

Short Communication

Photoacoustic monitoring of catalyst poisoning by petroleum trace metals

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Although it is recognized that the adsorption of metallics onto the surface of catalysts contributes to their poisoning, the subject has not received the attention it deserves. In the petroleum industry, problems caused by catalyst deactivation are of mounting concern. Metallics in the feed charge may be at trace levels, yet their accumulation over the catalyst can be very detrimental. Frequent analysis of the catalyst for adsorbed species is therefore essential. In this respect photoacoustic spectroscopy (PAS) provides rapid identification of such species.

The basic principle of the PAS technique is that, when a sample is irradiated with frequency-modulated monochromatic radiation, part of the radiation is absorbed by the sample and gives rise to a temperature fluctuation in the sample coupling medium. As a result, pressure waves are produced in the coupling medium which is in contact with the sample surface. The pressure waves are then detected by a sensitive microphone to indicate the power absorbed by the sample at the wavelength of the incident radiation [1, 2]. The recent reports on PAS have been concerned with the UV-visible or IR spectra because of the simplicity of spectral interpretation in these ranges. The structured IR spectrum, for example, has been used successfully for identification of organic solids [3]. However, the UV-visible range of the spectrum has been found to be informative only in cases of a few surface species with distinguishable well-separated absorption bands.

Our investigation was conducted by cracking gas oil over a silica-alumina catalyst in a fixed bed reactor at 350 °C. The catalyst was sampled after successive runs for PAS surface analysis. The photoacoustic spectrometer used has been described in an earlier publication [4]. It utilizes a 1000 W xenon arc lamp as a source of excitation at the optimum modulation frequency of 40 Hz. The equipment is completely controlled and operated by a microprocessor.

Spectra of both fresh and used cracking catalysts were determined. The UV-visible (Fig. 1) spectra reveal that, with an increase in the number of runs over the catalyst, there is an increase in the adsorbed species, as would

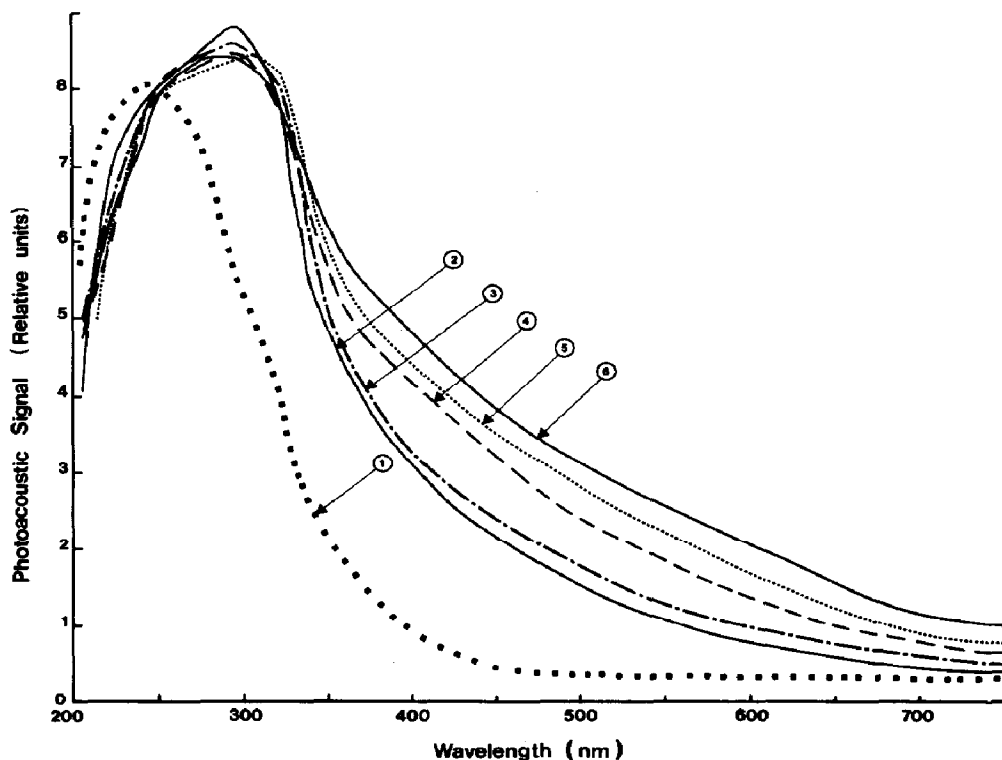


Fig. 1. UV-visible photoacoustic spectra of fresh and used silica-alumina catalysts: curve 1, fresh catalyst; curve 2, after 5 runs; curve 3, after 10 runs; curve 4, after 20 runs; curve 5, after 40 runs; curve 6, after 60 runs.

be expected. However, the overlapping of the spectral bands made it difficult to identify the trace metals adsorbed onto the catalyst. In contrast, the red-near-IR (Fig. 2) range of the spectrum provides a more complete identification of the trace metals.

The peaks at about $1.4 \mu\text{m}$ and at about $1.9 \mu\text{m}$ were found to be due to water absorbed by the silica. The characteristic peaks of silica near-IR photoacoustic spectra should appear at $1.38 \mu\text{m}$ (due to the surface silanol group) and at $2.22 \mu\text{m}$ (due to the bending and stretching vibration of the silanol groups) as explained in an earlier publication [4]. These two peaks are shifted slightly and overshadowed by the peaks of the absorbed water. However, they could easily be identified using a monochromator with higher resolution, but this would be at the expense of the signal-to-noise ratio of the overall spectrum. Since we were not interested in the spectrum of silica *per se*, we decided to sacrifice the spectrum resolution for better signal-to-noise ratio. The alumina spectrum is flat in the range $0.81 - 2.6 \mu\text{m}$. It does not exhibit any structure in that range of the spectrum.

There are two distinct sharp peaks at about 1.9 and $1.7 \mu\text{m}$ and a weak broad peak at about $0.84 \mu\text{m}$ in the spectra of the used catalysts. These three extra peaks did not appear in the spectrum of the fresh catalyst. Their relative intensities increase with the number of runs. The peaks are attributed to

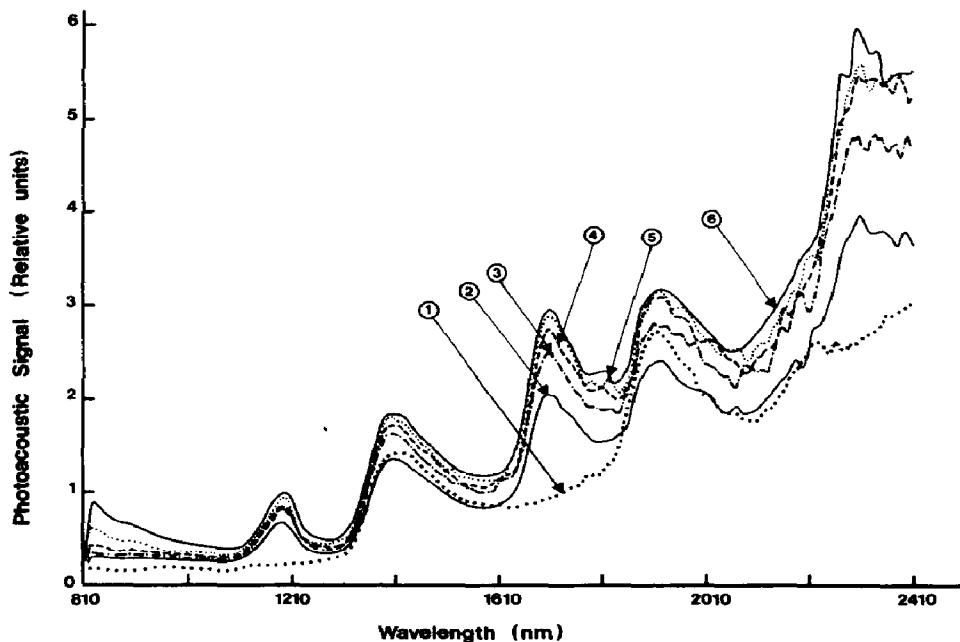


Fig. 2. Red-near-IR photoacoustic spectra of fresh and used silica-alumina catalysts: curve 1, fresh catalyst; curve 2, after 5 runs; curve 3, after 10 runs; curve 4, after 20 runs; curve 5, after 40 runs; curve 6, after 60 runs.

the spectrum of accumulated poisoning trace metals which increase with the number of runs. They are most probably due to the presence of OH groups on the surface of the poisoning trace metals. To substantiate this, the near-IR photoacoustic spectra of several Specpure salts (PbO , $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, CaCO_3 etc.) were obtained. Using these spectra we were able to identify the three extra peaks of the used catalysts. The peaks at 0.84, 1.19 and 1.7 μm were tentatively assigned to lead, calcium and magnesium poisoning trace metals. The presence of these trace metals in our used catalysts has been confirmed independently using an emission spectrographic analysis technique.

This preliminary result is being extended to monitor not only the retained metallic species but also non-metallic species that are the source of catalyst deactivation. Subsurface analysis of the cracking catalyst and other catalysts of industrial interest is also being undertaken.

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