

**Possible heterogeneous catalytic reactions of ethane
and propane on Mo₂C containing catalysts**

and

**Surface chemistry of HNCO and NCO
on Pd(100) single crystal**

Ph. D. thesis

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Szeged
2008

I. Introduction and aim

One of the main tasks of the heterogeneous catalytic research is to find new, more effective catalysts.

The catalytic properties of Mo_2C are similar to platinum metals, for this reason it is suitable to substitute them. Both catalysts are used for activate C-H bonds and produce $-\text{C}_x\text{H}_y$ species. Mo_2C is a “softer” catalyst and enhances the lifetime of formed $-\text{C}_x\text{H}_y$ species, providing an opportunity to stabilize these species by coupling or dehydrogenation. In the same reaction conditions the cracking of C-C bond occurs more likely on platinum metals than on Mo_2C containing catalysts. On the other hand Mo_2C is more resistant against catalytic poisons (like sulfur), and its price is lower than that of platinum metals.

We studied the dehydrogenation and aromatization processes of ethane and propane on Mo_2C containing catalysts. Besides methane, these two hydrocarbons occur in large quantities in the natural gas, but ethane and propane formed in a noticeable amount in the chemical industry, for example in the oil refinery. Transformation of these hydrocarbons to more valuable compound is a very important task for the industry. Benzene, toluene and xylenes produced by aromatization of ethane and propane are very important starting materials for the organic chemical industry. The dehydrogenation of ethane and propane results in the formation of ethylene and propylene, and the polymerization of the later products is one of the basic processes in the plastics industry. Propylene is also useful for producing branched hydrocarbons with higher carbon number to improve the octane number of gasoline. The products of both the aromatization and the dehydrogenation are counted on comprehensive use in the industry, and the starting materials of these reactions are available in great quantities and

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4. Kecskés T, **Németh R**, Raskó J, Kiss J
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at relatively low cost. At the same time the catalytic features of supported Mo₂C were not studied in these reactions, this explains our efforts in the characterization of these systems.

In the second part of our work we performed experiments in ultrahigh vacuum condition to study another catalytic problem, the surface chemistry of isocyanic acid and isocyanate species on Pd(100) single crystal surface.

The catalytic conversion of harmful gases arising from exhaust system of the vehicle is widely studied problem. The main processes are the reduction of nitrogen oxides (mainly nitrogen monoxide) to nitrogen, and the total oxidation of hydrocarbons and carbon monoxide (produced in the incomplete oxidation in the engine) to water and carbon dioxide. Oxygen atoms necessary for the CO oxidation to CO₂ come from O₂ cleavage or from NO reduction. The latter reaction is especially remarkable, because the oxygen atoms created by reduction of NO directly oxidize the CO molecule without other components (for example oxygen gas) or other reaction steps, while harmless nitrogen forms from the nitrogen monoxide. For this reason, the NO + CO reaction has been extensively studied in the past. The intermediate formed during the reaction is isocyanate, and investigation of this species is necessary to discover the reaction mechanism.

II. Experimental methods

Hexagonal Mo₂C was prepared by temperature programmed reaction of MoO₃ and a gas mixture containing 20 vol% methane and 80 vol% hydrogen.

Supported Mo₂C catalyst was prepared by the carburization of calcined MoO₃/SiO₂ or MoO₃/ZSM-5 in the catalytic reactor. MoO₃/SiO₂ and MoO₃/ZSM-5 catalysts were prepared by impregnating silica (Cab-O-Sil, surface area: 200 m²/g) or H-ZSM-5 (Si/Al = 55) with a basic solution of ammonium heptamolybdate to yield a nominal 2 wt% of MoO₃.

Catalytic reaction was carried out at 1 atm of pressure in a fixed-bed, continuous-flow reactor consisting of a quartz tube. In most cases the flow rate was 12 ml/min. The carrier gas was Ar. The ethane or propane content was 12,5 %, which was kept constant in all experiments. Generally 0,5 g of loosely compressed catalyst sample was used. Reaction products were analyzed gas chromatographically with a *Hewlett–Packard 5890 Series II* gas chromatograph and a Porapak QS column using both the thermal conductivity and flame ionization detectors. The selectivity values of product formation represent the fraction of ethane or propane that has been converted into specific products taking into account the number of carbon atoms in the molecules. The supplementary method used was temperature-programmed desorption (TPD) with a heating rate of 5 K/min.

Infrared spectra were recorded with a Biorad Fourier transform IR spectrometer (FTS 155), the resolution was 4 cm⁻¹. Catalysts were characterized by XPS (Kratos XSAM 800) measurements.

In the second part we used ultrahigh vacuum (UHV) system and reflection absorption infrared spectroscopy (RAIRS) to explore the surface chemistry of isocyanic acid and isocyanate species on Pd(100) single crystal surface. RAIRS experiments were completed with temperature-programmed desorption (TPD) measurements, in the course of which the desorbed species were detected by mass spectrometer (MS). Auger electron spectroscopy (AES) was applied to control the surface purity.

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9. T. Kecskés, **R. Németh**, J. Kiss
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10. J. Kiss, F. Solymosi, A. Erdőhelyi, A. Berkó, L. Deák, J. Raskó, É. Novákné Hajdú, L. Óvári, R. Barthos, **R. Németh**, A. Hancz, T. Kecskés, J. Szökő, A. Farkas
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11. R. Barthos, T. Bánsági, L. Deák, A. P. Farkas, Á. Koós, **R. Németh**, A. Széchenyi, A. Szőke, P. Tolmacsov, F. Solymosi
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Partial oxidation of methane on supported alkali molybdate catalysts
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New reaction route of HCOOH catalytic decomposition
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9. J. Kiss, **R. Németh**, Á. Koós, J. Raskó
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Total impact factor of the publications: **21,572**

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2. F. Solymosi, **R. Németh**, L. Óvári
Aromatization and oxidative dehydrogenation of ethane on supported
Mo₂C catalyst
*Symposium on Site Isolation and Phase Cooperation in Selective
Oxidation Catalysis*, Irsee, Germany, 2000.

3. A. Oszkó, **R. Németh**, J. Raskó, A. Erdőhelyi
Spectroscopic characterization of alkali metal molybdates
XIVth International Symposium on the Reactivity of Solids, Budapest,
Hungary, 2000.

4. F. Solymosi, **R. Németh**, L. Bugyi
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*International Chemical Congress of Pacific Basin Societies (PacifiChem
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Effects of CO₂ on the reaction of ethane over supported Mo₂C catalysts
17th North American Catalysis Society Meeting, Toronto, Canada, 2001.

The experiments were performed in a two-level UHV system with a base pressure of 5×10^{-10} mbar. The lower part of the chamber had facilities for Auger electron spectroscopy (AES, Physical Electronics) to control the surface purity and temperature-programmed desorption (TPD), in the course of which the desorbed species were detected by mass spectrometer (MS, Balzers Prisma QMS 200). The upper part was equipped with a single-beam Fourier transform IR (FTIR) spectrometer (*Mattson Unicam, Research Series*), which was used for reflection absorption infrared spectroscopic (RAIRS) measurements. All IR spectra were averaged over 512-1024 scans using an MCT detector cooled by liquid nitrogen at 4 cm^{-1} resolution.

The palladium single crystal was cleaned by cycles of argon ion bombardment at room temperature and at 650 K (ion current: 11 μA , ion energy: 1,5 keV) and a short annealing to 1200 K. The gases used in the experiments were of 99,99 % purity. The preparation of HNCO involves the dropwise addition of a saturated aqueous solution of potassium cyanate (KOCN, BDH Chemicals, 98 % purity) to concentrated phosphoric acid (Baker, 85 % by weight in water) under vacuum. The HNCO vapor produced in this reaction was condensed at 190 K cooled by a dry ice/acetone bath under dynamic vacuum conditions. This product was twice statically vacuum distilled from 240 to 190 K to remove impurities. The purity of HNCO has been checked by MS. The HNCO was stored at LN₂ temperature.

III. New scientific achievements

1. The oxidative dehydrogenation of ethane on Mo₂C/SiO₂ catalyst

- 1.1. The unsupported Mo₂C and the SiO₂ support exhibited a very low catalytic activity for the oxidative dehydrogenation of ethane by carbon-dioxide. Deposition of Mo₂C on SiO₂ caused a dramatic change in the catalytic performance and produced an effective catalyst. The reaction started about 800 K.
- 1.2. The non oxidative dehydrogenation of ethane exhibited a similar catalytic activity on Mo₂C/SiO₂ but the presence of CO₂ changed the products' distribution: the main product was ethylene and the formation rate of aromatic product strongly diminished, thus the selectivity of ethylene significantly increased. At 873 K the conversion of ethane was 14 % and the selectivity of ethylene was 89 %.
- 1.3. The cracking of ethane also occurred on Mo₂C/SiO₂ catalyst and produced methane. The presence of CO₂ had no direct effect to this reaction. At the earliest minutes of the reaction the formation rate of methane decreased rapidly, which was connected to the rapid decrease of the number of strongly acidic catalytic sites sufficient to cracking. We assumed that these sites were blocked by surface carbon.
- 1.4. The conversion of ethane had two main parallel reactions: the oxidative dehydrogenation and the cracking. The change of experimental conditions had oppositely effect to these reactions. Rise of the temperature or increase the contact time were favorable to the cracking, but the lower temperature or shorter contact time were advantageous for dehydrogenation.

IV. List of publications

Publications to the Ph. D. thesis:

1. F. Solymosi, **R. Németh**
The oxidative dehydrogenation of ethane with CO₂ over Mo₂C/SiO₂ catalyst
Catalysis Letters, **62** (1999) 197-200. IF: 2,051
2. F. Solymosi, **R. Németh**, L. Óvári, L. Egri
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3. F. Solymosi, **R. Németh**, A. Oszkó
The oxidative dehydrogenation of propane with CO₂ over supported Mo₂C catalyst
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4. **R. Németh**, J. Kiss, F. Solymosi
Surface chemistry of HNCO and NCO on Pd(100)
Journal of Physical Chemistry C **111** (2007) 1424-1427. IF: 4,115

Other publications:

5. A. Erdőhelyi, K. Fodor, **R. Németh**, A. Hancz, A. Oszkó
Partial oxidation of methane on silica supported different alkali metal molybdates
Journal of Catalysis, **199** (2001) 328-337. IF: 3,293
6. A. Erdőhelyi, **R. Németh**, A. Hancz, A. Oszkó
Partial oxidation of methane on potassium promoted WO₃/SiO₂ and on K₂WO₄/SiO₂
Applied Catalysis A: General, **211** (2001) 109-121. IF: 2,258
7. F. Solymosi, **R. Németh**, A. Széchenyi
Aromatization of *n*-butane over supported Mo₂C catalysts
Catalysis Letters. **82** (2002) 213-216. IF: 1,852

5. Surface chemistry of HNCO and NCO on Pd(100) single crystal

- 5.1. We found that HNCO adsorbed molecularly on Pd(100) surface at 100 K. With the rise of the temperature above 120 – 140 K HNCO dissociated forming hydrogen and adsorbed NCO species. NCO species was very unstable on a clean surface and totally decomposed to adsorbed CO and N atoms at 280 – 300 K.
- 5.2. Strong interaction was observed between adsorbed NCO molecules, and this interaction became weaker with the decrease of the surface coverage. Formed and added CO had no influence to the bond strength of adsorbed NCO.
- 5.3. The spectral property of CO produced by NCO decomposition and CO adsorbed on Pd(100) was different, due to the different surface geometry of carbon-monoxide. We assumed that the NCO and CO, and the NCO and O occupy different surface sites.
- 5.4. Preadsorbed oxygen promotes the dissociation of HNCO and resulted in about 50 % more adsorbed NCO. Preadsorbed oxygen also enhances the stability of NCO: its decomposition occurred only between 380 and 420 K. The oxygen also lowered the rate of decomposition up to 340 K. Preadsorbed or gas phase hydrogen had no effect on the stability of surface NCO.

2. Dehydrogenation of propane on Mo₂C and Mo₂C/SiO₂ catalysts

- 2.1. In the course of TPD measurement performed after propane adsorption at 298 K we found that propane didn't interact with SiO₂ support. We detected weakly bonded propane desorption from the unsupported Mo₂C surface. At higher temperature a small amount of propylene was also detected. In case of Mo₂C/SiO₂ catalyst physisorbed propane and at higher temperature strongly bonded ethylene and propylene desorbed from the sample. Our result was verified by IR measurements studied by our colleagues.
- 2.2. On unsupported Mo₂C catalyst the main process at 873 K was the dehydrogenation of propane to propylene. The conversion of propane was 7 % and the selectivity of propylene was 44 %. The cracking of propane also occurred: the selectivity of ethylene and methane was 33 % and 21 %. We didn't find any sign of aromatization processes.
- 2.3. The conversion of propylene on pure Mo₂C led to the formation of totally new products. We found C₄ and C₆ hydrocarbons and small amount of benzene. From this we concluded that the smaller hydrocarbons produced from the cracking of propane, not from the propylene created by the propane dehydrogenation. The dehydrogenation and the cracking of propane are two parallel processes.
- 2.4. The Mo₂C/SiO₂ catalyst was effective in the dehydrogenation of propane. At 873 K the conversion of propane was 31 %. The main process was the dehydrogenation of propane to propylene with high selectivity (38 %). Cracking of propane also occurred, the selectivity of ethylene and methane was 13 and 16 %. We also found aromatization processes. The total selectivity of benzene and toluene was 23 %. With the decrease of the temperature the dehydrogenation process gone to the

foreground, and the cracking and aromatization processes were diminished on Mo₂C/SiO₂ catalyst. Thus the selectivity of propylene increased with the decrease of temperature. At 813 K it was more than 80 %.

3. Dehydrogenation of propane on ZSM-5 and Mo₂C/ZSM-5 catalysts

- 3.1. We found that propane interacts strongly with H-ZSM-5 and Mo₂C/ZSM-5 catalysts. In the course of TPD measurement after propane adsorption at 298 K we found weakly bonded propane desorption from both catalysts at low temperature. At higher temperature ethylene, methane and propylene were detected from the strongly bonded surface species. Our TPD results were proved by IR measurements in separate studies.
- 3.2. The H-ZSM-5 support was an active catalyst in the conversion of propane, and the deposition of Mo₂C on it did not change the activity remarkably, but the products' distribution was very different. Due to the dehydrogenation effect of Mo₂C the selectivity of aromatic products increased, the selectivity of the cracking products, however, decreased.
- 3.3. We assumed that during the carburization of MoO₃/ZSM-5 the most active acidic sites of the catalyst reacted with the hydrocarbon content of the gas mixture, and the produced carbon decreased the activity of these centers. The other possibility effect is that the formed Mo₂C islands covered these centers, and decrease their acidic properties. The activity of remained acidic sites is enough to aromatization, but it is too weak for the cracking reaction detected on pure support.

4. Oxidative dehydrogenation of propane on Mo₂C/SiO₂ catalyst

- 4.1. It has been found that silica supported Mo₂C is an effective and selective catalyst for propane oxidative dehydrogenation by carbon-dioxide. The activity of the Mo₂C/SiO₂ catalyst lowered in the presence of CO₂. At 873 K the propane conversion was 31 % without CO₂ and reduced to 6 % in the presence of CO₂. The products' distribution, however, greatly altered. Due to the presence of CO₂ the main process was the dehydrogenation of propane, and the selectivity of propylene increased to 82 % from 38 %. Very little amount of aromatic products formed.
- 4.2. We assumed that CO₂ opened a new reaction route to the conversion of propane. The first step in the oxidative dehydrogenation process is the partial oxidation of Mo₂C with CO₂ and the formation of Mo oxycarbide. Propane adsorbs on the Mo₂C surface and reacts with the active oxygen attached to Mo to produce propylene and water. Due to this reaction mechanism the active oxygen left the system as water, and the adsorption of another CO₂ molecule was necessary to recover the activity of the catalytic site, to rebuild the Mo oxycarbide form. Our conception was strengthened by separate XPS measurements.
- 4.3. Reduction of contact time had no effect to the products' distribution. This indicates that the dehydrogenation reaction was independent from the cracking reaction. With the rise of the temperature the dehydrogenation of propane fell into the background and the cracking became the main process. The selectivity of ethylene and methane increased while the selectivity of propylene decreased.