

ETHANE AND PROPANE TRANSFORMATION ON SUPPORTED PLATINA METALS AND RHENIUM CATALYSTS

Ph.D. Thesis

Péter Tolmacsov

Supervisor:

Dr. Frigyes Solymosi

Member of the Hungarian Academy of Sciences

University of Szeged

Department of Solid State and Radiochemistry

Reaction Kinetics Research Group of the Hungarian Academy
of Sciences

2008

Introduction

In our days most products of the chemical industry are produced catalytically. Out of the various catalytical processes especially important are those involving mineral oil and natural gas. In these processes an ever greater role is played by various heterogeneous catalytic processes, since the separation, regeneration and reutilization of catalysts, is considerably easier than in the case of homogeneous catalytic processes.

In research special attention is given to the catalytic transformation of hydrocarbons (C_1 - C_4) since these feedstocks occur in great quantities in natural gas. Various ways of transformation are possible and widely researched such as coupling, aromatization, steam and dry reforming, and partial oxidation.

Numerous publications address issues of the decomposition of ethane and propane. Researchers devote considerable attention to supported platinum metal catalysts, especially to various zeolite support catalyst. It has been determined that the first step of the transformation is the dehydrogenation of alkane, followed by the oligomerization and aromatization of alkane. A necessary prerequisite of aromatization is the bifunctional nature of the catalyst. The metal applied to the support is responsible for the dehydrogenation of alkane, while acidic centers of zeolite are responsible for coupling and aromatization.

Various publications have reported on attempts to produce zeolite catalysts promoted with the help of other metals (Mo, Ni and Ga) and active in alkane aromatization processes. It has been proven that their catalytic activity is comparable to that of supported Pt metal catalysts.

One of the aims of reforming short chain alkanes is to produce synthesis gas. It can be gained directly from alkanes in three different ways: through steam reforming, dry reforming, and partial oxidation. A great advantage of dry reforming is that it involves a smaller degree of carbon deposit than steam reforming, and it is easier to control from the point of view of oxidation than partial oxidation. Natural gas often includes a great quantity of carbon-dioxide, which could be utilized easier through the process of dry reforming.

Relatively few publications discuss the dry reforming of propane, and most of those that do report on having investigated supported Ni catalysts. Even though these catalysts show very favorable characteristics, they also have a high level of structure sensitivity: they easily deactivated due to the aggregation of the metal particles as well as the result of the deposition of carbon.

Objectives

In this dissertation I seek to answer the question how dotation with rhenium affects the catalytic activity of H-ZSM-5 support in the process of the decomposition of ethane and propane, especially the change in the selectivity of benzene. I also want to find whether there is an ideal catalyst composition whose activity stands out during the investigated reactions.

In investigating the decomposition of propane I will compare the activity order of alumina supported Pt metals and their capacity. I will pay special attention to catalyst Rh/Al₂O₃, in the case of which I will investigate how different supports affect the catalytic character of this metal.

I also want to find whether the catalyst Re/Al₂O₃ can be compared, from a catalytic point of view, with the catalyst Rh/Al₂O₃ in the reaction of propane decomposition.

After this, I will investigate the process of dry reforming of propane on Pt metals and Re catalysts. I seek to answer, first, whether an ideal reaction gas mixture in the process of reforming, and, second, how temperature affects reforming. In the case of rhodium – similarly to the decomposition of propane – I will investigate the support effect as well.

After the measurements, I will also take TPR measures on used catalysts to determine the quantity and quality of the carbon deposited on the surface.

Methods

The catalysts were prepared by impregnating the supports with solutions of metal salts.

The impregnated Pt catalysts were dried at 383 K. The fragments of the dried catalysts were oxidized at 523 K for 30 min and reduced at 773 K in the catalytic reactor for 1 hour. The Re catalyst was dried at 383 K and calcinated at 773 K for 4 hours. Before the measurements the catalysts were reduced with hydrogen in the catalytic reactor for 1 hour.

The ethane and propane content were 12.5%. In the study of the propane + carbon-dioxide reaction we used a stoichiometric (1:3) gas mixture, where the propane content was again 12.5%.

The amount of catalysts used was 0.3 g. Catalytic measurements were carried out in a fixed-bed continuous-flow reactor. The system was operated at total pressure of 1 atm. Analyses of the exit gases were performed with a Hewlett-Packard 5890 GC.

Results

1. I have found that, regardless of the $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio of the H-ZSM-5 support, rhenium considerably increased the conversion and selectivity of benzene during the decomposition of ethane and propane. In the investigated processes the most active catalyst composition is 2% Re/H-ZSM-5 (30). Its activity is comparable to that of Pt metal catalysts in the investigated decomposition reactions. During the reaction the activity of the catalyst decreases due to carbon deposition, but it does not cease completely, as a result of the carbon migrating onto the support.
2. In investigating the decomposition of propane, in the case of alumina support, I established the following Pt metals activity order: $\text{Ru} > \text{Rh} > \text{Pd} > \text{Pt} \sim \text{Ir}$. The activity order of supported Rh catalysts decreases along the support order $\text{TiO}_2 > \text{Al}_2\text{O}_3 > \text{MgO} > \text{SiO}_2$. With the decrease of temperature, in the case of every catalyst processes of dehydrogenation became primary.
3. I have shown that during the reaction of dry reforming of propane, alumina supported Pt catalysts have kept the activity order seen in propane decomposition, and the activity order of supports did not change in the case of Rh catalysts either.
4. In the case of catalysts $\text{Rh}/\text{Al}_2\text{O}_3$ and $\text{Re}/\text{Al}_2\text{O}_3$ I have found that the gas mixture of 1:3 proportion, following the $\text{C}_3\text{H}_8 + 3 \text{CO}_2 \rightarrow 6 \text{CO} + 4 \text{H}_2$ reforming function, can be considered a threshold limit. A further increase in the quantity of carbon-dioxide does not considerably affect the H_2/CO ratio.

5. I have shown that in the case of catalysts Rh/Al₂O₃ and Re/Al₂O₃, the order of propane is zero at 923 K during the process of dry reforming of propane, and the order of carbon-dioxide is fractional (0.4-0.45 for Rh/Al₂O₃; 0.6 for Re/Al₂O₃).
6. As a result of the TPR measurement following the catalytic examination alumina supported Pt metals, I have found that after the decomposition of propane and dry reforming of propane only a single amorphous carbon form can be found on the surface, which can be hydrogenated in the 850-1100 K temperature range. During the dry reforming of propane I have determined carbon deposit of the order of *one* less than in the process of the decomposition of propane.
7. TPR measurements carried out on rhenium catalysts have shown that after the decomposition of propane and dry reforming of propane carbon forms of similar kinds but of various activity form on the surface, which can be hydrogenated in the 650-950 K temperature range.

Publications

Papers related to this thesis:

- 1. Decomposition of propane and its reactions with CO₂ over alumina-supported Pt metals**
F. Solymosi, P. Tolmacsov
Catalysis Letters, 83 (2002) 183-186
I.F.: 1.852
- 2. CO₂ reforming of propane over supported Rh**
F. Solymosi, P. Tolmacsov, K. Kedves
Journal of Catalysis, 216 (2003) 377-385
I.F.: 3.276
- 3. Conversion of ethane into benzene on Re/ZSM-5**
F. Solymosi, P. Tolmacsov
Catalysis Letters, 93 (2004) 7-11
I.F.: 1.904
- 4. Reactions of propane and n-butane on Re/ZSM-5 catalyst**
F. Solymosi, P. Tolmacsov, A. Széchenyi
Studies in Surface Science and Catalysis, 147 (2004) 559-564
I.F.: 0.489
- 5. Dry reforming of propane over supported Re catalyst**
F. Solymosi, P. Tolmacsov, T. Sili Zakar
Journal of Catalysis, 233 (2005) 51-59
I.F.: 4.780

Papers not related to this thesis:

- 6. Adsorption and Reaction of CO₂ on Mo₂C Catalyst**
F. Solymosi, A. Oszkó, T. Bánsági, P. Tolmacsov
Journal of Physical Chemistry B, 106 (2002) 9613-9618
I.F.: 3.379

Impact factor of the papers: **15.680**

Conference presentations and posters related to this thesis:

1. CO₂ reforming of propane over supported Pt catalyst

F. Solymosi, P. Tolmacsov, K. Kedves

18st North American Catalysis Society Meeting
Cancun, Mexico (June 1-6, 2003)

2. Reaction of propane and n-butane on Re/ZSM-5 catalyst

F. Solymosi, P. Tolmacsov, A. Széchenyi

7th Natural Gas Conversion Symposium
Dalian, China, (June 6-10, 2004)

Conference presentations and posters not related to this thesis:

3. The synthesis of dimethyl carbonate from methanol and carbon dioxide

P. Tolmacsov, K. Almusaiter, F. Solymosi

1st European Chemistry Congress
Budapest, Hungary (August 27-31, 2006)