5. F. Solymosi, **A. Széchenyi**: Aromatization of isooctane on Mo_2C catalysts
Catalytic Processing of Renewable Sources: Fuel, Energy, Chemicals
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6. **A. Széchenyi**, F. Solymosi: Aromatization of n-octane on Mo_2C-containing catalysts
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C_4 and C_8 hydrocarbons transformation on Mo_2C and Re contaning catalysts

PhD Thesis

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Introduction

One of the largest challenges of these days is the development and introduction of the ecologically accepted chemical technologies. The heterogeneous catalysis has a main role in it, so the development of the new catalysts and processes is of high importance.

The upgrading of lower alkanes is an important subject of heterogeneous catalysis. One of the great challenges in this area is to transform methane into higher hydrocarbons with high conversion and selectivities, which represents one route of converting the cheap raw materials into more valuable compounds. The discovery that methane can be converted into benzene on MoO_3/ZSM-5 opened a new route for the utilization of methane. It turned out, however, that not the MoO_3 but Mo_2C is the key component for the activation of methane, which is formed from MoO_3 during the induction period of the reaction. In the subsequent works a great attention has been devoted to the formation, structure and reactivity of Mo_2C on ZSM-5.

Objects

In our laboratory we continued our work in two directions: elaborating the effect of Mo_2C on the aromatization of hydrocarbons, and studying the chemistry of hydrocarbon fragments, C_xH_y, the primary products of the activation of the above compounds, on Mo_2C/Mo(100) in UHV by several spectroscopic methods.

As a continuation of this research program the reaction of C_4 és a C_8 hydrocarbons has been investigated on the same Mo_2C/ZSM-5 catalyst used in previous works. Attention is paid to the low temperature interaction of butane with the catalyst, to the effects of the composition of ZSM-5 on the catalytic performance of Mo_2C, to the influence of preparation and pretreatments of the

10. **A**. **Széchenyi,** F. Solymosi
Production of hydrogen in the decomposition of ethanol and methanol over unsupported Mo_2C catalyst
J. Phys. Chem. B 111 (2007) 9509.

Impact factor of the papers: 17,780

Conference lectures and posters related to this thesis:

1. F. Solymosi, **A. Széchenyi** and R. Németh
Aromatization of n-butane over supported Mo_2C catalysts
18th North American Catalysis Society Meeting
Cancun, Mexico, June 1-6. 2003, lecture.

2. F. Solymosi, P. Tolmacsov, **A. Széchenyi**
Reaction of propane and n-butane on Re/ZSM-5 catalyst
7th Natural Gas Conversion Symposium
Dalian, Kína, June 6-10. 2004, lecture

3. **A. Széchenyi**, F. Solymosi
C_4 szénhidrogének átalakulása Mo_2C tartalmú hordozós katalizátorokon
Katalízis Munkabizottság és a Felületkémia és Nanoszerkezet Munkabizottság ülése
Szeged, May 19-20. 2005, lecture

4. **A. Széchenyi**
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Matematikai és Természettudományi Kuratórium, Fiatal kutatók meghalgatása
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n-Octane aromatization on Mo_2C-containing catalysts
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Impact factor: 2.630

Impact factor of the papers related to this thesis **10,630**

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6. M. Szekeres, **A. Széchenyi**, K. Stepan, T. Haraszti, I. Dékány
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Aromatization of ethanol on Mo_2C/ZSM catalysts
Catal. Lett. 110 (2006) 85.

Impact factor: 1.772

8. R. Barthos, **A. Széchenyi,** F**.** Solymosi
Decomposition and aromatization of ethanol on ZSM-based catalysts
J. Phys. Chem. B 110 (2006) 21816.

Impact factor: 4.115

9. R. Barthos, **A. Széchenyi,** F**.** Solymosi
The decomposition of ethanol over Mo_2C/carbon catalysts
Appl. Catal. A 327 (2007) 95.

catalysts. Detailed measurements are also performed on Mo_2C deposited on different inactive oxide supports. In order to obtain a deeper insight into the mechanism of the formation of aromatics, the reaction of unsaturated products, assuming that the starting compound in the formation of benzene, is also examined on Mo_2C-containing catalysts.

Methods

Mo_2C was prepared by the carburization of MoO_3 as was described by M.L.H. Green and coworkers. The oxide was heated under 10% v/v C_2H_6/H_2 gas mixture from 300 K to 900 K at a heating rate of 0.8 K/min. The MoO_3 supported samples were prepared by impregnating the support with a basic solution of ammonium-heptamolybdate. Supported Mo_2C catalysts have been made in the same way as the pure Mo_2C, by the carburization of MoO_3-containing supports with C_2H_6/H_2 gas mixture. All the catalysts used in the study have been characterized by XPS and FTIR measurements.

Catalytic reaction was carried out at 1 atm of pressure in a fixed-bed, continuous flow reactor consisting of a quartz tube. Generally 0.3 g of loosely compressed catalyst sample was used. Reaction products were analyzed gas chromatographically using a Hewlett-Packard 5890 gas chromatograph with a 60 m long GS-GASPRO column, and Agilent 4890 gas chromatograph equipped with HP-PLOT Al_2O_3 30 m long capillary column and PORAPAQ Q+S pocked column. The amount of coke deposited on the catalyst during the reaction was determined by temperature programmed reaction (TPR).

Results

1. Deposition of Mo_2C changed the catalytic performance of the ZSM-5, and promoted the dehydrogenation and aromatization processes**.**

2. Reaction products determined at zero conversion on Mo_2C/ZSM-5 samples suggested that aromatics are formed in the secondary processes very likely in the reactions of olefins formed in the primary reactions**.**

3. Mo_2C catalyzed the dehydrogenation and aromatization of examined hydrocarbons even when it was deposited on an inactive silica support, which suggested that the oligomerization and aromatization processes of hydrocarbons might proceed on the Lewis sites of the Mo_2C/SiO_2**.**

4. As Mo_2C exerted much less influences on the reaction of 1-butene occurring on ZSM-5 and only slightly enhanced the formation of aromatics, it was inferred that the alkyl species, the primary product of the activation of hydrocarbons on Mo_2C, is effectively converted to a compound leading to aromatics.

5. The Re catalyzed the dehydrogenation and aromatization of n-butane even when it was deposited on an inactive silica support.

6. Unsupported Mo_2C is an active catalyst in the dehydrogenation of n-octane yielding various octenes, and also in its the aromatization at 723-873 K. The main aromatic products are o-xylene, ethylbenzene, toluene and benzene in decreasing selectivity. It is assumed that the monofunctional mechanism operates.

7. The catalytic performance of Mo_2C is considerably enhanced when it was dispersed on Al_2O_3, SiO_2 and ZSM-5. The distribution of aromatics depended on the nature of the support. On Mo_2C/Al_2O_3 C_8 aromatics were the dominant products, whereas on Mo_2C/SiO_2 and Mo_2C/ZSM-5, their hydrogenolysis occurred to yield benzene and toluene. The results are explained by the bifunctional mechanism.

Publications

Papers related to this thesis:

1. F. Solymosi, R. Németh, **A**. **Széchenyi**
Aromatization of n-butane over supported Mo_2C catalysts
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Impact factor: 1.559

2. F. Solymosi, **A**. **Széchenyi**
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3. F. Solymosi, P. Tolmacsov, **A. Széchenyi**
Reactions of propane and n-butane on Re/ZSM catalyst
Stud. Surf. Sci. Catal. 147 (2004) 559.

4. F. Solymosi, **A**. **Széchenyi**
Aromatization of isobutane and isobutene over Mo_2C/ZSM-5 catalyst
Appl. Catal. A 278 (2004) 111.

Impact factor: 2.378