GAMMA-RESONANCE SPECTROSCOPY OF ZIEGLER-NATTA TYPE HOMOGENEOUS-HETEROGENEOUS CATALYSTS
A. Khlystov, A. Brodskii, N. Noskova, D. Sokolsky

To cite this version:

HAL Id: jpa-00219611
https://hal.archives-ouvertes.fr/jpa-00219611
Submitted on 1 Jan 1980

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
GAMMA-RESONANCE SPECTROSCOPY OF ZIEGLER-NATTA TYPE HOMOGENEOUS-HETEROGENEOUS CATALYSTS

A.S. Khlystov, A.R. Brodskii, N.F. Noskova and D.V. Sokolsky

Institute of Organic Catalysis and Electrochemistry, Kazakh Academy of Sciences, Alma-Ata.

The paper is devoted to the study of Ziegler-Natta type metallo-organic catalysts on an iron stearate base.

In the chemical reaction between Fe(C_{17}H_{35}COO)\_2 and Al(C_{2}H_{5})\_3 complexes are formed the nature of which depends on the Al/Fe ratio. Earlier /1,2/ three stages were distinguished for the catalytic system formation and analyzed. At a molar ratio of Al/Fe=2 when the component interaction process is only slightly complicated by oxidation-reduction transformations, the usual reaction of AlR\_3 addition to stearate ligand and carbonyl with preservation of the initial iron stearate structure takes place. At 2\leq Al/Fe \leq 4 molar ratios as a result of oxidation reduction interactions complexes are formed containing Fe(II) and Fe(III). At Al/Fe \geq 4 multinuclear associated systems appear in which Fe(II) and Fe(III) are bound to aluminium alkyl. Further increase of the AlR\_3 concentration leads only to associate sizes growth due to the aluminium alkyl coordination.

In the process of the hydrogenation reaction associates and complexes with different iron valent forms are in a dynamic balance, their ratios depend on conditions in which the process is carried out and on the hydrogenated compound and the nature of the solvent.

Depending on the unsaturated compound nature there occurs change of the Al/Fe ratio at which the hydrogenation proceeds with the highest rate. Thus, for methylinoleate the optimal Al/Fe is 6\pm 8. Fig. 1 presents Mossbauer spectra of the samples taken at various stages of methylinoleate hydrogenation in toluol and heptane; Fig. 2 shows final results of their treatment.

![Mossbauer spectra of the Fe(C\_{17}H\_{35}COO)\_2\cdot Al(C\_{2}H\_{5})\_3 catalytic complex in heptane (a) and toluol (b). 1-the formed complex; 2-methylinoleate introduction; 3-1/2 mole H\_2 addition; 4- 1 mole H\_2 addition.](image)

In conformity with the idea about the Fe(C\_{17}H\_{35}COO)\_2 /1, 2/ structure, associates may be considered to be the active centre in which methylinoleate hydrogenation proceeds. In GR-spectra the iron form corresponding to associates is designated by us as Fe(X). It may be assumed that in the case of toluol the unsaturated compound is activated on associates acting as an acceptor. The acceptor character of methylinoleate is seen in the fact of the continuous (J_E \_1) isomeric shift decrease for Fe(X) in the hydrogenation process. Such a decrease may occur due to decrease of d-electrones.
screening action as a result of their being drawn off by the unsaturated compound. Sharp decrease of the relative Fe(II) content when introducing methylstearate and a smoother one in hydrogenation points out partial destruction of the associated complex in the hydrogenation process; the catalyst with low Fe(II) content is not active. The conclusion about associates destruction may also proceed from the fact of the increase of the relative Fe(II) content proportional to decrease of the Fe(II) amount because in this case increase of the Fe(II) amount may occur only due to the Fe(II) form (the relative Fe(II) content practically is not changed). Furthermore, the changes occurring in the system with introduction of the unsaturated compound are shown by increase of the quadrupole ($\Delta E_Q$) splitting for Fe(II) while in the hydrogenation process $\Delta E_Q$ practically is not changed.

![Diagram](image)

Fig. 2 Change of GR-parameters and of the content of I - Fe(III), II - Fe(II), III - Fe(I) iron forms depending on the stage of process in toluol (a) and heptane (b) (1, 2, 3, 4 see Fig. 1).

in the case of heptane it should be noted that both Fe(II) and Fe(III) react upon introduction of the unsaturated compound, and in contrast to the case of toluol with unsaturated compound introduction, the relative Fe(II) content increases and only later its behaviour in the hydrogenation process becomes the same as in toluol. Increase of the Fe(II) amount with methylstearate introduction is proportional to decrease of the relative Fe(II) amount.

There are two possible explanations for methylstearate hydrogenation differences depending on a solvent. It may be assumed that in heptane with introduction of unsaturated compound there occurs Fe(III) bond break in an associate, a part of Fe(III) appears to be unblocked and able to participate in the oxidation-reduction process involving Fe(II). As a result of it, at the stage of the unsaturated compound introduction there may be formed some additional Fe(II) amount. Another possible explanation is that the unsaturated compound activation occurs also on Fe(II). In favour of this assumption speaks the character of $\delta E_I$ and $E_Q$ change for Fe(II) as well as the $\delta E_I$ behaviour change for Fe(II) in comparison with that was observed in toluol. At the present time it is not possible to choose between these two assumptions.

Deposition of Fe(C$_{17}$H$_{35}$COO)$_2$ over Ni(OH)$_2$ leads to a several-times increase of the hydrogenation rate without a considerable change of the supported iron stearate and AlR$_2$ interaction mechanism and the hydrogenation mechanism. Some difference consists in the formation of complex-containing Fe(II) and Fe(III) as well as associates at lower Al/Fe ratios. This fact may be accounted for by the stabilizing affect of the carrier acting in the catalytic complex as a ligand.

\cite{1, 2/ A.R.Brodskii, et all, J.Organometall. Chem. Vol 178/2, Vol.179(in press)}