SPECTRAL AND CATALYTIC PROPERTIES OF A CHROMIUM–CONTAINING POLYMERIC COMPLEX

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Received November 1, 1977
Accepted March 20, 1978

The spectral and catalytic properties of octahedrally coordinated polymeric Cr$^{3+}$ ions are compared with those of the same ions in α-Cr$_2$O$_3$. A relationship between the character of the nearest ligand environment of the Cr$^{3+}$ ion (according to spectral data) and the catalytic activity was found. The exchange interaction between Cr$^{3+}$ ions of the polymer chain exerts no significant influence on the catalytic activity.

Chromium ions exhibit different catalytic properties in oxide systems. The study of their catalytic and physical properties when present in other types of solid substances in an octahedral oxygen environment was judged to be of interest in order to elucidate some general aspects of the catalytic activity.

A polymer of the proposed composition

$$\{\text{Cr}(\text{CH}_3\text{COCOCH}_3)\{\text{OP(C}_6\text{H}_5\text{O})_2\}_{\text{n}}\}$$

prepared according to Ref. /1/ from chromium acetylacetonate and diphenylphosphinic acid at 200 $^\circ$C was investigated. Cr$^{3+}$ polymer ions are octahedrally coordinated with
the chelating oxygen atoms of diphenylphosphinic acid and acetylacetonate, while
the individual coordination moieties are bonded in spirals /2/:

![Chemical structure](image)

The studies were conducted using two fractions of the polymer, a benzene soluble
fraction (CrPCBF) of molecular weight 2000–2600, \( n = 4−5 /1/ \), containing 8.4 wt. %
chromium, and an insoluble fraction (CrPCNS) of higher molecular weight (several
tens of thousands) containing 4.5 wt. % of chromium. Elemental analysis and IR
spectra corroborate the suggested structure /1, 2/.

Reflectance spectra of the samples taken on a VSU-2p-Carl Zeiss spectrometer
in the 340–700 nm region revealed \( 4A_{2g} \rightarrow 4T_{2g}, 4A_{2g} \rightarrow 4T_{1g} \) and \( 4A_{2g} \rightarrow 4T_{2g} \)
transitions typical for \( Cr^{3+} \) in an octahedral environment /3/. The experimental
spectra were used as a basis for calculating the crystal field splitting of the d-levels
\( \Delta(4A_{2g} \rightarrow 4T_{2g} \) transition) and the electron repulsion parameter \( B_{35} /3/:

\[
B_{35} = \frac{\Delta E}{15} \left( \frac{\Delta - \delta E}{0.8 \Delta - \delta E} \right)
\]

where \( \delta E \) is the energy difference between the \( 4T_{2g} \) and \( 4A_{1g} \) terms. The spectral
data listed in the Table support the proposed structure of the polymer /1, 2/.