Ph. D. Thesis

INFRARED STUDY OF SURFACE SPECIES AND INTERMEDIATES FORMED IN THE REACTION OF SMALL MOLECULES

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1. PRECEDING WORKS AND AIMS OF THIS STUDY

Data on the properties of the adsorbed species and/or surface intermediates playing decisive role in the catalityc reactions have been previously obtained only indirectly through the study of the kinetics of the whole reaction, or through isotope exchange investigations. Vibration spectroscopic studies in the infrared rauge, however, give direct proofs on the structure of adsorbed forms. The infrared spectroscopy became one of the most effective surface science methods due to its easy handling and cheapness.

Infrared spectroscopic studies showed the formation of isocyanate surface complex in the NO + CO reaction on supported noble metal catalysts. As this surface complex plays decisive role in the undersived side reaction of the catalytic transformation of the auto exhaust gases, great attention should be payed to its properties and to the mechanism of its formation. For this purpose the interaction of NO + CO gas mixture with supported gold, palladium and rhodium catalysts was investigated.

Interests in the CO_2 catalytic chemistry has been growing in the couple of recent years. A possible way of the CO_2 transformation is its catalytic hydrogenation. In line of the aboves the surface interactions between H_2, CO_2 and supported rhenium catalysts were studied.

The interaction between butyl iodide and supported Mo_2C catalysts is important from both theoretical and environmental aspects. Due its cheapness and better catalytic activity Mo_2C would be excelently used instead of platium metals which are good and very expensive catalysts in many reactions.

One of most advantageous H_2 productions is the decomposition of ethanol produced in renewable process. The study of ethanol adsorption on different catalysts may serve usefull data on catalytic H_2 formation from ethanol.

2. EXPERIMENTAL METHODS

The IR studies were performed in a metal-glass vacuum system capable for maintaing $p \leq 5\times10^{-6}$ Torr (1 Torr = 133 Pa) vacuum. The length of the infrared cell

was approximately 10 cm, closed by CaF_2 windows at both end. Experiments at lower temperatures were made with the help of a copper block cooled by liquid nitrogen. The pretreatments of catalysts and the experiments at T > 300 K were performed in the upper part of the IR cell heated by an outer furnance.

Infrared spectra (in transmission mode) were recorded with a Biorad (Digilab Div. FTS 155) instrument with a wavenumber accuracy of ± 4 cm^{-1}. All the spectra presented in this study are difference spectra. Spectra of pretreated catalysts and the adsorbing gases were subtracted from the actual spectra. All subtractions were taken without the use of a scaling factor (f=1,0000). The optical path was purged by CO_2- and H_2O-free air produced by Balston 75-62 FTIR Purge Gas Generator.

The gas phase composition was monitored by a quadropole mass spectrometer.

The catalysts were produced by impregnation of the supports by the appropriate metal salt solution; after impregnation the samples were dried at 383 K. The dried porous catalysts were pressed into self-supporting wafers (10-60 cm^2) the pretreatment of which was made in the IR cell. The pretreatment consisted of evacuation at high temperature, oxidation and reduction.

3. NEW SCIENTIFIC RESULTS

1. Although very limited dissociation of NO was observed on reduced Au catalyst, catalytic tests showed that all the samples used effectively catalyse the NO+CO reaction above 573 K.

2. By means of FTIR spectroscopy several new absorption bands have been detected on the Au samples, the positions of new bands depended on the nature of the support. It was 2212 cm^{-1} for Au/TiO_2 2220-2230 cm^{-1} for Au/MgO 2256 cm^{-1} for Au/Al_2O_3 and 2305 cm^{-1} for Au/SiO_2. These bands were attributed to the asymmetric stretch of NCO attached to the oxides. This idea was strengthened by the results obtained following HNCO adsorption on supports alone which gave the same absorption bands.

3. It was demonstrated and assumed that NCO species is formed on Au crystallites, and then migrates from the Au onto the acceptor sites of support where it is accumulated and stabilized.

4. For clarifying the contradiction appeared in the literature we have studied the spectral parameters of NCO formed int he NO + CO reaction and in the dissociative adsorption of HNCO on Pd/SiO_2. We have assigned the band due to Pd – NCO (2183 cm^{-1}) and to Si – NCO (2305 cm^{-1}) excluding the possibility that the band at 2258 cm^{-1} appeared in the NO + CO reaction on Pd(111) single crystal surface at 600 – 650 K is due to Pd – NCO surface species.

5. It was shown that when the reaction between NO and CO set in two absorption bands appeared in the FTIR spectra of Rh/CeO_2 at 2180 and 2210 cm^{-1}, which were not observed following the adsorption of reactants and products. Adsorption of HNCO on pure CeO_2 at 200 and 300 K yielded the same spectral features suggesting that these bands belong to adsorbed isocyanate, NCO, species bonded to the CeO_2. These results suggest that the spillover process of NCO from the Rh onto support proceeds even in the case of CeO_2 used as a solid oxidizer in the three way catalyst . NCO attached to ceria reacts with H_2O resulting in the release of NH_3.

6. The adsorption of CO_2 on Re supported by Al_2O_3, TiO_2, MgO and SiO_2 have been investigated by FT-IR spectroscopy. The dissociation of CO_2 was not experienced on the Re/Al_2O_3 reduced at 673 K, it occured, however, ont he sample reduced at 1073 K.

7. Addition of H_2 to CO_2, initiated the dissociation on all catalysts as indicated by CO bands at 2022 – 2053 cm^{-1}. Besides, new spectral features were developed at 1600 – 1550, 1395 and 1365 cm^{-1} attributed to formate species. This assumption was confirmed by the adsorption of HCOOH vapor on these solids.

8. No bands due to formate were detected on Re/SiO_2. Adding methane and ethane to CO_2 also led to the appearance of CO bands, the

intensities of which were much less compared to the H_2 + CO_2 co-adsorption. The formation of formate also occurred to a small extent.

9. No formate was detected following the co-adsorption of CO_2-containing gas mixture on the supporting oxides alone. It was assumed that the formate species identified in the surface interactions is located on the support, where it is stabilized.

10. The adsorption and reactions of butyl iodide on Mo_2C/ZSM-5 and Mo_2C/SiO_2 have been investigated by means of FTIR spectroscopy and mass spectrometry. Adsorption bands observed following the adsorption of butyl iodide at 200-230 K corresponds well to the vibrations of molecularly adsorbed C_4H_9I. At higher adsorption temperatures bands due to the adsorbed butene and butylidyne also appeared.

11. From the comparison of the adsorption and desorption characteristics determined on pure and Mo_2C-containing ZSM-5 it was concluded that the majority of butyl iodide is attached to ZSM-5.

12. The presence of Mo_2C on ZSM-5 and SiO_2, however, enhanced the rate of the decomposition, promoted the coupling of butyl species and catalyzed the formation of xylene and benzene. It was assumed that Mo_2C interacting with the acidic sites of the support is the active center for the latter processes.

13. Ethanol adsorbs and dissociates mainly on ZSM-5, SiO_2 and CeO_2 supports. Aromatics in the catalytic reactions of ethanol possibly form via the reaction between crotonaldehyde and acetaldehyde.

4. POSSIBLE APPLICATIONS OF THE RESULTS IN THE PRACTICE

The results are of basic scientific character, their use would be important in theoretical considerations. On the basis of these results the production of more effective catalysts can be possible, the conclusions would contribute, to the development of new, effective catalysts.

5. LIST OF PUBLICATIONS

Impact factors

1. **Süli Zakar T.**, Hannus I., Kiricsi I.: A zeolitok karrierje – V. Kísérletek zeolittal.
   A Kémia Tanítása (2002) 3-5.

2. F. Solymosi, P. Tolmacsov, **T. Süli Zakar**: Dry reforming of propane over supported Re catalyst
   Journal of Catalysis **233 (1)** (2005) 51-59. **4.063**

Publications to the Ph.D thesis:

3. F. Solymosi, T. Bánsági, **T. Süli Zakar**: Infrared study of the NO + CO interaction over Au/TiO_2 catalyst.
   Catalysis Letters **87** (2003) 7-10. **1.904**

4. F. Solymosi, T. Bánsági, **T. Süli Zakar**: Surface interaction and reaction of NO + CO on supported Au catalyst.
   PCCP **5** (2003) 4724-4730. **2.076**

5. F. Solymosi, T. Bánsági, **T. Süli Zakar**: Comment on „Combined in situ infrared and kinetic study of the catalytic CO+NO reaction on Pd (111) at pressures up to 240 mbar”
   J. Phys. Chem. B **108** (2004) 14178-14180. **3.834**

6. F. Solymosi, T. Bánsági, **T. Süli Zakar**: Adsorption and reactions of butyl species over Mo_2C catalyst.
   J. Mol. Cat. A-Chemical **225 (2)** (2005) 217-223. **2.316**

7. F. Solymosi, T. Bánsági, **T. Süli Zakar**: FT-IR study on the interaction of CO_2 with H_2 and hydrocarbons over supported Re.
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6. PERFORMANCES

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2. F. Solymosi, T. Bánsági, **T. Süli Zakar**: Infrared spectroscopy study of the interaction between NO and CO on supported Au catalyst.
   The 10th Symposium on Analytical and Environmental Problems, Szeged, 29 September 2003

3. Solymosi F., Bánsági T., **Süli Zakar T.**: NO + CO reakció infravörös spektroszkópiai vizsgálata oxid hordozós arany katalizátorokon.
   XXVI. Kémiai Előadói Napok, Szeged, 2003. október 27-29.