5. F. Solymosi, A. Széchenyi: Aromatization of isooctane on Mo$_2$C catalysts
Catalytic Processing of Renewable Sources: Fuel, Energy, Chemicals

6. A. Széchenyi, F. Solymosi: Aromatization of n-octane on Mo$_2$C-containing catalysts
8$^{th}$ Pannonian International Symposium on Catalysis
Szeged, July 4-7. 2006, poster.

C$_4$ and C$_8$ hydrocarbons transformation on Mo$_2$C and Re containing 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$_2$C 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$_2$C on ZSM-5.

Objects

In our laboratory we continued our work in two directions: elaborating the effect of Mo$_2$C on the aromatization of hydrocarbons, and studying the chemistry of hydrocarbon fragments, C$_x$H$_y$, the primary products of the activation of the above compounds, on Mo$_2$C/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$_2$C/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$_2$C, to the influence of preparation and pretreatments of the catalyst.

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$_2$C catalysts
18$^{th}$ 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
7$^{th}$ Natural Gas Conversion Symposium
Dalian, China, June 6-10, 2004, lecture

3. A. Széchenyi, F. Solymosi
C$_4$ szénhidrogének átalakulása Mo$_2$C tartalmú hordozós katalizátorokon
Katalízis Munkabizottság és a Felületkémia és Nanoszerkezet Munkabizottság ülése
Szeged, May 19-20, 2005, lecture

4. A. Széchenyi
Izobután és izobutén aromatizációja Mo$_2$/ZSM-5 katalizátoron
Matematikai és Természettudományi Kuratórium, Fiatal kutatók meghallgatása
Budapest, June 10, 2005, lecture

10. A. Széchenyi, F. Solymosi
Production of hydrogen in the decomposition of ethanol and methanol over unsupported Mo$_2$C catalyst
5. A. Széchenyi, F. Solymosi

n-Octane aromatization on Mo$_2$C-containing catalysts

Impact factor: 2.630

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

Papers not related to this thesis:

Layer-by-layer self-assembly preparation of layered double hydroxide/polyelectrolyte nanofilms monitored by surface plasmon resonance spectroscopy

Impact factor: 1.263

7. A. Széchenyi, R. Barthos, F. Solymosi
Aromatization of ethanol on Mo$_2$C/ZSM catalysts

Impact factor: 1.772

8. R. Barthos, A. Széchenyi, F. Solymosi
Decomposition and aromatization of ethanol on ZSM-based catalysts

Impact factor: 4.115

9. R. Barthos, A. Széchenyi, F. Solymosi
The decomposition of ethanol over Mo$_2$C/carbon catalysts

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$_2$O$_3$ 30 m long capillary column and PORAPAQ Q+S packed column. The amount of coke deposited on the catalyst during the reaction was determined by temperature programmed reaction (TPR).
Results

1. Deposition of Mo$_2$C changed the catalytic performance of the ZSM-5, and promoted the dehydrogenation and aromatization processes.

2. Reaction products determined at zero conversion on Mo$_2$C/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$_2$C 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$_2$C/SiO$_2$.

4. As Mo$_2$C 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$_2$C, 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$_2$C 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$_2$C is considerably enhanced when it was dispersed on Al$_2$O$_3$, SiO$_2$ and ZSM-5. The distribution of aromatics depended on the nature of the support. On Mo$_2$C/Al$_2$O$_3$ C$_8$ aromatics were the dominant products, whereas on Mo$_2$C/SiO$_2$ and Mo$_2$C/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$_2$C catalysts

2. F. Solymosi, A. Széchenyi
   Aromatization of n-butane and 1-butene over supported Mo$_2$C catalyst

3. F. Solymosi, P. Tolmacsov, A. Széchenyi
   Reactions of propane and n-butane on Re/ZSM catalyst

4. F. Solymosi, A. Széchenyi
   Aromatization of isobutane and isobutene over Mo$_2$C/ZSM-5 catalyst