Sample preparation and electron microscopy of hydrocracking catalysts

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Abstract. This work focuses on the preparation of zeolite and alumina hydrocracking catalysts for investigation by electron energy-loss spectroscopy (EELS). EELS can potentially give new insights into the location and structure of coke which can result in catalyst deactivation. Three sample preparation techniques have been used – microtoming, focussed ion beam milling (FIB) and conventional ion beam milling. Crushing and grinding the catalyst pellets has been discounted as a preparation technique as the spatial relationship between the coke and the catalyst is lost using this method. Microtomed sections show some mechanical damage while sections milled in a single beam FIB microscope show gallium decoration in pores and were too thick for EELS. Conventional ion beam milling has proved to be most successful as it results in extensive thin regions and maintains the spatial distribution of the zeolite and alumina phases.

1. Introduction

Hydrocracking catalysts, which are used in refineries to produce transportation fuels from heavier oil fractions, often contain zeolite Y because of its high acidity and reasonable accessibility. Other catalyst components are an alumina binder and a mixed sulphide (Ni/W) hydrogenation function. In use, over time, such catalysts accumulate coke (carbonaceous deposit) on their surface, with a detrimental effect on their catalytic performance. To really understand this phenomenon it is of paramount importance to know where the coke is deposited - e.g., on the binder, on the outside of the zeolitic crystallites, or inside the zeolite pores -- and what its structure is. The aim of this project is to characterise the location and structure of coke using electron energy-loss spectroscopy (EELS) in a scanning transmission electron microscope (STEM). The preparation of thin samples suitable for STEM- EELS studies is the focus of this contribution.

Grinding and microtoming are the most common techniques for preparing thin sections of catalysts. While grinding is a simple procedure, the spatial distribution of the phases is destroyed [1,2] and varying sample thicknesses make EELS and energy dispersive x-ray analysis (EDX) difficult. Consequently it has not been considered for this study. Microtoming produces large areas of thin, uniform sections that are suitable for chemical analysis but can result in mechanical damage to the samples. A more recent development in sample preparation is focussed ion beam (FIB) milling that provides site specific investigation of a sample although gallium implantation and material redeposition are problems associated with this technique. Images from these two methods will be
discussed and compared. Conventional, or broad, argon ion beam milling has also been carried out. While this is an established technique, conventional sample preparation on zeolites is scarcely documented in literature and preliminary results will be shown.

2. Materials and experimental methods

In this study, four samples were examined: one fresh zeolite Y/alumina catalyst, and three spent (coked) NiW/zeolite Y/alumina catalysts, derived from it by subjecting it to process conditions of various severity. All samples are in the form of extrudates. Transmission electron microscopy (TEM) was carried out on a JEOL 2000FX and JEOL 2010 at 200kV. Chemical analysis was done on the JEOL 2010 using Noran System Six microanalysis software.

The first step of microtoming involves vacuum embedding the specimen in resin that is cured at 50ºC for two days. The specimen is trimmed and an ultra-microtome produces thin sections by moving the specimen past a knife blade. Thin sections float on distilled water near the knife edge and are collected on grids. The thickness of a section can be identified by interference colours. [3]

An FEI Strata™ FIB200TEM single beam instrument was used for FIB milling. FIB systems raster a beam of focussed gallium ions across a sample [4]. When the ions impact on a material, sputtering takes place that allows thin sections to be produced from bulk samples. All milling in this work took place at 30kV and a beam current of 100pA was used for final thinning at a sample tilt of ± 1°. The three coked samples were obtained using ex-situ liftout (EXLO). In EXLO the section is thinned and the entire sample is removed from the microscope. The section is then manipulated from bulk sample to a mesh grid. In-situ liftout (INLO) was used for the fresh sample as it was charging due to an absence of carbon. In this procedure all thinning and manipulation is done in the microscope. The samples were embedded in conducting resin as zeolites are insulating materials that are difficult to image in a FIB system.

For conventional ion beam milling, catalyst extrudates were embedded in a brass tube and were cut, ground and polished to a thickness of 80 μm using a disc grinder finishing with a 1 μm diamond suspension. The sample was milled in a Precision Ion Polishing System (PIPS) at 8°. After perforation, milling continued at 4° for 30 minutes. A beam energy of 4keV was used at all times.

3. Results and discussion

Fig 1 shows that the spatial distribution of zeolite and alumina is maintained in a FIB system but not in a microtome. Fig 1a) reveals that the FIB section has stayed completely intact and consequently zeolite grains, binder and porosity can be identified. Fig 1b) shows that microtoming causes extensive material damage which makes it difficult to identify phases and to differentiate between a real pore in the catalyst and a hole that has been produced as a consequence of sectioning. Damage is seen because of the mechanics involved in microtoming and due to alumina being a hard material that fractures easily when cut.
Fig 1 - TEM image of a coked catalyst prepared by a) FIB and b) microtome

Fig 2 shows the presence of artefacts when a FIB system is used. While some artefacts are inevitable, Fig 2a) shows pores that contain regions of extensive amorphous contrast. STEM x-ray analysis shows these areas to be rich in gallium (Ga) and platinum (Pt). In a FIB system Pt metal is deposited by ion beam assisted chemical vapour deposition of a precursor organometallic gas. The gas molecules are adsorbed on the surface and they decompose when the Ga beam strikes. Repetitive adsorption and decomposition result in the buildup of Pt and Ga and this is being seen in Figs 2b) and 2c).

Fig 2 a) TEM image of a coked pellet sectioned by FIB showing amorphous contrast (arrows), b) Ga STEM x-ray map and c) STEM Pt x-ray map
Fig 3 shows that conventional ion beam milling is a good sample preparation method. The spatial distribution of zeolite and alumina is comparable to FIB sections yet a larger thin region can be obtained. Hence this method is being pursued further for EELS.

Fig 3 - TEM image of a coked pellet prepared by conventional ion beam milling

4. Conclusions
Both microtoming and single beam FIB milling are unsuitable for STEM-EELS. All spatial information is lost in microtomed sections and phase identification is not possible due to material damage. Microtomed and FIB sections contain pores that are infiltrated with resin that are carbon based. These sections are unsuitable for EELS as carbon K edges in EEL spectra will be investigated to determine the structure of coke. While FIB sections remain intact, they are too thick for EELS and the location of Ga and Pt has been observed at some pores. Conventional ion beam milling creates a large thin region that maintains all spatial information and is therefore the most suitable technique for STEM-EELS.

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6. References
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