INVESTIGATION OF THE EFFECT OF H_2S ON THE CATALYTIC TRANSFORMATION OF CARBON-DIOXIDE AND METHANE

PhD Theses

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Preliminaries and Objectives

The industrial realisation of the CO_2+CH_4 reaction could be a solution for both reducing the concentration of greenhouse gases and the utilisation of natural gases with high amount of inert gas content. The products, CO and H_2, could take the role of petroleum which is an important energy source and a row material of chemical industry.

Supported noble metals were found to active catalysts in the CH_4+CO_2 reaction contrary to the Ni samples on which much surface carbon was formed. The sulphur-containing compounds which are present in the raw materials, were less investigated. That's why we chose to investigate the effect of H_2S in the dry reforming of methane. We also paid attention to the secondary processes (CO_2+H_2, CO+H_2, and CH_4+H_2O) and to the interaction of the reactants and the catalysts (CO_2 adsorption, CO disproportionation, CH_4 decomposition, H_2S adsorption).

Our goal was to better understand the mechanism of H_2S poisoning and find a good explanation for the phenomena observed in the experiments.

Experimental methods

The catalysts were made with impregnating of the supports (TiO_2, SiO_2, Al_2O_3, CeO_2, ZrO_2, and MgO) with the aqueous solution of metal-chlorides (Rh, Ru, Pd, Pt). Treatments of the catalyst pellets were made in the reactor in situ.

The reactions were carried out in a continuous flow quartz reactor. The flow rate was 40-300 ml/min, the amount of the catalysts was 0.3-0.5 g. The analyses were made by GC. The reactions were examined with gas mixtures of stoichiometric composition and in the presence of 20 % Ar as diluting gas. When the effect of H_2S was studied the mixture contained 22 or 116 ppm pollutant.

The amount and reactivity of surface carbon formed after 1 hour of the reaction were determined by TPR. The heating rate was 10 K/min.

TPD experiments were made in a quartz reactor, too. The flow rate was 40 ml/min, the heating rate 20 K/min. The analyses was performed by MS.

Results

1. Investigation of CO_2+CH_4 reaction

1.1. Comparing Rh/TiO_2 and Rh/SiO_2 in the reaction of CH_4 with CO_2 it could be seen that Rh/SiO_2 is less active than Rh/TiO_2. H_2S decreases the conversion on all of the catalysts, but while on the noble metals supported on TiO_2 the CO/H_2 ratio increased, it did not changed on SiO_2 supported samples. This indicates that the effect of H_2S on the secondary processes differs on SiO_2 and TiO_2 supported samples. Pre-treating Rh/TiO_2 with H_2S at different temperatures we did not find any deactivation while the amount of surface carbon decreased in such an extent that corresponds to the amount of H_2S mixed to the reactants. This shows that H_2S is bonded on the surface and decreases carbon formation.

1.2. On TiO_2 supported noble metals we found low amount of surface carbon. H_2S decreases the amount of surface residues. The decrease is more than calculated from the activity loss. So the H_2S has an important role in the formation of surface carbon or/and in the removal of it. On supported Rh samples the position of the CH_4-peak in the TPR experiments was at the same temperature independent of the support which suggests that the carbon connects to the metal, not to the support. In this case, too, H_2S suppresses the carbon formation, but on Rh/SiO_2 a new, more inactive carbon was formed which is more prominent in the presence of more H_2S.

2. Investigation of the CO_2+CH_4 reaction's secondary processes

2.1. Among the secondary processes, CO_2 hydrogenation seemed to be interesting. In this case, Rh/TiO_2 is far more active than Rh/SiO_2. The initial behaviour of the catalysts is totally different since we found notable initial activity on Rh/TiO_2 depending on the reduction temperature, which ceased in 40 seconds or could be stopped with a small amount of CO_2 or H_2O.

2.2. In the presence of 22 ppm H_2S the rate of CH_4 formation is higher than in the absence of sulphur. This was also found on titania-supported Ru and Pd. To produce this phenomenon H_2S must be in contact with the fresh sample. On used catalysts H_2S poisoned the reaction. Rh/CeO_2 showed similar activity enhancement. This support is reducible just as TiO_2. On other supports the poisoning effect of H_2S was observed. In the $CO+H_2$ and CH_4+H_2O reactions only the inhibiting effect of H_2S was established.

2.3. In the $CO+H_2$ and CH_4+H_2O reactions only the inhibiting effect of H_2S was established.

3. Elementary steps of the CO_2+CH_4 reaction

3.1. The adsorption of CO_2 on TiO_2 reduced at high temperature resulted in adsorbed CO.

3.2. The disproportionation of CO was enhanced on Rh/TiO_2, and decreased on Rh/SiO_2 by H_2S. It did not influence the reactivity of surface carbon on Rh/TiO_2, but on Rh/SiO_2 the H_2S increased the amount of inactive carbon.

3.3. While CH_4 pulses were added onto Rh/TiO_2 an interesting temperature dependent phenomenon was observed: at 548 K H_2S increases, at 773 K it decreases H_2 formation which is opposite of the changing of the amount of surface carbon. In an oxygen-free environment on Rh/TiO_2 we found CO formation, which suggests that TiO_2 can give O to the CH_x species. H_2S did not influence the ethane formation but decreased the CO formation. The amount of H_2 measured in the TPR experiments decreased not only in the range of CH_4 formation, but at higher temperature, as well, which means that TiO_2 is reduced. In the same process the H_2S did not influence the H_2 formation on Rh/SiO_2. The amount of surface carbon on Rh/SiO_2 is much higher than on Rh/TiO_2. In the case of Rh/SiO_2 H_2S increases the amount of surface carbon formed in the reaction.

3.4. In TPD experiments after H_2S adsorption we got only SO_2 as a product on TiO_2 supported noble metals and on Rh/CeO_2. The explanation for this could be that H_2S is built into the lattice of TiO_2 and CeO_2. This was showed on Rh/TiO_2 by XPS, too.

Conclusions

We explained the different effects of H_2S on TiO_2 and SiO_2 supported samples with the variation of reducibility and surface structure. The fact that notable CH_4 evolution was found in the first seconds of the CO_2+H_2 reaction could lead to the conclusion that during the reduction of TiO_2 supported catalysts O-vacancies are formed close to the metal particles which take part in the reaction. Increasing the reduction temperature this effect became more prehanced. The vacancies are poisoned by water formed in CO_2 hydrogenation. These phenomena were not detected on Rh/SiO_2. Following the above considerations it is probable that sulphur is built into the defect sites of TiO_2 formed during reduction on the titania-metal interface, and this became the active centre for the CO_2+H_2 reaction, which is stable against the water. Further explanation could be that sulphur built into the support, oxidizes the metal, so the rate of CO_2+H_2 reaction increases. Nevertheless this effect would enhance CO hydrogenation, as well. That's why we have to propose a mechanism, in which CO_2 dissociates on the metal-TiO_2 interfaces so the O-vacancies play an important role. Literature data show that while sulphur originating from H_2S leaves the surface, it removes O-atoms, which produces new O-vacancies. Naturally we cannot disregard that sulphur may modify the electron distribution of the catalyst and this affects reaction rates.

H_2 formed in the CO_2+CH_4 reaction in the presence of H_2S may react with CO_2. This process is faster on Rh/TiO_2 than on Rh/SiO_2. H_2 consumption and CO enhanced formation in the CO_2+H_2 process could lead to the increase of the CO/H_2 ratio. The poisoning of the catalysts by H_2S in the CO_2+CH_4 reaction could be explained easily with strong sulphur-metal interaction. The key for further explanation may be surface carbon. H_2S can decrease the formation of surface carbon in two ways. The first is well-known in the literature, which includes that the sulphur poisons those very active metal particles or surface sites where the CH_4 decomposition would be very fast. We think the second alternative may be that sulphur built into the titania creates a physical barrier around the metal for the CH_x groups. This barrier does not allow them to spill over to the support, where they could be accumulated and cause the deactivation of the catalyst.

Publications related to the dissertation

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