermocouple located in the catalyst bed. After catalyst reduction, the sample was purged with helium at the same temperature for 30 mins and then cooled to room temperature. The catalysts were exposed to CO gas at room temperature by injecting 0.16 ml pulses into helium carrier gas the continually flowed through the catalyst until no additional adsorption was detected at the detector outlet and then heated in a programmed schedule (10°C/min) in flowing helium. The off gases were monitored by G.C. system. Flow rates were between 30-40 cm^3/min, and the experiment was performed at

atmospheric pressure. All gases used were provided by Air Products Ltd, and were used without further purfication.

The following sequence was employed in the TPD/TPR studies after initial reduction:

Step 1 CO was pulsed over the catalyst, until no further adsorption was detected. The catalyst sample was then heated in flowing helium to 450°C (TPD) at 10°C/min. During this period the concentration of CO and CO_2 were monitored as a function of temperature. The sample was then cooled to toom temperature.

Step 2. The helium flow to the reactor was then curtailed and a 10 ml/min flow of hydrogen was introduced. The catalyst was then heated in flowing hydrogen to 450°C at 10°C/min. During this period the concentration of methane, ethane and ethene in the hydrogen stream were recorded as a function of temperature.

Step 3. After cooling in hydrogen again to room temperature, the catalyst was pulsed with CO and heated in hydrogen to 450°C at 10°C/min. Products were detected in the same manner as in step (ii).

Three catalyst Ru:Mn/Al_2O_3 (100:00, 100:10 and 100:20) and pure Mn/Al_2O_3 were studied.

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