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Vibrational spectra of titanium chlorides and magnesium chlorides used for the Ziegler-Natta catalyst

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Ziegler-Natta catalyst (ZNc) composed of titanium chlorides and magnesium chlorides has been used for the production of highly stereospecific polyolefins. Although a large number of studies have been made on this catalyst, its catalytic mechanism has not yet been clear. In order to clarify its catalytic mechanism, it is important to perform the in situ observation of the catalytic reaction on a model thin film ZNc by vibrational spectroscopy. For this observation, vibrational spectra of crystalline $TiCl_n$ (n=2, 3, and 4) and $MgCl_2$ thin film are necessary as the basic data. The aims of this work are (1) to obtain vibrational data of $TiCl_n$ (n=2,3,and 4) by Raman scattering, and (2) to establish the production method of crystalline $MgCl_2$ thin film available for the vibrational spectroscopic observation.

The observed Raman spectra of $TiCl_n$ are shown in Fig. 1. The Raman spectrum of crystalline $TiCl_2$ shown in Fig. 1 is the first data, so far as we know. In the spectrum of crystalline α-$TiCl_3$, five clear Raman bands are seen. The frequencies of these five bands are different from those reported in Ref. 1. Four clear Raman bands are seen in the spectrum of $TiCl_4$. The frequencies of these observed bands agree well with those reported in Ref. 2 and 3. In order to make assignments of these observed bands in Fig. 1, normal modes were calculated by the GF method. Through the calculation, we find that the Ti-Cl stretching force constant increases as the oxidation number of the Ti increases. This result provides important information for the investigation of the catalytic reaction , because the Ti-Cl stretching force constant can be a good indicator of the catalytic activity.

Next, the Raman observation of ball-milled α-$TiCl_3$ was performed to investigate the milling effect leading to an increase in the activity of ZNc. A new band appears at 224 cm^{-1} for ball-milled α-$TiCl_3$. This band probably results from the breakdown of the crystal symmetry.

In order to prepare the $MgCl_2$ film, $MgCl_2$ was sublimed from a glass crucible heated at about 420℃ and deposited on a Ag film in UHV. The observed Raman spectrum of the $MgCl_2$ thin film is shown in Fig. 2. Two Raman modes A_{1g} and E_g are clearly seen in the spectrum. Due to the SERS (surface enhanced Raman scattering) effect of Ag film substrate the observation Raman scattering from the very thin $MgCl_2$ film has become possible. Since observed band frequencies agree with those of $MgCl_2$ crystal and the observed band widthes are not so broad, we conclude that the crystallinity of the deposited film is good.

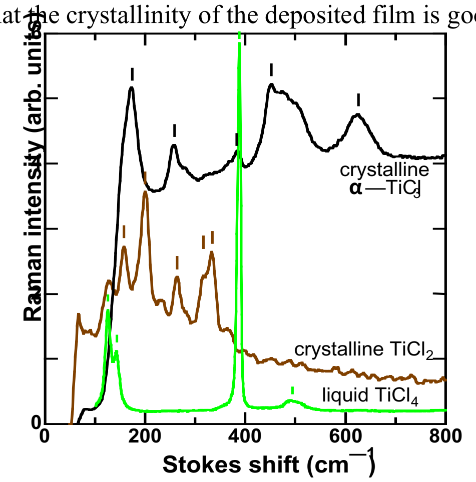

Fig. 1: Raman spectra of $TiCl_n$ (n=2, 3, 4)

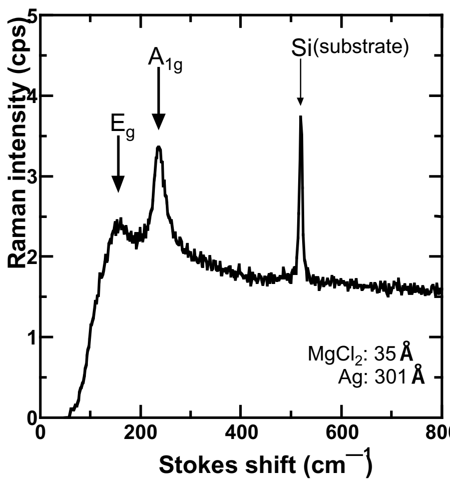

Fig. 2: Raman spectrum of $MgCl_2$ thin film

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