

Interfaces studied with XPS, AFM, SEM, FTIR and Raman techniques

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Abstract

This short overview of recent activity within my research interests is devoted to professor Ference Billes at his 80th birthday. We have known each other for some years now (time passes by very quickly at our age) and thanks to our common interest on vibrating molecules and your nice personality, I got another very good friend.

The research activities I included in this short overview are from various research areas, but all of them have a common denominator namely interfacial structures. It is about the effect of water contamination on automatic transmission fluids, surface properties of magnetite particles and their possible modification to improve pelletizing of iron ore concentrate, how inorganic ions may influence the efficiency of surfactants as a washing powder constituent, and last but not least the synthesis of thin zeolite films on supports such as porous alfa-alumina, supports that may have complex geometry.

Introduction

Szia Feri,

I am pleased to have the opportunity to present this limited overview of recent IRS activity at my division as a personal contribution to the 80th birthday of a very good and appreciated friend. I hope it will at least to some extent make your birthday even more delightful and I wish you all the best in the future.

The summary below is about my recent activity at our laboratories where knowledge about interfacial structures and properties are of high importance from a technological point of view and of course vibration spectroscopy is an important technique used to elucidate the structures of these interfaces. The combination with other techniques makes vibration spectroscopy even more powerful.

I will start with a system where lubricants are involved and especially their properties as automotive transmission fluids in humid environments. As I remember, you are not a big fan of cars, not even cars with an automotive transmission, I suppose. I remember very well how you preferred to take a walk to the shopping center in Luleå, although the distance to this center (Storheden) was about 10 km one way and despite the fact that local bus transport was available ☺.

However, at longer distances e.g. on iceroads to the Luleå archipelago or through landscapes where the roads were surrounded by deep forests, car transportation was more or less unavoidable. The investigation involved FTIR spectroscopy, traditional friction tests, as well as XPS and is summarized in section I below.

Another example of recent spectroscopy and microscopy activity concerns magnetite particles and their surface properties. These studies are of course related to the pelletizing of iron ore concentrate, since most of the research was funded by LKAB via the Hjalmar Lundbom Research Center (HLRC). Spectroscopy (FTIR) and microscopy (AFM) results are described in section II.

Thirdly, I will present some recent results also involving iron oxide particles but with an objective different from agglomeration of the particles. In this case the ultimate goal was to detach particles from natural or synthetic fibers and the chemicals used you may find in your laundry. The exact formulation of this washing powder is of course surrounded by secrecy, so in section III I have tried to fulfill our agreements with the international company (Unilever) that supported our research. No PhD student was involved here since the possibility to publish the results was rather restricted. However, one publication was approved by the company so far.

Finally, section IV is about recent progress in our synthesis of thin zeolite films. As you know, zeolites are frequently used in washing powders as well, but in this case they are grown as a film on a porous support and can be used as a molecular filter based on their microporosity and adsorption properties. My own research activity during the past few years has been very much focused on the synthesis of these films onto supports prepared by a new method in order to circumvent existing international patents. Our own international patent application was handed in to the European Patent Office (EPO) just a month ago, implying that only manuscripts are prepared but nothing is published yet. Publications has to await the comments from EPO, according to the patent bureau we have used.

As you already noticed, this short overview is kind of a soup with many ingredients. I hope it will taste good, in a scientific sense, although it will certainly not be as delicious as the home-made goulash soup you invited me to some years ago ☺.

I. Degradation Mechanism of Automatic Transmission Fluid by Water as a Contaminant.

Concerning automotive transmissions, a lowest possible friction is not the ultimate goal but rather a controlled increase in the coefficient of friction (COF) during the change from one gear to another. The friction has to be controlled in order to obtain a smooth gear transmission.

In this project, the degradation mechanism of water contaminated Automatic Transmission Fluids (ATF) was investigated experimentally. The work presented here was a cooperation between the tribology group at the division of Mechanical Engineering and the division of Chemical Engineering, at LTU.

The water contaminated ATF was tribotested in a full-scale wet clutch test rig to monitor the friction durability during clutch ageing. The lubricant was also statically aged in an oven to evaluate the interaction of ATF with water. The bulk properties and the chemical nature of the ATF were analyzed using viscosity measurements, Fourier Transform Infrared Spectroscopy (ATR-FTIR), and Thermogravimetric Analysis (TGA). It was shown that the presence of water in the

ATF could increase the mean friction coefficient over a short time period, though in the long-term perspective there is a high loss of mean friction. Water in oil forms a water-in-oil emulsion. Phase separation of this water-in-oil emulsion by centrifugation at 20000 rpm made it possible to examine the water phase using infrared spectroscopy. The spectroscopic analysis revealed the hydrophilic nature of certain ATF constituents, although the impact of water on the bulk properties like lubricant viscosity and thermal stability was insignificant. The analysis of the tribotests showed that the friction increase after water contamination was a short-term effect and likely due to the interaction between polar surface-active additives and water. Even though no significant change was found neither for the thermal degradation of ATF nor for the bulk properties of the lubricant, the initially changed action of the water soluble additives and generation of high friction resulted in a total deterioration of the clutch performance during long term use.

The following figure may illustrate what the scientific problem was. Our aim was to explain, on molecular level, why the friction coefficient suddenly increased when the ATF was contaminated by water (Fig. 1).

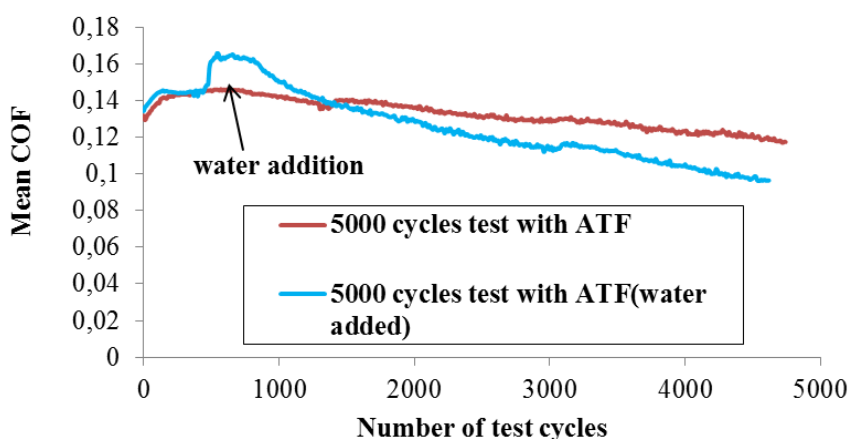


Fig. 1. The figure above shows the change in the Coefficient of Friction (COF) as a function of the number of test cycles before and after addition of water to the ATF.

Water as a polar compound can interact with polar additives like surfactants, detergents, and friction modifier. Although the extracted and dried fraction from the centrifuged ATF/water emulsion (10 volume-% water) will increase the concentration of water soluble additives on the surface of the ATR crystal, it should be emphasized that additives in solution and additives in dry state may not show identical IR spectra. However, dominant absorbance bands of the possible additives in ATF can be seen in the spectrum of the water extract (as shown in the figure below), which were hidden behind the dominant base oil spectra in the spectrum of the water contaminated new ATF. The carbonyl bands between 1700 and 1730 cm^{-1} were, however, also observed in spectra recorded for water contaminated new ATF. The spectra also showed possible OH- bending at 1404 cm^{-1} and bending vibration

of methyl groups at 1380 cm^{-1} . There are also prominent bands in the $1150\text{-}1000\text{ cm}^{-1}$ range, which probably corresponds to compounds containing phosphate (PO_4^{3-}). However, one important result from our FTIR investigation of the water contaminated base oil is the fact that additives in the base oil were shown to accumulate in the water phase of the water in ATF emulsion formed upon adding water.

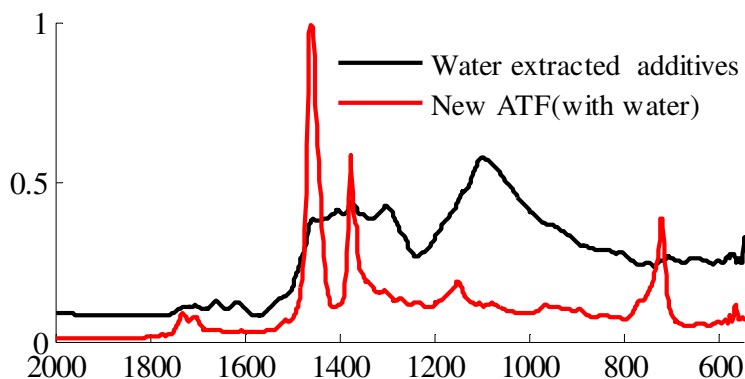


Fig. 2.

The next challenge was to compare the layers formed on friction and reaction plates before and after addition of water to the ATF. The FTIR spectra of the plates were carefully analysed to identify the functional groups according to their characteristic bands. The friction plate was made of a cellulose based material and the reaction plate is made of steel and is in contact with the friction plate during the test cycles.

In the interpretation of infrared spectra, we had good help from XPS studies described below.

Here, ab initio calculations could be helpful, Feri, but the problem is that all these additives in ATFs are not officially known, but a company secret. There is an obvious conflict here. The company wants to have scientific support but refuse to disclose what they know about the formulation of the ATF ☹.

The XPS results from the friction plate (FP) and the reaction plate (RP) showed that the water contaminated sample FPWW (With Water) had higher concentration of N, O and P. Moreover, FPWW also confirmed the presence of Fe and Si, which are absent in the uncontaminated FP without Water (WOW). The possible source of Fe on the cellulose surface is the wear product from the steel plate and Si should originate from the cellulose friction liner or from the ATF additives since its concentration in the steel plate was very low. A detailed analysis of the high resolution spectra showed that chemical species containing Ca, P, Zn, S and N are similar in both samples. Fe, Ca and Zn are found on the surfaces in oxide forms. N, P and partly S appear to be coupled with the organic matrix (C-N, $-\text{PO}_4$, S-CH_x , $\text{CH}_x\text{-SO}_2$). The presence of C-N, $\text{CH}_x\text{-SO}_2$ and $-\text{PO}_4$ indicates interaction involving aramid fiber in friction liner, over-based Ca-sulphonate, and ZDDP or phosphoric acids of friction modifiers (FMs), respectively. Possible sources of S-

Me, and CaO chemical species in both samples can be the anti-wear additives ZDDP and Ca(OH)₂. The curve fit of the C 1s showed higher amount (17.1%) of C-O/C-N in the formed tribofilm for water contaminated ATF (FPWW) than in the uncontaminated FPWOW system (2.9%). It was also notable that the tribofilm on FPWW showed presence of O-C=O species for C 1s and C-O/SiOC species in the O 1s curve fitting. O-C=O suggests the presence of carbonyl groups, ester and/or carboxylic acid groups on the liner. The possible metal in Me-O found in both cases for O 1s curve fitting can be Zn or Ca. *All these findings were in accordance with the FTIR results.*

This investigation presents an experimental approach to evaluate degradation of water contaminated ATF and to detect the particular reason responsible for the change in the wet clutch system's friction behavior due to water contamination. The following conclusions were drawn from this work:

It clarified the impact of water presence on ATF performance. The dynamic viscosity was almost unchanged at the operating temperatures. In addition, the thermal stability of the tested water contaminated ATFs showed a minor impact of the water contamination in the ATF even after 5000 test cycles. Therefore, no substantial influence of water on the base oil's rheological properties and durability can be liable for the sudden increase in COF when water was added to the ATF.

The friction data indicated the quick loss of mean COF for long test duration. Consequently, this confirmed the increase in friction to be a short-term effect after water contamination of ATF.

The FTIR spectra and the DTG curves of the tested ATFs showed the absence of water in

the lubricant already after about thousand clutch engagements in the test rig. This finding also supports the change in friction behavior.

There is not any notable change in the FTIR spectra of the tested water contaminated ATF in comparison with the tested uncontaminated ATF. This indicates that the key functional groups in the water contaminated ATF are unaffected after test.

However, one important result from the performed FTIR investigation of the water contaminated ATF is the fact that some of the surface active additives in the base oil are shown to accumulate in the water phase of the water-in-oil emulsion. So the current study indicates two possible mechanisms of ATF degradation for water contamination: i) rapid reverse micelle formations (responsible for the sudden increase in friction around 500 cycles due to inadequate additive action) and ii) promoting ageing (responsible for gradually decrease in friction after 1500 cycles). The later was considered as an impact of water since water evaporated during the test, but the degradation still proceeded and can also be responsible for the previously observed fast degradation in the friction interfaces, implying permanent change of the clutch system.

The water contaminated reaction plate showed absence of Ca, S, Zn and comparatively higher P content on its surface, which originates mostly from the regular metallic detergents and anti-wear agents used also for stabilizing the friction.

The presence of O-C=O and O-C-O in the tribofilm of the water contaminated friction plate studied by both XPS and FTIR spectroscopy suggest that water affected the adsorption of detergents and friction modifiers.

More detailed information about this research project will soon be found in forthcoming publications and references therein:

1) Nowshir Fatima*, Allan Holmgren, Ichiro Minami, Pär Marklund, and Roland Larsson: Degradation mechanism of Automatic transmission fluid by water as a contaminant. Manuscript submitted to *Journal of Engineering Tribology*.

2) Nowshir Fatima*, Ichiro Minami, Allan Holmgren, Pär Marklund, and Roland Larsson: Degradation Mechanism of Water Contaminated Automatic Transmission Fluid. Manuscript to be submitted to *Journal of Engineering Tribology* 2014.

II. Surface properties of magnetite particles and their possible modification to improve pelletizing.

As you know Feri, mining of iron ore is very important to Sweden but also to EU since the major part of iron ore production within EU is located in Sweden. LKAB has invested a lot of money (via eg. HLRC) to improve their product. They wanted to get better knowledge about the surface properties of magnetite and to improve the strength of so called green pellets i.e. pellets before sintering.

The following summary is just the recent achievements within this area. Unfortunately, LKAB currently seems to have lost their interest in the surface chemistry of magnetite particles or may be there are other important perspectives they have to focus on first. Viability is always the lodestar for all companies and what's viable depends on the persons involved in various decisions ☺.

Anyhow, we were generously funded to explore the properties of magnetite surfaces implying many publications, but here I will describe just recent results that I have been involved in. The funding stopped 2 years ago.

Since most of all minerals are not transparent to infrared radiation, ATR elements coated with thin films of mineral particles are commonly applied in the adsorption studies by ATR-FTIR spectroscopy. Natural mineral particles are not always appropriate for this type of measurements since they may have relatively low surface area resulting in a low signal-to-noise ratio and may contain impurities that would complicate the interpretation of the spectroscopic results. For that reason, synthetic mineral particles with high surface area are commonly applied in the adsorption studies by ATR-FTIR spectroscopy. The interactions between iron oxides and flotation reagents are important, not only for the performance in flotation of apatite from magnetite, but also for the subsequent agglomeration of magnetite concentrate to produce iron ore pellets. Reduced wetting of the magnetite concentrate due to adsorption of a flotation collector has been shown to result in lower pellet strength and may hamper the production capacity of a pelletizing plant. The scope of the present work was to characterise the interfacial properties of natural magnetite particles cleaned by magnetic separation and flotation and to compare with the properties of the synthetic magnetite nanoparticles used in our

previous experimental work, especially to test whether the conclusions drawn regarding adsorption behaviour and wettability of synthetic magnetite are valid for mineral particles. Whereas this aspect is seldom addressed in the literature, the difference in interfacial properties of synthetic and natural materials is an important issue to consider when substituting synthetic particles for their mineral analogue in experimental work.

It was shown in this work that previously reported results obtained from a model system, concerning adsorption of a carboxylate surfactant and sodium metasilicate onto synthetic magnetite nanoparticles, as obtained by in situ ATR-FTIR spectroscopy and contact angle measurements, are applicable to adsorption of flotation reagents on magnetite concentrate. Additionally, the problem of restoring magnetite wetting after flotation is addressed since good wetting of a magnetite concentrate is required to produce iron ore pellets by wet agglomeration. The results from the present work indicate that the wettability of both synthetic magnetite coated with surfactant and magnetite concentrate after flotation can be improved by adsorbing a hydrophilizing agent such as silicate or polyacrylate.

In spite of differences in surface properties and morphology of synthetic and natural magnetite particles, similar tendencies were observed for adsorption of calcium ions, soluble silicates, anionic carboxylate surfactants, and polyacrylate polymers on these materials, as illustrated by contact angle measurements. It was confirmed that the wettability of magnetite was reduced by collector adsorption when calcium ions were present in the system, despite pre-conditioning with water glass. Wettability of the flotated magnetite concentrate could be significantly improved by prolonged treatment with water glass or rather short conditioning with sodium polyacrylate, in agreement with the results obtained for the synthetic magnetite nanoparticles. Better wetting of the concentrate would facilitate wet agglomeration and could possibly increase the strength of iron ore pellets produced. The figure below is a tentative explanation to the observed behaviour of sodium polyacrylate (Fig. 3).

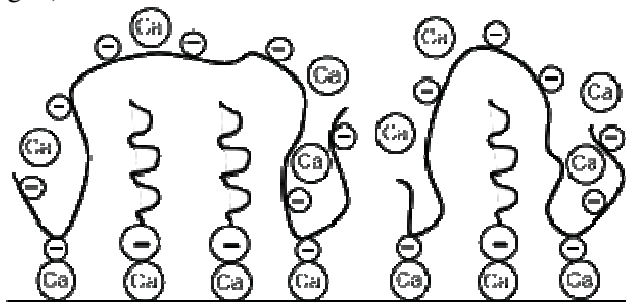


Fig. 3.

In a collaboration between the division of Physics and the division of Chemical Engineering, at LTU, we also investigated force interactions between microsize-microsize and microsize-nanosize magnetite particles in Ca^{2+} solution and examined the effect of calcium concentration and pH on their mutual interaction, by using AFM.

The colloidal probe technique was applied to the measurement of the force interactions and pH was varied between 4 and 10. The statistical treatment of data from retracting experiments used in this work showed the applicability of the AFM technique for studying adhesion forces with high sensitivity despite predicted difficulties arising from the roughness of the particles.

Accordingly, all measured adhesion forces must be regarded as semiquantitative since the inter-particle distances reported do not reflect the true adhesion force that would have resulted from the interaction. Further, force interactions between magnetite, silica, and bentonite were studied using AFM.

In this work, the measurements were performed between magnetite-magnetite, bentonite-magnetite, silica-bentonite, and silica-magnetite particles in 1 mM CaCl₂ solution at various pH values. By analyzing AFM approach curves, it was possible to determine whether the interaction between particles at different conditions was attractive or repulsive. The observed trends were in good agreement with what could be expected from the measured zeta-potential values for the particles at the same conditions.

Particle aggregation was studied by measuring the adhesion force. Absolute values of adhesion forces for different systems could not be compared due to the difference in particle size and contact geometry. Therefore, the relative change of adhesion force between pH 6 and 10 was used for comparison. The adhesion force slightly decreased for the magnetite-magnetite and bentonite-silica systems and increased for the magnetite-bentonite system at pH 10 as compared to pH 6, whereas a pronounced decrease in adhesion force was observed in the magnetite-silica system at the same conditions. Thus, the presence of silica particles on the magnetite surface could have a negative impact on the interaction between magnetite and bentonite in balling due to the reduction of the adhesion force.

More detailed information about the projects can be found in the following publications and references therein:

1) E. Potapova*, X. Yang, M. Westerstrand, M. Grahn, A. Holmgren and J. Hedlund. Interfacial properties of natural magnetite particles compared with their synthetic analogue. *Minerals Engineering* 36–38 (2012) 187–194.

2) Elisaveta Potapova* and Allan Holmgren. Surface modification of magnetite for improved pelletization of iron ore. *5th Asian Particle Technology Symposium 2-5 July 2012, Singapore*.

3) Illia Dobryden*, Xiaofang Yang, Nils Almquist, Allan Holmgren, and Hans Weber. An atomic force microscopy study of the interaction between magnetite particles: The effect of Ca²⁺ ions and pH. *Powder Technology* 233 (2013) 116–122.

4) Elisaveta Potapova*, Allan Holmgren & Jonas Hedlund, Illia Dobryden, Nils Almquist & Hans Weber. Force interactions between magnetite, silica, and bentonite studied with atomic force microscopy. Manuscript submitted to *Minerals Engineering* 2014.

III. The Effect of Inorganic Ions on Dodecylbenzenesulfonate Adsorption onto Hematite: an ATR-FTIR Study

This project was funded by Unilever and the goal of the project was to obtain molecular information on the adsorption of various tensides and complex binders onto hematite. It was an interesting project where we could observe that certain formulations were very efficient and even washed away the iron oxide layer we had deposited on the ATR crystal to monitor the adsorption process. The loss of the IR signal from species adsorbed on hematite became a good measure of the washing efficiency. The text below is a summary of a paper recently accepted for publication and also the only material we got permission to publish so far.

In the present study, we investigated the effect of calcium and carbonate ions on the desorption of sodium dodecylbenzenesulfonate (SDBS) on hematite at pH 8 and 10.5, using in-situ ATR-FTIR spectroscopy. The goal was to acquire a better understanding of the intricate chemistry occurring with this important surfactant during adsorption from complex solutions. To the best of our knowledge, this is the first in-situ spectroscopic study considering SDBS adsorption onto hematite in the presence of several co-adsorbing inorganic ions.

Linear alkylbenzenesulfonates (LAS) are an important group of anionic surfactants within the detergent industry and have also been suggested for use in mineral flotation and enhanced oil recovery. Because of its great industrial importance, there are a number of publications on the adsorption of LAS on metal oxides; however, the effect of co-adsorbing inorganic species on LAS adsorption has rarely been addressed.

DBS adsorption on hematite was found to increase as pH was decreased from 10.5 to 8. Calcium ions promoted accumulation of DBS on hematite, with a larger amount of DBS on the surface at pH 10.5. Carbonate ions did not have any major effect on DBS adsorption on hematite. In the presence of both calcium and carbonate, the amount of DBS on the hematite surface was higher than without the two co-adsorbing ions but lower than with calcium ions alone. Likely, precipitation of calcite reduced the total concentration of calcium ions available for the interaction with DBS on the hematite surface.

In the figure below, the absorbance of the CH₂ symmetric stretching vibration band in the spectra of DBS adsorbed on hematite at pH 8 and 10.5 and in the presence of different inorganic salts is shown (Fig. 4).

The adsorption time at each pH was 1 h. In forthcoming work we intend to implement the developed method to study the effect of inorganic ions on the adsorption of surfactants from binary anionic/non-ionic surfactant mixtures, common for many industrial applications.

The results presented in this work clearly indicate the importance of water chemistry for DBS adsorption and allow predicting adsorption behavior of DBS on iron oxides from natural and process waters of different chemistry, which is important for the industrial applications of DBS and the fate of DBS in the environment. It deserves to mention that the variation in the infrared absorption of the bending mode of water at the solid-water interface served here, as in many

others of our adsorption studies, to assess whether the surface became more or less hydrophilic upon adsorption of a certain species.

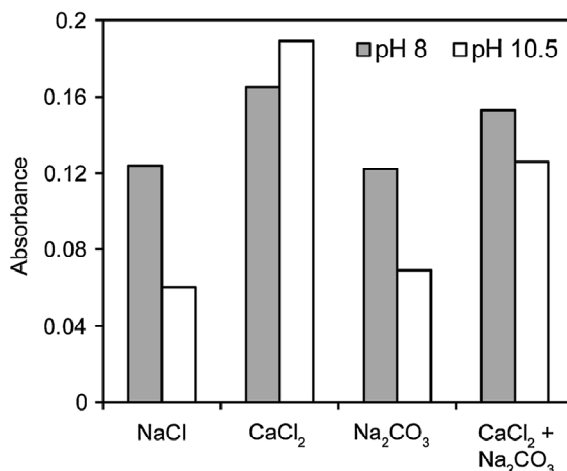


Fig. 4.

IV. Preparing thin zeolite films on supports with complex geometry

The last few years, I have focused my work on a new method to make thin zeolite membranes on porous tubular alumina supports. The method is different from methods to make membranes on porous disc supports and innovative enough (we think) to be subject of a patent application. An international patent application was filed to the European Patent Office on the 14th of March this year.

The innovation enables preparation of high flux zeolite membranes with a very well defined pore diameter.nm. The high flux is due to the thickness of the membrane, which in our case is only 500 nm. Still the membranes are virtually free from defects. Because zeolites are inorganic materials, the membranes are much more chemically resistant than polymeric membranes and can therefore be used in harsh environments. They are thermally stable, do not suffer from swell-induced plasticization by carbon dioxide and incorporation of hydrocarbons, and have well-defined molecular sized pores allowing for molecular sieving based on size and shape of the molecules to be separated. Thin zeolite membranes with well-defined pores lead to high flux and selectivity. These membranes can for instance selectively separate CO₂ from synthesis gas, natural gas and biogas and to separate 1000 kg CO₂/h, it is sufficient with a membrane area as low as 2.6 m². This enables very cost and energy effective separation of CO₂ compared to conventional techniques such as amine scrubbing and competing membrane techniques. Since CO₂ separation currently is a major cost, these zeolite membranes can potentially reduce the overall production costs significantly in many processes. Examples are ammonia and methanol production and upgrading of natural gas and biogas. The membranes are also isomer selective and can separate p-xylene from other xylene isomers (and reduce production costs of p-xylene) and can also separate linear hydrocarbons from branched hydrocarbons (to increase the octane number).

The method we have developed enables the synthesis of zeolite membranes on the inside of the tubes even though the inner diameter is small. The picture below shows a typical module and inside the tubes we can synthesize thin zeolite membranes.



Fig. 5.

In a Commercial process many such modules are used to separate e.g. carbon dioxide from gas stream containing carbon dioxide and methane. On the upper side of the module, you can see the outlet for the gas that has passed through the membrane. Compared to conventional processes used to separate carbon dioxide from methane (amine scrubber) the installation costs of a membrane process with the same capacity is about 10 times lower and the operating costs about 100 times lower.

As an aid in the development of these membranes we usually make use of SEM and the following figure shows an SEM picture of a membrane synthesized on the surface inside the tube of a porous alumina substrate.

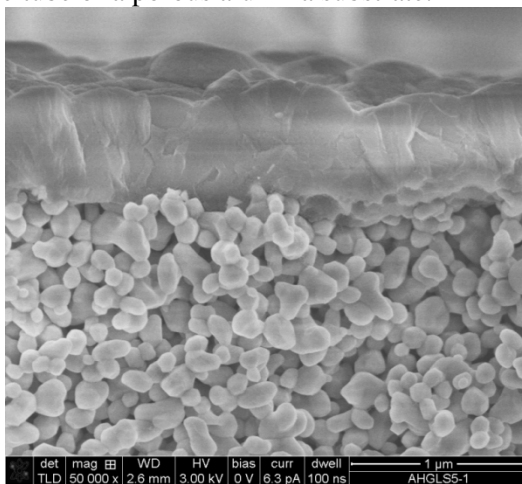


Fig. 6.

However, we have also used in-situ ATR FTIR spectroscopy to find out the optimal way to prepare the support in order to prohibit the synthesis solution to enter the porous support structure. These investigations have not been published yet because of patent considerations. Raman microscopy is another efficient technique to probe the result of the membrane synthesis e.g. the crystallinity and the variation

in the thickness of the membrane. The following picture is an example of such an attempt (Fig. 7).

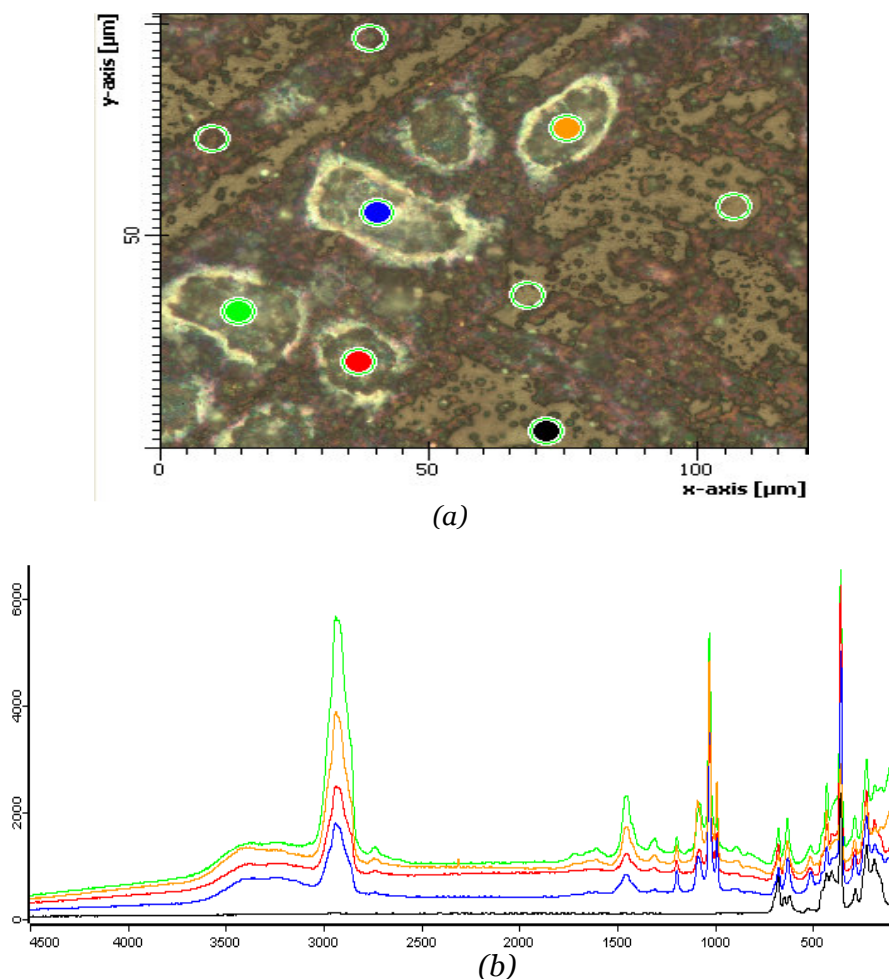


Fig. 7. Membrane (a) the surface points probed (b) the Raman spectrum at different points on the surface of the zeolite membrane

This membrane was a bit too thick, but illustrates how the thickness of the membrane may vary for different sample points and also the influence of the substrate (black trace), which was ZnS in this case. It also clearly shows the organic template used to synthesize the porous zeolite film.

Feri, I hope that this short overview gave you a glimpse of what I have been doing the last few years and once again I wish you a happy birthday and all the best for the future.

Barátsággal,

Allan