Thermochimica Acta, 133 (1988) 137–142
Elsevier Science Publishers B.V., Amsterdam

TEMPERATURE PROGRAMMED DESORPTION INVESTIGATION OF SOME NICKEL/ALUMINA CATALYSTS FOR CARBON MONOXIDE METHANATION

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ABSTRACT

Various Ni/Al_2O_3 catalysts were investigated by the high vacuum temperature programmed (HV-TPD) technique. Both the CO disproportionation yield and the CO methanation efficiency were calculated as a function of temperature and nickel particle size. The dependence on the temperature of the adsorption capacity of the catalytic surface was tested too. A model which explains the CO adsorption modes and consequently the existence of the two reaction mechanisms of the CO methanation was imagined.

INTRODUCTION

According to the literature [1-5] the CO methanation on nickel catalysts is a structure-sensitive reaction for nickel particle sizes up to 8 nm. As far as the Ni/Al_2O_3 catalysts with larger nickel particle sizes are concerned, their activity for the CO methanation is structure-insensitive and similar to the activity of (100) and (111) nickel single-crystal faces [1,5-8]. The above mentioned modification in structure-sensitivity seems to be correlated with the variation of the ratio between the number of corner atoms plus edge atoms and the total number of surface atoms [9] as a function of nickel particle size.

As far as the mechanism of CO methanation on nickel catalysts is concerned, the reported kinetic data are consistent with either hydrogenation of molecular absorbed carbon monoxide, $(CO)_s$, followed by subsequent dehydration [1,6,10,11], or with the CO dissociation followed by subsequent hydrogenation of the surface carbon, C_s [1,12,13]. According to Van Ho and Harriott [14] the gasification of C_s could become the limiting step at high temperature, thus suggesting a modification in mechanism with the temperature increase.

Finally we mention the work of Zagli [15], who, based on TPD and temperature programmed reaction measurements, concluded that the CO methanation on nickel

0040-6031/88/$03.50

catalysts occurs through dissociation of CO followed by C_s hydrogenation.

This paper deals with some results concerning the methanation of CO on Ni/Al_2O_3 catalysts using HV-TPD technique. From the measurements carried out in this work, we tried to obtain information concerning the structure-sensitivity of the reaction and its modification with the temperature and, as far as possible, to draw some conclusions about the reaction mechanisms.

EXPERIMENTAL

Six Ni/Al_2O_3 catalysts prepared industrially or in laboratory were used. Two of them, denoted E and F, were commercial ICI and BASF catalysts. High purity H_2 and CO were used for adsorption.

The TPD measurements were carried out in high vacuum, the desorbed gases being evacuated through the ionization chamber of a MCX-4 (USSR) time-of-flight mass spectrometer. Each catalyst sample was reduced prior the TPD experiment at 773 K in flowing hydrogen. After reduction each sample was submitted to the following sequence of adsorptions followed by the corresponding temperature programmed desorptions: hydrogen adsorption at 293 K, CO adsorption at 293 K, CO adsorption and CO adsorption followed by H_2 adsorption at temperatures between 473 and 673 K. For each TPD experiment the adsorption pressure was 21 torr irrespective of the gas used and of the adsorption temperature. The adsorption time, 30 min, was also the same in all experiments.

The sequence of TPD experiments was begun by one in which H_2 was adsorbed at 293 K. This kind of experiment was repeated until we obtained reproducible TPD curves. We consider that in this moment the catalytic surface is stabilized and cleaned.

After preparing the surface, the TPD experiment with CO adsorption at 293 K was carried out. The purposes of this experiment were to characterize the interactions of the nickel surface with CO and to determine the CO disproportionation yield for each catalyst.

After this we carried out the TPD experiments with CO adsorption and those with CO adsorption followed by H_2 adsorption at high temperatures. These two kinds of TPD experiments were carried out in order to determine the $(CO)_s$ methanation yield, ε, as a function of temperature for each studied catalyst.

Another kind of TPD experiment was carried out in order to test the exposed nickel surface capacity for CO adsorption at various temperatures. These experiments were carried out on fresh samples.

RESULTS AND DISCUSSION

As shown above, the sequence of the TPD experiments was begun by a circle of TPD experiments with H_2 adsorption at 293 K. Two maxima could be observed in the final TPD-curves of every catalyst sample, located at ~353 K and 463 K, the first one probably corresponding to the physical adsorption [16]. The ratio between the peak areas of the two maxima were different for different catalysts, thus indicating differences between the amounts of the two kinds of adsorption centers.

In the following experiments CO was adsorbed at 293 K, but during the temperature programmed desorption both CO and CO_2 were detected. Between 293 and 773 K the TPD curve exhibited three CO maxima and only one for CO_2, irrespective of the catalyst sample. The first two maxima, located at ~348 and 423 K, are characteristic of metallic nondispersed nickel [17], while the third CO maximum, located at 723 K, is characteristic of highly dispersed nickel [18]. This last maximum is probably due to desorption of $(CO)_s$, adsorbed on the nickel centers located on the edges and corners of the crystallites. The CO_2 maximum was located at 523 K, irrespective of the sample. The CO_2 observed in desorption is due to the disproportionation of the $(CO)_s$ adsorbed on the crystal edges [18], whose maximum is located in desorption at 723 K.

Calculating the efficiency, R, of the disproportionation reaction of $(CO)_s$, as the disproportioned fraction of $(C)_s$, we obtained the following values: catalyst D, R=2.4%; catalyst E, R=32%; catalyst F, R=42%. Taking into account the fact that the sample F consists of particles of 5-6 nm, the sample E consists of crystallites of 5-6 nm plus 7% particles of 10 nm and the sample D consists of particles of 5-6 nm, 10nm, 30 nm and even 60 nm, the results mentioned above show that the disproportionation of $(CO)_s$ exhibits a kind of structure-sensitivity from the standpoint of efficiency, which decreases when the particle size increases. One can observe that this structure-sensitivity is opposite to the structure-sensitivity for the CO methanation. However, this observation cannot be a conclusion and should be treated carefully because of the differences between the experimental conditions for the activity measurements and for TPD measurements.

To get comparable results concerning the CO methanation and the CO disproportionation, TPD experiments with CO adsorption and CO adsorption followed by H_2 adsorption, at high temperatures, were carried out. These experiments enabled us to determine the methanation yield of every catalyst sample [18]. For all the six catalyst samples the fraction of the methanated $(CO)_s$ depends on temperature. In figure 1 one can see how the yield depends on temperature for the catalysts D, E and F, well characterized by electron microscopy with respect to their different nickel particle sizes.

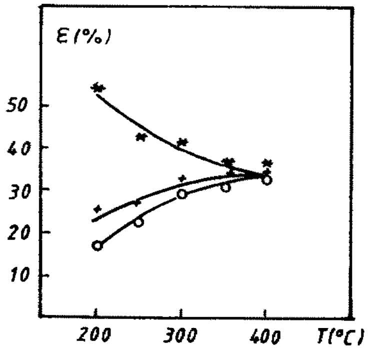

Fig. 1. Temperature dependence of the yield of methanation of the surface species for the D (*), E (+) and F (o) catalyst samples.

One can see that the temperature dependence of the yield ε for the three catalysts is different from one another; it depends on the nickel particle sizes too. This data shows that indeed the methanation yield of the $(CO)_s$ depends on structure in an opposite way than the disproportionation yield of the $(CO)_s$. This fact suggests that, at least at 473 K, the methanation of CO on nickel particles with sizes larger than 20 nm occurs preferably by the hydrogenation of $(CO)_s$ followed by dehydration, and not by the dissociation of $(CO)_s$ followed by C_s gasification.

The decrease of the methanation yield with the temperature increase, exhibited by the catalyst sample D, and the increase of the same yield with the temperature increase for the catalysts E and F, leading at high temperatures to the same value of the yield, suggest, at least for sample D, a modification in the methanation reaction and CO adsorption mechanisms when the temperature increases.

The TPD experiments carried out to test the CO adsorption capacity of the catalytic surface as a function of temperature showed [18] that the adsorption mechanism of CO is modified when the temperature increases: the adsorption capacity for CO increases when the temperature increases.

Taking into account: (a) the reported results, (c) the existence of the two kinds of adsorption centers on the nickel surface, represented by the corner and edge atoms and by the remaining surface atoms, whose ratio varies with the nickel particle size, (c) the gasification of C_s which becomes the limiting step of the CO methanation when the temperature increases and (d) that the difference between the gasification rate and the overall methanation rate decrease when the temperature increases [14], it is obvious that the methanation mechanism depends on the nature of the CO adsorption centers. We suppose that the centers which consist of corner and edge atoms are responsible for the methanation which takes place by dissociation of $(CO)_s$ followed by the gasification of C_s; on the other centers the methanation occurs through hydrogenation of $(CO)_s$ followed by dehydration.

Another assumption is that as the temperature increases, the adsorption mechanism of CO on the "interior" centers changes. As a consequence, the adsorption capacity increases and the methanation reaction mechanism changes from the hydrogenation of $(CO)_s$ followed by dehydration to the dissociation of $(CO)_s$ followed by the gasification of C_s. Therefore for nickel catalysts, no matter what the particle size is, the two mechanisms coexist, only their extent being structure-influenced.

Taking into account the above mentioned assumptions, the literature data as well as our data could be explained in a satisfactory way. Consequently one can conclude the following tentative conclusions.

CONCLUSIONS

At low temperatures, of about 473 K, the methanation of carbon monoxide occurs on the interior nickel centers by hydrogenation of $(CO)_s$ followed by dehydration. As the temperature increases, on these centers the methanation mechanism modifies; at high temperature (~673 K) the methanation only proceeds by the dissociation of $(CO)_s$ followed by hydrogenation of C_s. On the corner and edge nickel centers, the methanation of CO occurs by dissociation of $(CO)_s$ followed by the hydrogenation of C_s. The reaction mechanism on these centers does not modify with temperature.

At temperatures lower than 673 K the methanation of CO occurs by both mechanisms. The extent of each mechanism depends on the catalyst structure and temperature.

The methanation of $(CO)_s$, as it results from our TPD experiments, exhibits a kind of structure-sensitivity at temperatures between 473 and 673 K. The structure-sensitivity is favoured at low temperatures. At 673 K the methanation becomes structure-insensitive.

The methanation activity of Ni/Al_2O_3 catalysts with large particles decreases with the temperature increase, whereas the activity of Ni/Al_2O_3 catalysts with small particles increases with the temperature increase.

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