Deactivation study on zeolite materials using XPS and STEM characterization

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Zeolites are porous materials, widely used in heterogeneous catalysis. The availability of well-defined porous structure makes it a versatile catalyst for industrial applications [1]. However, the zeolites have higher tendency for carbonaceous species (coke) formation under operating conditions and hence blockage of the porous structure, limiting its catalytic stability for a long-term usage [2] and regeneration of the zeolite. Therefore, it is necessary to study the coke formation on zeolite in the operation conditions. In this work, we have studied the coke formation on three zeolites such as fresh ZSM-5 catalyst with Si:Al ratio of 30 and spent ZSM-5 catalysts; one acquired from Vapor-Phase Upgrading (VPU) vessel (spent-VPU) and the other one from the reactor after the experiment was finished (spent). The coke formation was studied by X-ray photoelectron spectroscopy (XPS) and scanning transmission electron microscopy (STEM) to estimate the carbon concentration.

XPS powder samples were prepared by dispersing the samples on a two-sided tape fixed to a clean glass slide. The samples were later inserted on the XPS instrument and wide energy spectrum (0-1200 eV) was acquired to determine the elements present on each sample. Next, a narrow range spectrum was acquired on each detected element. TEM samples were prepared by standard drop-cast method on the TEM grid. TEM images and the elemental distribution was determined using an aberration corrected JEM-ARM200F NEOARM operating at 200kV, which is equipped with a cold field emission gun (Cold-FEG), a next generation Cs corrector (ASCOR) equipped with energy dispersive X-ray spectroscopy (EDS) system using dual JEOL 100 mm^2 silicon-drift detectors (SDD) and a Gatan Quantum electron energy loss (EEL) spectrometer for chemical analysis.

Figure 1 is the XPS spectra on the three samples. Figure 1 a confirms the presence of C, O, Al and Si in each sample. The fresh catalyst exhibits the least amount of C by an order of magnitude, 4 at. %. The other two spent catalysts exhibit less Si, O, and Al due to the overlayer of carbonaceous material, however significantly higher C level than the fresh sample. The atomic percentage of each element is similar in both spent catalysts (for instance, 44.1 and 42.8 at. % of C in the spent-VPU and spent, respectively). Figure 1 b compares the C 1s, O1s, Al 2p, and Si 2p for the three samples. The spectra for the fresh sample were slightly wider than the spent samples due to charging effect. The charging was not found in the spent catalysts because of the presence of carbon film on the surface. The shape of the C 1s for the two spent catalysts indicate an amorphous type of carbon that is likely a form of coke. The O 1s, Al 2p, and Si 2p were all consistent with Al-O and Si-O bonding indicating oxide composition.

Figure 2a shows the HAADF-STEM image and EDS elemental mapping of C, O, Al and Si acquired from the fresh ZSM-5, while Figure 2b shows the HAADF-STEM image with corresponding EDS elemental maps of C, O, Al and Si generated from the spent ZSM-5. The preliminary data shows that there is a uniform distribution of O and Si on both catalysts. However, the difference in C intensity

between the fresh and spent ZSM-5 indicates that the surface C concentration increases on the spent catalyst. The preliminary EELS data suggest presence of surface carbon on the catalyst, which further supports EDS results. There is some local variation in Al distribution in both catalysts, which requires further study.

Our study provides preliminary insights into coke formation and its distribution throughout the spent ZSM-5. Therefore, XPS in combination with STEM-EDS and EELS mapping is a key characterization technique to study deactivation mechanisms [3].
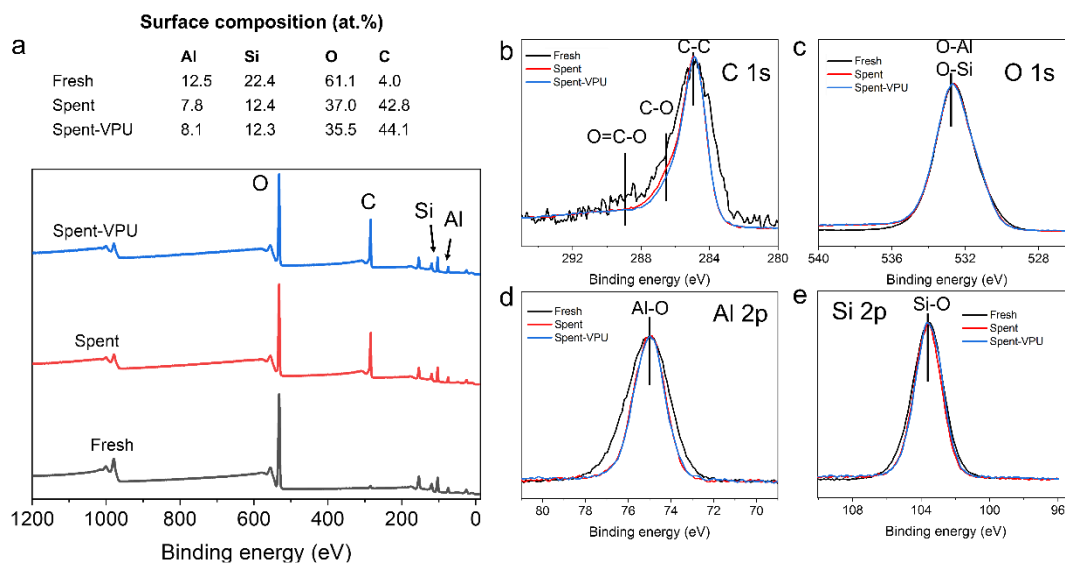
Figure 1. XPS of fresh, spent and spent-VPU ZSM-5 catalyst a) in a wide energy range, with respective atomic percentage of the surface elements such as Al, Si, O and C, b-e) in a narrow energy range, core level spectra.
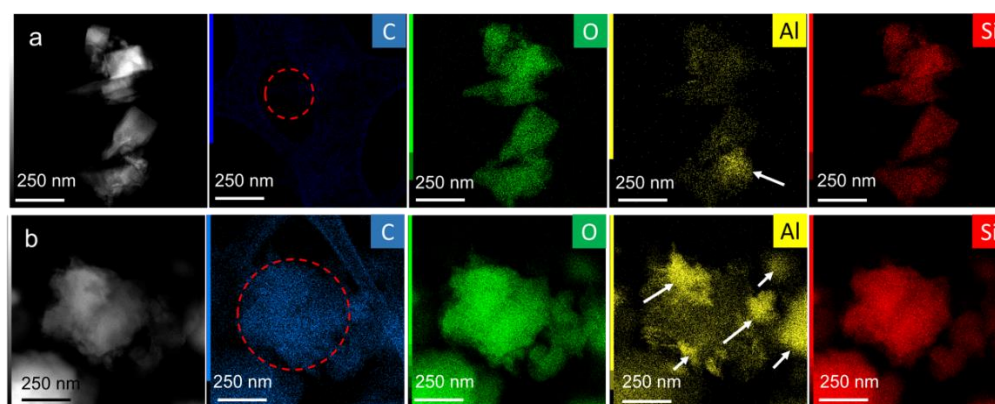
Figure 2. a) HAADF-STEM image of a) fresh and b) spent ZSM-5 with associated EDS elemental maps showing distribution of C, O, Al, Si. The red dotted circle in C maps corresponds to the surface C and white arrows on the Al maps highlights local Al variations in distribution.

References:

[1] EM Gallego et al., Science **355** (2017), p. 1051.
[2] N Chaouati et al., **344** (2016) p. 354.