

## PHOTOACOUSTIC SPECTRUM OF A NICKEL OXIDE-ALUMINA CO-PRECIPIATED AEROGEL CATALYST\*\*

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Received July 7th, 1982

The near UV and visible spectrum of a NiO-Al<sub>2</sub>O<sub>3</sub> aerogel hydrogenation catalyst (bulk weight of about 50 mg/cm<sup>3</sup>; 23 wt.% of Ni) was measured using photoacoustic detection. Within the 300–900 nm region, the sample (about 5 mg) showed a single band at 310 ± 5 nm. The band is assigned to an electron transfer from oxygen ligands to Ni<sup>2+</sup> ions incorporated in the lattice of the co-precipitated aerogel. The absorption spectra of the sample in the near and middle infrared regions (900–10 000 nm) obtained by classical transmission technique are presented for comparison.

In the previous work<sup>1</sup> the co-precipitated NiO-Al<sub>2</sub>O<sub>3</sub> catalyst was used as a sorbent for gaseous benzene and hexadeuteriobenzene. The sorption of benzene *in vacuo* (about 1 · 10<sup>-3</sup> Pa) was studied by IR absorption spectroscopy (4 000–1 100 cm<sup>-1</sup>). In order to improve the transparency of the co-precipitated catalyst, it was prepared in the form of self-supporting aerogel plates. The grey plates were sufficiently transparent in the middle- and near-infrared but opaque in the visible and near-ultraviolet regions.

Studies of sorption of aromatic hydrocarbons by electronic spectroscopy are of great interest for catalytic research, too. In cases of dark sorbents, the reflectance spectroscopy is not applicable and therefore the photoacoustic (PA) or optoacoustic method of detection of absorbed light<sup>2-5</sup> is now the only available method which can be used in the visible and near-ultraviolet regions.

The aim of this work was to measure the electronic spectrum of bare aerogel catalyst on air and to determine the region of the spectrum suitable for studies of chemisorbed molecules.

### EXPERIMENTAL

*Preparation of the co-precipitated NiO-Al<sub>2</sub>O<sub>3</sub> aerogel plates.* The procedure proposed for preparation of the pure  $\gamma$ -alumina aerogel<sup>6</sup> was used. The starting sol of aluminum acetate was prepared according to Heard<sup>7</sup>, the only modification was the use of mercuric oxide solution in glacial acetic acid<sup>8</sup> instead of mercuric nitrate to catalyse the dissolution of metallic aluminum.

\* Part LXVI in the series Catalysis by Metal Complexes; Part LXV: This Journal 47, 719 (1982).

\*\* Presented at the 12th Czechoslovak Symposium on Homogeneous Catalysis, Liblice near Prague, October 6–8th, 1980.

After centrifugation at 30 000*g*, the clear sol was mixed with an aqueous solution of nickel acetate (*puriss.*, Merck) in a desired Ni:Al ratio. The co-precipitation of Ni and Al hydroxides was carried out on a mercury pool by gaseous  $\text{NH}_3$ . The obtained hydrogel cake of the co-precipitated hydroxides was repeatedly washed with water and then changed to an alcogel using dried methanol. The resulting alcogel cake was cut into pieces (about  $2 \times 3 \text{ cm}^2$ ) which were transferred into an autoclave. Then, practically all methanol was slowly boiled off above its critical temperature from the autoclave, to avoid a destruction of the aerogel structure of the precipitate. The aerogel plates obtained were calcined on air at about 450°C for several hours. The resulting plates of the  $\text{NiO-Al}_2\text{O}_3$  aerogel were used for the spectral measurements on air.

The plates were about 3 mm thick, for each the total weight was about 80 mg, *i.e.*, the bulk weight was about 50  $\text{mg/cm}^3$ . The content of Ni, determined gravimetrically, was 23 wt.%. Even after a heat treatment of the plates in  $\text{H}_2$  atmosphere, X-ray diffraction showed only the lines of NiO and  $\gamma\text{-Al}_2\text{O}_3$ .

*Photoacoustic spectrometer.* The PA spectrum of the  $\text{NiO-Al}_2\text{O}_3$  aerogel sample of about 5 mg in the near UV and visible regions (300–900 nm) was measured on a single-beam, home-made instrument (linear in wavelength): a 100 W high-pressure short-arc Xe lamp (type XBO 101, Narva, G.D.R.), a quartz parabolic lens, a mechanical chopper, a grating monochromator of the Littrow type ( $f/10$ ; 1.6 nm/mm; constant geometrical slit width 1.8 mm; Optica-Milano, Italy), a PA cell of our construction (sensitivity of about 100 mV/Pa) with a membrane condenser microphone (about 5 mV/Pa; Tesla, Czechoslovakia), a lock-in nanovoltmeter (type 232B; Unipan, Poland), and a conventional line recorder. A similar instrument was described in more detail elsewhere<sup>9</sup>.

*Photoacoustic measurements.* The focused beam of polychromatic light was chopped mechanically (12.5 Hz) and the reference signal for the lock-in detection was taken from a photodiode behind the chopper. A freshly prepared carbon black, deposited on a quartz disc, was used as the reference standard. The maximum PA signals of the sample and the reference standard were adjusted at 465 nm, being about 140 and 550  $\mu\text{V}$ , respectively. The PA spectra, taken during night time at a scan rate 33 nm/min and at a time constant 1 s, were reproducible. The spectrum of the sample was normalized using a programmable desk-top calculator Hewlett-Packard, model 9830A, and an HP-plotter, model 9862A.

*Infrared spectrometers.* Two double-beam instruments from Beckman were used: the model IR-7 with the NaCl fore-prisms/grating optics, linear in wavenumber 1 100–4 000  $\text{cm}^{-1}$ , and the model DK-2A with the quartz prism within the 20 000–3 000  $\text{cm}^{-1}$  region (linear in wavelength; PbS detector).

## RESULTS

The normalized PA spectrum (300–800 nm) of the  $\text{NiO-Al}_2\text{O}_3$  aerogel plate is in Fig. 1, the ordinate scale of which is in arbitrary units<sup>1</sup> for the photoacoustic signal (PAS). The single peak is located at  $310 \pm 5 \text{ nm}$  and its irregular shape around the maximum is presumably due to the point-by-point normalization procedure.

The IR absorption spectra of the  $\text{NiO-Al}_2\text{O}_3$  aerogel plate, obtained by usual transmission technique, are presented in Figs 2 (near IR) and 3 (middle IR) for comparison. A huge IR absorption by the untreated sample in the 2 700–3 300 nm region (3 700–3 000  $\text{cm}^{-1}$ ) is due to H-bonded OH groups (adsorbed  $\text{H}_2\text{O}$  and Al—OH groups) and can be practically removed by heating *in vacuo* (400–450°C).

## DISCUSSION

Doyle and Lonergan<sup>10</sup> have studied thin films of NiO deposited on quartz windows by transmission technique. In the 200–1 000 nm region, their NiO samples revealed two absorption maxima at 240 and 280 nm. The band at 280 nm has been assigned to electron transitions from the highest full band to the first exciton level<sup>10</sup>. Since NiO does not show photoconductivity between 250 and 800 nm, this transition requires that the exciton is not thermally dissociated at room temperature<sup>10</sup>. In other words, the 280 nm band is associated with electron transfer from negative to positive ion<sup>10</sup>.

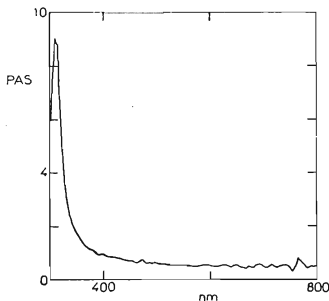


FIG. 1

The photoacoustic spectrum in the near ultraviolet and visible regions (linear in wavelength) of the NiO-Al<sub>2</sub>O<sub>3</sub> aerogel plate before the treatment (cf. Fig. 3)

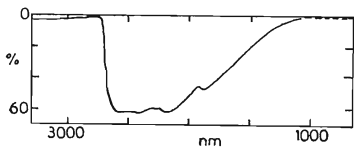


FIG. 2

The near infrared absorption spectrum obtained by classical transmission technique (linear in wavelength) of the NiO-Al<sub>2</sub>O<sub>3</sub> aerogel plate before the treatment (cf. Fig. 3), using a PbS detector for the whole region

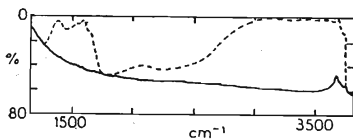


FIG. 3

The middle infrared absorption spectrum obtained by classical transmission technique (linear in wave number) of the NiO-Al<sub>2</sub>O<sub>3</sub> aerogel plate. After the treatment at about 450°C *in vacuo* (full line); before the treatment (dashed line)

In agreement with this interpretation we ascribe the band at 310 nm to an electron transfer from  $O^{2-}$  to  $Ni^{2+}$  ions incorporated in the lattice of the co-precipitated  $NiO-Al_2O_3$  aerogel.

Summarizing, the PA spectrum is sufficiently simple in the 320–800 nm region to allow spectral studies of coloured compounds adsorbed on the catalyst. The PA spectrum below 300 nm is also of interest, since the first absorption band, *e.g.*, of free benzene molecules is centered around 250 nm. It requires, however, a higher output of the xenon lamp to improve the signal-to-noise ratio in this region.

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Translated by the author