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Citation	Applied Catalysis A: General, 437-438: 24-27
Issue Date	2012-06-15
Type	Journal Article
Text version	author
URL	http://hdl.handle.net/10119/11451
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Description	

Validation of BET Specific Surface Area for Heterogeneous Ziegler-Natta Catalysts based on α_S -Plot

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ABSTRACT: Specific surface area based on the BET method in N₂ adsorption has historically posed poor correlation with olefin polymerization activity of heterogeneous Ziegler-Natta (ZN) catalysts. We have investigated the validity of the BET surface area for ZN catalysts based on the α_s -plot method, where non-porous core-shell MgO/MgCl₂/TiCl₄ catalysts were used as a reference material. The α_s -plots for typical industrial ZN catalysts clarified the presence of two classes of micropores and resultant difficulty to isolate a multilayer adsorption region for the BET method. The results cast doubt on the application of the BET method to evaluate the surface area of heterogeneous ZN catalysts.

KEYWORDS: Ziegler-Natta polymerization; polyolefin; nitrogen adsorption; BET method; α_s -plot

1. Introduction

Specific surface area is one of the most fundamental characteristics of heterogeneous catalysts, especially in terms of catalytic activity. The BET method [1] in N_2 adsorption has been routinely employed for this purpose. Similarly in heterogeneous Ziegler-Natta (ZN) catalysts for industrial olefin polymerization, the specific surface area evaluated by the BET method has been frequently attached as a kind of specs. However, it has been recognized that the BET surface area contains some intrinsic problem(s), probably arising from uncertainty in pore structures and/or the presence of internal donors that are more or less volatile. For example, Marigo et al. showed quite poor correlation between two kinds of specific surface area measured by the BET method and by small-angle X-ray scattering (SAXS) for ZN catalysts prepared through precipitation of $MgCl_2$ -alcohol adduct [2]. The BET surface area was poorly correlated with propylene polymerization activity, while the SAXS surface area gave some level of correlation [2]. Rönkkö et al. reported that a self-supported ZN catalyst prepared by an emulsion technique [3] offered a good activity ($\sim$ several tens $kg/g\cdot cat\cdot h$) in propylene polymerization in spite of extremely low BET surface area ($\sim 2\text{ m}^2/g$) [4]. Furthermore, the catalyst underwent relatively homogeneous fragmentation during the polymerization, even though it was assumed in N_2 adsorption that there were few spaces for reagents to diffuse inside the catalyst particles [5].

In general, the application of the BET method requires careful attention in evaluating the surface area of materials with unknown pore structures. Especially, the monolayer capacity (V_m) in the BET equation is not decided for microporous materials, thus leading to physically meaningless surface area. One of the most difficult cases is that a material apparently gives an

isotherm typical for the types II or IV in IUPAC classification but contribution from micropore filling is hidden. The α_s -plot method is an empirical approach for the determination of a surface area and the identification of pore structures [6], which utilizes the invariant nature of multilayer adsorption of N₂. Unlike to the t -plot method [7], it requires only a non-porous or macroporous reference material, whose surface chemistry resembles that of a sample of interest. The adsorption isotherm of a reference material is used to construct an α_s curve as a function of p/p_0 and the isotherm of a sample of interest is plotted against the obtained α_s curve. Although an advantage of the α_s -plot method is for the validation of the BET surface area [8], it has been never applied to heterogeneous ZN catalysts. The largest difficulty exists in the preparation of a non-porous or macroporous ZN catalyst as reference, since typical ZN catalysts consist of irregular and hierarchical agglomeration of unknown building units bearing a variety of pore sizes and shapes.

Recently we have prepared novel core-shell MgO/MgCl₂/TiCl₄ catalysts by chlorinating single-crystal MgO nanoparticles with refluxing TiCl₄, where the original MgO nanoparticles as non-fragmentable core were thinly covered by TiCl₄/MgCl₂ catalytic overlayer [9]. Since the catalysts were free from internal pores, a series of the core-shell catalysts with controlled surface area were obtained from the MgO nanoparticles having different sizes. The state of supported Ti species studied with X-ray photoelectron spectroscopy was identical to that of typical ZN catalysts (TiCl₄ supported on MgCl₂) irrespectively of the catalyst surface area. Propylene polymerization with these catalysts firstly revealed a completely linear relationship between the catalyst BET surface area and propylene polymerization activity, while the activity was not dependent on the content of supported Ti species [9]. In this communication, the

non-porous feature of $\text{MgO/MgCl}_2/\text{TiCl}_4$ catalysts was exploited as a reference material for the α_s -plot method, and the validity of the BET specific surface area analysis in typical heterogeneous ZN catalysts was firstly studied.

2. Experimental

2.1. Materials

The core-shell $\text{MgO/MgCl}_2/\text{TiCl}_4$ catalysts were synthesized according to our previous literature [9]. Briefly, $\text{MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ prepared from $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ solution in ethanol was calcined at 800, 750, or 650°C, leading to single-crystal (*i.e.* poreless) MgO nanoparticles with the crystallite size of 32.0, 19.5 or 12.8 nm, respectively (designated as MgO1, MgO2, and MgO3). The crystallite sizes determined with the Scherrer equation for the (200) peak of MgO in X-ray diffraction coincided well with the sizes estimated from transmission electron microscope (TEM) and the BET specific surface area. The MgO nanoparticles were partially chlorinated by refluxing with TiCl_4 for 2 h to obtain the core-shell MgO1-3/ $\text{MgCl}_2/\text{TiCl}_4$ catalysts with the sizes of MgO core kept almost unchanged after the chlorination [9]. The Ti contents were 0.88, 2.39, and 7.72 wt.-% for MgO1-3/ $\text{MgCl}_2/\text{TiCl}_4$, respectively, which increased as the catalyst surface area increased.

Two kinds of typical industrial ZN catalysts were prepared in this study. The first catalyst (designated as Cat-S) was synthesized based on precipitation from MgCl_2 -alcohol solution [10,11]. 10 g of MgCl_2 co-dissolved by 52 ml of 2-ethylhexanol and 5 ml of di-*n*-butylphthalate (DNBP) in anhydrous decane was dropwisely added to 400 ml of TiCl_4 kept at -15°C for 1 h, and heated at 110°C . The resultant precipitate was washed with anhydrous heptane, again

treated with 200 ml of TiCl_4 at 110°C and repeatedly washed with heptane to obtain the catalyst. The second catalyst (designated as Cat-C) was obtained by chemically converting $\text{Mg}(\text{OEt})_2$ precursor into MgCl_2 using TiCl_4 [11,12]. 80 ml of TiCl_4 was dropwisely added into 40 g of $\text{Mg}(\text{OEt})_2$ dispersed in 240 ml of toluene. The temperature was once increased up to 90°C to introduce 6 ml of DNBP, and then kept at 110°C for 2 h. The obtained solid was washed with toluene, additionally treated with 80 ml of TiCl_4 in 200 ml of toluene at 110°C for 2 h, and repeatedly washed with heptane to yield the catalyst. The Ti contents were 2.1 and 2.7 wt.-% for Cat-S and Cat-C, respectively.

2.2. Characterizations

The particle morphology of the above-mentioned catalysts was acquired by using scanning electron microscope (SEM, Hitachi S-4100). Samples for SEM measurements were prepared in a glove bag under N_2 atmosphere, then transferred to a deposition device (Hitachi E-1030 Ion Sputter) for Pt-Pd coating, and finally transferred to a SEM chamber, during which the contact of samples with air was minimized [13].

N_2 adsorption / desorption isotherms at 77 K were measured on Belsorp-max. Samples were filled in a tube under N_2 atmosphere and then outgassed for 2 h at 80°C prior to the measurements. In the α_s -plot method, the adsorption volume ($V_{\text{ads}}(p/p_0)$) normalized at $V_{\text{ads}}(0.4)$ for a reference material is regarded as $\alpha_s(p/p_0)$, which is used as a new x-axis to plot the adsorption isotherms for samples of interest. The discrete adsorption data for the reference were numerically interpolated to generate a continuous α_s axis.

3. Results and discussion

Fig. 1 shows the N₂ adsorption / desorption isotherms for Cat-S and Cat-C as typical ZN catalysts. Their adsorption isotherms are apparently classified as the types IV and II, respectively, even though contribution of micropore filling to the isotherms could not be judged as was mentioned in the introduction. The BET surface area was determined to be 302 and 267 m²/g for Cat-S and Cat-C, respectively. The presence of a hysteresis loop is associated with the capillary condensation taking place in mesopores, while the unrestricted sorption limit in type II is generally observed for macroporous adsorbent. The hysteresis loop for Cat-S belongs to the type H2, indicative of the presence of irregular mesopores in size and shape, made by agglomeration of spheroidal particles [14]. On the other hand, the hysteresis loop for Cat-C belongs to the type H3, typical for slit-shaped mesopores, whose sizes and shapes are again non-uniform [12]. These suggestions for the shapes of mesopores are consistent with the morphology of the two catalysts: building units are spheroidal for Cat-S and lamellar for Cat-C as can be seen in their cross-sectional SEM images (Fig. 2).

The core-shell MgO/MgCl₂/TiCl₄ catalysts were believed to keep the non-porous morphology of the single-crystal MgO nanoparticles, since the crystallite dimension of the MgO core as well as the particle surface area were almost kept unchanged after the formation of the TiCl₄/MgCl₂ catalytic overlayer [9]. Further, the perfectly proportional relationship between the BET surface area and propylene polymerization activity [9] was a sort of indicator of the absence of internal micropore structures (since the BET method does not correctly evaluate the surface area of microporous materials). Thus, the core-shell MgO/MgCl₂/TiCl₄ catalysts were regarded as an ideal reference material for ZN catalysts in the α_s -plot method.

Fig. 3 displays the N₂ adsorption / desorption isotherms of the core-shell MgO/MgCl₂/TiCl₄ catalysts. The MgO1/MgCl₂/TiCl₄ catalyst having the largest particle size exhibits the type II adsorption isotherm without prominent rise at $p/p_0 < 0.1$ and with a marginal hysteresis at $p/p_0 > 0.9$, which indicates the dominant presence of macropores (> 50 nm). These macropores absolutely belong to inter-particle pores since their sizes are above the particle size of 32 nm. The other two catalysts with smaller particle sizes showed similar isotherms except downward shift of the hysteresis closure point due to smaller inter-particle pore sizes. The BET surface area was evaluated to be 33, 100 and 149 m²/g for MgO1-3/MgCl₂/TiCl₄, respectively.

Although it appeared that all the core-shell catalysts were free from pore filling at least up to $p/p_0 = 0.4$ (the BET method utilizes $0.05 < p/p_0 < 0.35$), we have employed the adsorption isotherm of the MgO1/MgCl₂/TiCl₄ catalyst to construct an α_s curve due to its largest inter-particle pores, where the α_s value was set to unity at $p/p_0 = 0.4$. Fig. 4 summarizes α_s -plots for all the catalysts. The α_s -plots for the smaller core-shell MgO2,3/MgCl₂/TiCl₄ catalysts were substantially linear up to $\alpha_s = 1.5$ (corresponding to $p/p_0 \sim 0.66$), even though the smallest MgO3/MgCl₂/TiCl₄ exhibited a hysteresis around the corresponding pressure. This result indicates that most of the N₂ uptake arose from monolayer and multilayer adsorption of N₂. In this way, the non-porous feature of the core-shell MgO/MgCl₂/TiCl₄ catalysts held irrespectively of their particle sizes. The surface area calculated from the gradients, 99 m²/g for MgO2/MgCl₂/TiCl₄ and 151 m²/g for MgO3/MgCl₂/TiCl₄, well coincided with the BET surface area (given above), validating the BET method for the core-shell system. On the other hand, the α_s -plots for the two typical ZN catalysts were far from being linear: the gradient once decreased around 0.1-0.3 of α_s , then increased from *ca.* 0.7 of α_s and finally decreased gradually from *ca.*

1.0 of α_s . These results suggest the presence of at least two steps of pore filling, one at very low α_s associated with pores of molecular dimensions and the other at *ca.* 0.7-1.0 of α_s associated with pores involving quasi-multilayer formation [12]. Thus, we found with the aid of the α_s -plot method that typical ZN catalysts contain at least two classes of micropores, and it is not possible to isolate a multilayer adsorption region from the pore filling (critical for the BET method). These results clearly cast doubt on the validity of the BET surface area measurement for ZN catalysts, which is believed as one of the reasons why the BET surface area has posed poor correlation with olefin polymerization activity [2,4,15] in contrast to the perfectly linear relationship observed for the core-shell MgO/MgCl₂/TiCl₄ catalysts [9].

4. Conclusions

In order to identify an origin of poor correlation between the BET specific surface area and olefin polymerization activity of heterogeneous ZN catalysts, the validity of the BET method was examined by means of the α_s -plot method. A standard α_s curve was constructed from non-porous core-shell MgO/MgCl₂/TiCl₄ catalysts, whose BET surface area had exhibited perfectly linear correlation with propylene polymerization activity [9]. The N₂ adsorption isotherms for two kinds of typical industrial ZN catalysts were apparently classified into the types II and IV, to which the BET method is usually applicable. However, the α_s -plots revealed the presence of two classes of micropores, making the isolation of a multilayer adsorption region for the BET method almost impossible. It was concluded that the validity of the BET specific surface area of heterogeneous ZN catalysts is questionable, which is believed as one of the causes for the reported poor correlation with olefin polymerization activity.

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Figure captions

Fig. 1. N₂ adsorption / desorption isotherms for (open / filled circles) Cat-S and (open / filled triangles) Cat-C

Fig. 2. Cross-sectional SEM images of (upper) Cat-S and (lower) Cat-C. The images in the left side are magnified in the right side.

Fig. 3. N₂ adsorption / desorption isotherms for (open / filled circles) MgO1/MgCl₂/TiCl₄, (open / filled triangles) MgO2/MgCl₂/TiCl₄, and (open / filled diamonds) MgO3/MgCl₂/TiCl₄

Fig. 4. α_s -plot for (circle) MgO1/MgCl₂/TiCl₄ as reference, (triangle) MgO2/MgCl₂/TiCl₄, (diamond) MgO3/MgCl₂/TiCl₄, (square) Cat-S, and (positive sign) Cat-C

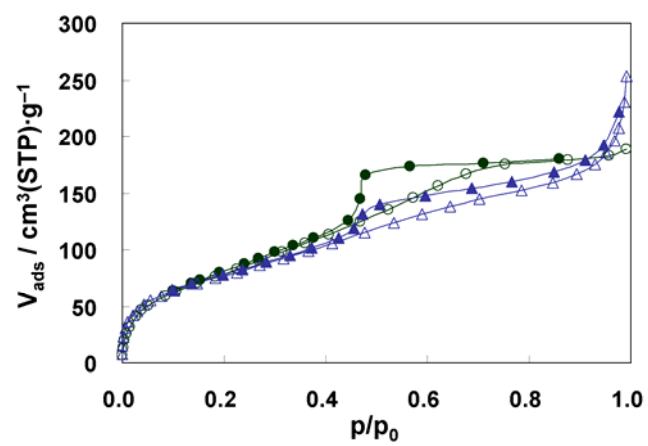


Fig. 1.

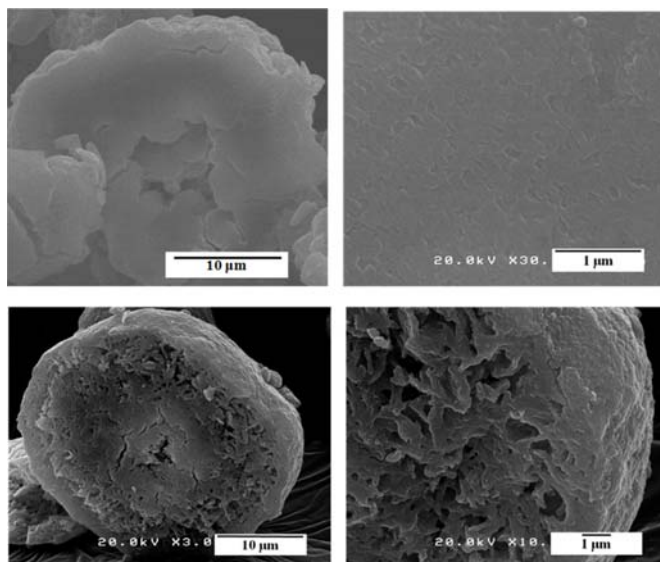


Fig. 2.

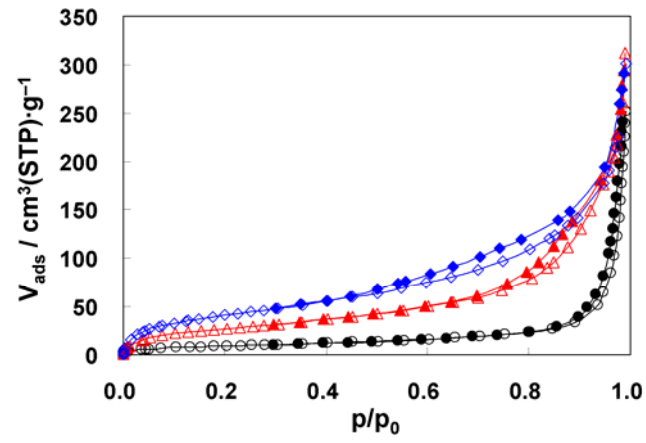


Fig. 3.

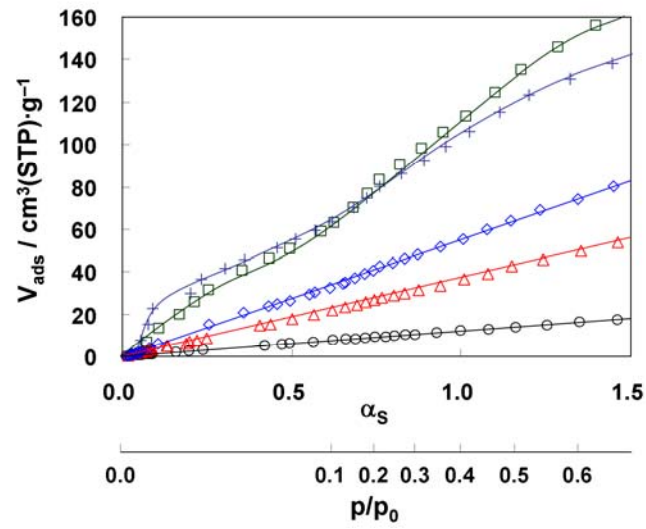


Fig. 4.