

## NOTE

## A Neutron Scattering Study of Molecular Motions in Toluene Adsorbed on Alumina and on Chromia Supported on Alumina

Heterogeneous catalysis requires the chemisorption of reactant molecules, and for this reason information concerning the structure and dynamics of adsorbed molecules can be of interest for the understanding of the catalytic process itself. As heats of chemisorption are of the order of 10 to 100 kcal/mol, the external molecular motions are appreciably changed when the molecule is adsorbed on a catalyst (1). Details about the dynamic behavior of adsorbed molecules may be obtained by infrared and Raman spectroscopy, by nuclear magnetic resonance, and by slow neutron scattering. The neutron scattering method has been used in the study of physical adsorption of water on  $\gamma$ -alumina (2) and zeolites (3), of methane, ethylene, acetylene and hydrogen on activated charcoal (4, 5), and of methane on zeolites (6). The use of the neutron scattering method as a tool for the investigation of molecular motions in condensed systems, and particularly to chemical problems, has been extensively described in the literature (6-8) and is not discussed here.

This article presents the results of preliminary measurements on the inelastic scattering of beryllium-filtered neutrons by toluene adsorbed at different temperatures on  $\eta$ -alumina and on chromia supported on  $\eta$ -alumina.

The neutron scattering measurements have been performed with a conventional time-of-flight spectrometer (9). An incoming, quasimonochromatic beryllium-filtered neutron beam, having a mean energy

of 3.5 MeV ( $28 \text{ cm}^{-1}$ ), is scattered by the studied sample. A chopper, placed between the beryllium filter and the sample, gives periodic neutron bursts and allows the time-of-flight analysis of scattered neutrons, which are detected by three banks of  $\text{B}^{10}\text{F}_3$  counters disposed at scattering angles of 40, 60 and  $80^\circ$ . After background subtraction, the measured intensities were corrected for counter efficiency, air attenuation, and attenuation by absorption and scattering in the sample.

The  $\eta$ -alumina, of area  $210 \text{ m}^2/\text{g}$ , has been prepared by calcining hydrated alumina for 6 hr at  $600^\circ\text{C}$ . The chromia-alumina catalyst, prepared from  $\eta$ -alumina impregnated with  $\text{CrO}_3$ , contained 18%  $\text{Cr}_2\text{O}_3$  and had an active area of  $175 \text{ m}^2/\text{g}$ .

The adsorbents were introduced in tight containers, made of a row of thin walled aluminum tubes, 8 mm in diameter. In order to reduce the multiple neutron scattering in the sample, the tubes were separated during the spectra measurements by cadmium sheets. The samples, coupled to a vacuum system, were outgassed for 12 hr at  $450^\circ\text{C}$  and  $10^{-3}$  Torr pressure. Toluene was admitted into the outgassed sample container at room temperature after which the unadsorbed substance was removed by an additional evacuation. The final surface coverage was about 90%. For liquid toluene the sample container was a plane aluminum box; the thickness of liquid film was 0.5 mm. The measurements with adsorbed toluene were performed first with the samples prepared as mentioned above,

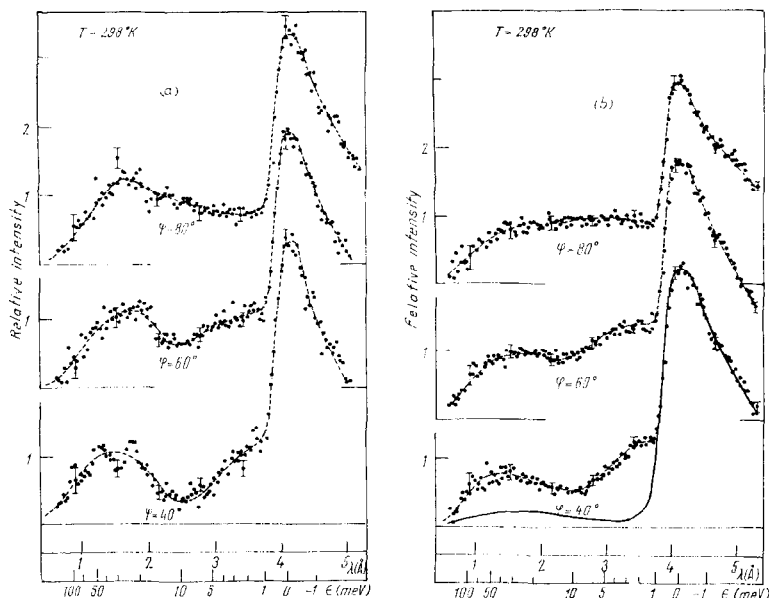


FIG. 1. The wavelength distribution of beryllium-filtered neutrons scattered at room temperature by samples containing the adsorbent and the toluene remaining adsorbed after 3 hr evacuation at 463°K. The adsorbents were (a)  $\eta$ -alumina and (b) chromia supported on  $\eta$ -alumina. (—) The spectrum of beryllium-filtered neutrons scattered by the outgassed  $\eta$ -alumina.

and then the measurements were repeated with the same samples additionally outgassed at 463 and 823°K. All the spectra were measured at room temperature.

In Fig. 1 are given the spectra of beryllium-filtered neutrons scattered at room temperature by the  $\eta$ -alumina and chromia catalyst samples filled with toluene, and then evacuated for about 3 hr at 463°K. At room temperature, the cold neutrons are scattered practically elastically by the outgassed alumina and chromia-alumina catalysts. The solid line shows the spectrum of cold neutrons scattered by the outgassed alumina sample which, apart from the resolution distortions, does not differ from the spectrum of the incoming neutrons. Therefore, the inelastic part of the spectra is given by the adsorbed toluene solely, while in the elastic peak the contribution of adsorbed toluene is overlapped by that of the adsorbent. The separation of the toluene contribution in the region of the elastic peak is affected by large statistical errors and is not considered in the present discussion. A characteristic

feature of all the spectra is the presence of an inelastic peak centered at about 40 MeV ( $320\text{ cm}^{-1}$ ) and a low energy band extended at energy transfers smaller than 10 MeV, which may be ascribed to the molecular modes of adsorbed toluene. At room temperature, the chemisorbed molecules have a small mobility on the surface and the peaks observed in the spectra may be assigned to the torsional vibrations of the methyl group, to the translational and librational modes of the whole molecule, and to the distortional vibrations of the toluene skeleton. In the low frequency band are accumulated the contributions of molecular modes which involve great effective mass, for example the center of mass oscillations and the librations of the whole molecule. In principle, three vibrational modes of the toluene molecule, namely,  $\nu_{11} = 216\text{ cm}^{-1}$ ,  $\nu_{18b} = 340\text{ cm}^{-1}$ , and  $\nu_{16a} = 405\text{ cm}^{-1}$  (10), and the torsional oscillations of the methyl group, may be associated with the  $320\text{ cm}^{-1}$  peak. In the assignment of this peak to a given molecular mode, some characteristic features of

neutron scattering have to be considered.

The intensity of an inelastic peak, which arises from the de-excitation of a vibrational mode, is proportional to the square of the corresponding vibrational amplitude. As the neutron incoherent scattering cross-section of hydrogen is appreciably greater than that of other nuclei (11), the molecular vibrational modes, which imply large amplitude proton oscillations, are associated with intense inelastic peaks in the spectrum of scattered neutrons (6-8). Due to the low rotational mass of hydrogen atoms in the methyl group, it may be supposed that the main contribution in the  $320\text{ cm}^{-1}$  peak results from the 1-0 transition of torsional oscillations of the methyl group. The assignment given is consistent with previous experimental data concerning the scattering of beryllium-filtered neutrons by benzene and methylbenzene (12-15). In the spectra of liquid benzene the contribution of intramolecular vibrational modes appear as an inelastic band which is several times less intense than the low frequency band associated with the whole molecule motions (12). If the spectrum of liquid toluene is compared with that of liquid benzene, their difference shows an intense broad peak which originates in the de-excitation of hindered rotational levels of the methyl group (14). As Fig. 2A for liquid toluene shows, the  $\text{CH}_3$  rotational peak and the low frequency band are not separated but blend into a single band. In solid methylbenzenes, where the methyl group performs torsional oscillations, the corresponding peak is distinct from other contributions (12, 13, 15).

If the barrier to free rotations of the methyl group in chemisorbed toluene is supposed to be a cosine potential,  $V = \frac{1}{2}V_0(1 - \cos 3\alpha)$ , the value  $V_0$  derived in the harmonic approximation is 6.3 kcal/mol.

As the adsorption temperature increases, the intensity of the peak centered at  $320\text{ cm}^{-1}$  decreases in the spectra of toluene adsorbed on the chromia-alumina catalyst and remains practically constant in the spectra of toluene adsorbed on  $\eta$ -alumina. For all the spectra the low frequency band

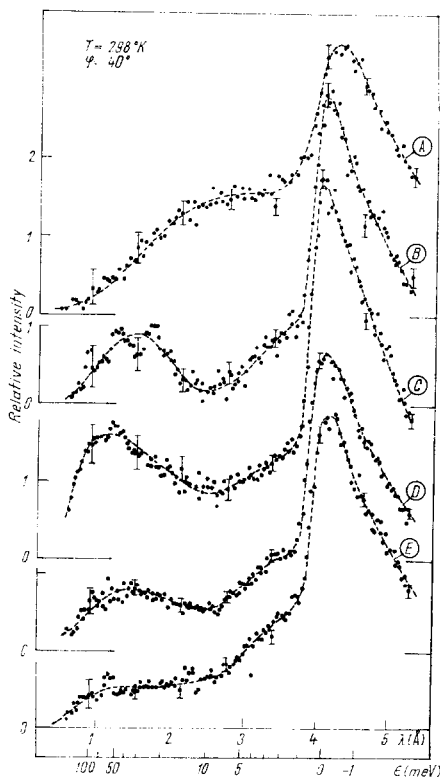


FIG. 2. The wavelength distribution of beryllium-filtered neutrons scattered at room temperature and scattering angle  $\theta = 40^\circ$  by: (A) liquid toluene; (B) sample +  $\eta$ -alumina + toluene evacuated at  $463^\circ\text{K}$ ; (C) sample + chromia supported on  $\eta$ -alumina + toluene evacuated at room temperature; (D) as (C) but toluene evacuated at  $463^\circ\text{K}$ ; and (E) as (C) but toluene evacuated at  $823^\circ\text{K}$ .

does not depend sensitively on the adsorption temperature (Fig. 2). This fact may be ascribed to the splitting of the C-C bond and the decomposition of toluene into benzene which remains adsorbed on the chromia catalyst and methane which is desorbed. Except for the decrease in the peak intensity of the  $320\text{ cm}^{-1}$  band there is not a noticeable difference between the spectra of toluene adsorbed on  $\eta$ -alumina and those of toluene adsorbed on chromia supported on  $\eta$ -alumina. It may be concluded that the presence of chromia on the surface of alumina does not change essentially the dynamic behavior of adsorbed toluene molecules.

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