

Hydrodechlorination of the chlorinated hydrocarbons over Pt- and Pd-containing zeolites

Ph.D. thesis

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1. Introduction

People, while making effort to satisfy the claims of civilisation, to save health and improve life conditions, transform the surrounding world according to their own short-distance needs.

The chemical industry produces about 70000 kinds of molecules and materials relatively in high amounts and during the production about 7000000 kinds of secondary products are also formed. We know only in part their environmental and health effects, a full survey would almost be impossible. A lot of chemicals produced in high quantities were proven to be toxic, carcinogenic and mutagenic and they are accumulating in the environment, endangering all living organisms. The halogen-containing organic compounds also have effects like these, especially the chlorinated hydrocarbons. Because of their favourable chemical and physical properties these compounds were and still are applied in high amounts in industry, agriculture and public health.

The secondary products and the chlorine-containing hydrocarbons not needed any more cannot be simply deposited in the waste-yard or emitted into the atmosphere. In one way or another these compounds must be destroyed.

Decomposition of chlorinated hydrocarbons can take place in oxidative or reductive ways. The first process results in favourable case carbon monoxide, water and halogen-containing inorganic compounds, not too dangerous for the environment. The reductive process results in reusable products, however, instead of cheap air the relatively expensive hydrogen has to be used. The purity and the worth of products produced determine the economy of this procedure. Thus, the aim is to develop catalysts on which reusable products are formed in high selectivities.

2. Aims

Our aims were to answer the following problems concerning the reductive decomposition of chlorinated hydrocarbons and the hydrodechlorination reactions.

Preparation and characterisation of noble metal containing zeolite catalysts by various physical-chemical methods. From these experiments one can conclude (i) changes in the structure of zeolite, (ii) size of metal nanoparticles formed upon reduction and (iii) the quantity of acid groups formed in the zeolite.

The differently pretreated catalysts can usually tremendously influence the nature of active centres and their chemical environment. The characterisation results of zeolites used and variously pretreated may show whether the (i) acidity of catalysts, (ii) situation of metal nanoparticles formed, and (iii) size of metal particles depend on changing the pretreatment conditions or not.

From following the reaction by IR spectroscopy we aimed to learn about the surface products and the nature of the reaction. In the knowledge of the parent materials, the secondary surface products and the final products we hoped to be able to present a suggestion for the possible mechanism of the transformation.

The reactor-experiments were hoped to serve with quantitative data to better understand the qualitative relationship between the reactants and products formed. These pieces of information were essential in exploring the reaction mechanism.

3. Experimental

We synthesised zeolites of various types and compositions: NaY-FAU, NaM-MOR, NaZSM-5-MFI and their ion-exchanged (exchanged with hydrogen-, cobalt-, platinum- and palladium ions), and their impregnated forms.

Pretreatment of the zeolite samples occurred with oxidative and oxidative-reductive methods. The catalysts prepared and pretreated were characterised by several instrumental methods.

Adsorbed molecules formed on the surface of the catalysts were detected by IR spectroscopy just as the products and by-products formed during the reaction. For these measurements an IR cell system was necessary, which allowed studying the catalysts at higher temperatures and lower pressures.

We determined the content of Pt and Pd by ICP, the content of Co by complexometry and UV-VIS spectroscopy. In the KBr technique 2 mg of used zeolite was weighed into 200 mg of KBr matrix and from this blend we pressed wafer with 1 cm of diameter and recorded its spectrum. With this method we could investigate changes in the zeolite framework after the reaction.

For the acidity measurement we introduced 10 Torr of pyridine onto the samples pretreated, after that slowly heated up to 100, 200, 300 and 400 °C. After 1 h adsorption the cell was evacuated for 1 h and cooled to room temperature and the spectra were recorded on a Mattson Genesis 1 FT-IR instrument equipped with a LaTiO₃ detector with a resolution of 1 cm⁻¹.

The size of Pt and Pd particles was characterised by transmission electron microscopy. For the registering the images a CM10 microscope with 100 kV acceleration voltage was used.

The X-ray diffraction measurements allowed us to investigate changes occurring in the zeolite lattice. These measurements were carried out on a DRON-2 diffractometer. The diffractograms were recorded within the $2\theta = 4^\circ - 40^\circ$ range.

The NMR measurements were performed on a BRUKER MSL 400 type instrument. The ²³Na, ²⁷Al, ²⁹Si MAS NMR (Magic Angle Spinning NMR spectroscopy) measurements serve valuable information about the adsorption and whether changes occurred during the surface reaction or not. Furthermore, the ¹³C and ¹⁹F NMR techniques serve information on the quantitative and qualitative nature of the surface reactions. The zeolite samples were

placed into a special NMR tube and were evacuated at 450 °C for 2 h, after that the activated samples were loaded with the reactants in a ratio of 0.01 g_{CFC}/0.05 g_{zeolite}. Then, the NMR tube was sealed. The spectra were recorded at different temperatures.

The reactor experiments were carried out in a standing-bed reactor, the products were analysed by gas chromatography.

4. New scientific results

1. During the work leading to this dissertation we prepared Pt- and Pd-containing zeolites by the ion-exchange and the incipient wetness methods and fully characterised them with special emphasis on the effects of various pretreatment and reduction methods and the quantitative determination of Brønsted and Lewis acid sites by pyridine adsorption.
2. Transmission electron microscopy and X-ray diffractometry were applied to determine the size of noble metal (Pt, Pd) clusters formed upon reduction in the zeolite samples of various methods prepared by ion-exchange and impregnation. It was established that for the impregnated samples the metal particles were on the outer surface of zeolite crystals averaging ~20 nm in diameter, while for the ion-exchanged samples they were uniformly dispersed in the large cavity of the zeolite with smaller than 2 nm in diameter. In the latter case the crystallinity of the zeolite decreased.
3. The earlier mechanistic suggestion that during the interaction between freons (CCl₂F₂, CHClF₂) and zeolites the fluor content of freons reacts with the aluminium of zeolite forming AlF₃ in the zeolite was proven by solid-state NMR. This reaction resulted in the dealumination of the zeolites, while the zeolite skeleton partially or totally collapsed. The extent of dealumination parallels with the loss in crystallinity and decreases with the increasing Si/Al ratio in the following order: FAU>MOR>ZSM-5.
4. It was established that in hydrogen atmosphere the interaction between Pt,NaY-FAU and CHClF₂ was not hydrodechlorination but a reaction with the oxygen content of the zeolite serving CO as the final product. CO adsorbed on Pt was identified by infrared spectroscopy.
5. During the interaction between carbon tetrachloride and Pt,NaY-FAU in the absence of hydrogen we experienced the formation of phosgene in complete agreement with literature data, which shows the reaction is rather stoichiometric than catalytic. In hydrogen atmosphere CH₄ and HCl as main products were detected. At lower temperatures (100 °C and 200 °C) chloroform was obtained in high amount. The amount of this secondary product is shown to go through a maximum with the increase in temperature. In spite of applying hydrogen

atmosphere, at lower temperature on the ion-exchanged Pt,NaY-FAU zeolite having considerable amount Brønsted acidic centres phosgene was also formed. We could not observe the same phenomenon on the impregnated samples not having Brønsted centres that means the active centre of hydrodechlorination reaction was the noble metal cluster, while that of the reaction with the zeolite was the Brønsted acid centre.

6. On Pt-containing zeolites during the hydrodechlorination of trichloroethylene and tetrachloroethane predominantly ethane and HCl were detected. The reactor experiments evidenced that incorporation of Co next to Pt decreased the selectivity of ethane, while on the zeolite containing only Co partial hydrodechlorination occurred resulting in ethyl chloride, dichloroethane and high amount of trichloroethane.

7. On Pd,NaY-FAU zeolite during the hydrodechlorination of CCl₄ we could also detect the by-product phosgene in low amount, but in contrast with the results obtained on Pt,NaY-FAU chloroform was not detected, the main product was not methane, but ethane and the reaction took place at higher temperature.

8. On the basis of our experiments it could be established that the activity and selectivity of the Pt,NaY-FAU and the Pd,NaY-FAU samples were different. Since Pt is „more noble” than Pd, the adsorption of carbon tetrachloride and the secondary product are stronger over Pd particles, thus, the probability of hydrogen insertion is higher on Pd than on Pt. It explains well that on the Pd-containing zeolite chloroform was not formed and the main product was ethane instead of methane.

5. Utilisation of results

The presented results in spite of the fundamental nature of the research may be used when environmental safety is of concern. It is well known the halogen-containing compounds mean danger for not only the biosphere but for the ozone layer of our planet. During our work we investigated the simplest members of these compounds. We were interested in whether they can be transformed to more valuable products like hydrocarbons under heterogeneous catalytic conditions applying hydrogen. In our experience this process under suitable conditions is possible, the technology can be applied in certain cases and under conditions in the industry as well.

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