

Metallophosphate-Supported Ziegler-Natta Catalysts for Ethylene Polymerization

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Synopsis

Several catalysts for ethylene polymerization were obtained by TiCl_4 deposition on a series of mixed metallophosphates at 100°C and were evaluated in suspension polymerization at 70°C and 14.6-atm ethylene pressure. Kinetic parameters of these polymerization reactions (initial activity, rate of deactivation, stability, etc.) were compared with properties of supports and catalysts themselves. Statistical analysis of the correlations between catalyst performance and properties shows that, in the case of Al-containing supports, the principal property of a catalyst influencing its activity is its specific surface area. An inverse dependence was found between catalyst activity and stability in ethylene polymerization. The presence of aluminum in the supports is essential for high catalytic activity, whereas the addition of other metals (non-transition or transition) does not influence the catalysts to any significant degree.

INTRODUCTION

Many approaches have been evaluated to modify the activity and properties of supported catalysts for ethylene polymerization. Commonly used supports include SiO_2 , Al_2O_3 , mixed SiO_2 - Al_2O_3 , MgO , MgCl_2 , and various inert polymers.^{1,2} Recent work in modifying the nature of the support has resulted in the identification of alumina-aluminum phosphate supports as possessing unique properties for chromium-based ethylene polymerization catalysts.^{3,4} This article reports results of the evaluation of titanium-based systems derived from TiCl_4 using a series of mixed metallophosphate supports containing various nontransition and transition metals (Al, Zr, Zn, Mg, Cu, Co, Ti, Fe, and La).

EXPERIMENTAL

Table I contains information on the composition and specific surface areas of mixed metallophosphate supports used in this study. The list includes monometallic (Zr) mixtures of phosphate and oxide, and corresponding bimetallic, trimetallic, and tetrametallic cation mixtures with various ratios of phosphate and oxide components. One of the metals in all cases was Zr. Specific surface area of these supports varies over a wide range—from 319 to $44 \text{ m}^2/\text{g}$. The supports were prepared by mixing two aqueous solutions, one containing $\text{ZrO}(\text{NO}_3)_2$ and apparent metal nitrate, and the second containing $(\text{NH}_4)_2\text{HPO}_4$. Constant pH during the mixing was maintained by adding aqueous NH_3 . Precipitates were washed, dried at 120°C , sized to 60–80 mesh, and air calcinated at 300°C for 6 h.

TABLE I
Composition and Activity of Supported Catalysts

No.	Cations ^a	Supports			Catalysts			$K_p C_m C_1^*$ (g/min)	$K_p C_m C_2^*$ (g/min)	K_d (min ⁻¹)	$K_p C_m C_1^*$ $K_p C_m C_2^*$	Stable centers, fraction ^d	Unstable centers, fraction ^e	Yield after 1 h
		M	Al	Zr	PO ₄ ^c	S ₀ (m ² /g)	Ti (wt %)							
1	Co	16.7		83.3	75	98	1.67	70	0.237	0.582	0.0167	0.289	0.711	36.4
2	Fe	16.7	0	83.3	100	46	2.70	41	0.220	0.136	0.0090	0.618	0.318	19.0
3	La	16.7	0	83.3	100	44	2.30	30	0.100	0.305	0.0157	0.247	0.753	18.0
4	Cu	16.7	0	83.3	75	83	1.99	55	0.116	0.270	0.0300	0.300	0.700	14.2
5	Mg	16.7	0	83.3	75	73	1.38	60	0.216	0.427	0.0118	0.336	0.664	14.5
6	Al	0	90	10	33	273	4.97	198	0.133	0.584	0.0236	0.185	0.815	25.0
7	Al	0	90	10	67	200	1.47	167	0.252	0.628	0.0177	0.206	0.794	33.4
8	Al	0	25	75	36	319	4.85	227	0.566	1.836	0.0259	0.244	0.756	39.0
9	Cu,Al	16.6	41.7	41.7	50	220	7.25	95	0.183	0.803	0.0285	0.236	0.764	61.9
10	Zn,Al	16.7	62.5	20.8	75	215	3.22	159	0.246	0.855	0.0157	0.186	0.814	29.0
11	Ti,Al	16.7	62.5	20.8	75	250	—	200	0.208	0.686	0.0248	0.223	0.777	48.1
12	Cu,Al, Mg	1.5 1.7	62.5	20.8	75	175	4.00	122	0.167	0.682	0.0260	0.233	0.767	34.2
13	—	—	100	0	10	166	4.58	118	0.080	0.110	0.0265	0.197	0.803	30.5
14	—	—	100	0	30	148	3.19	116	0.098	0.116	0.0114	0.421	0.579	8.2
15	—	—	100	0	70	93	2.00	65	0.044	0.070	0.0210	0.458	0.542	11.1
16	Al ₂ O ₃	—	100	0	0	—	3.10	172	0.191	0.685	0.0249	0.218	0.782	32.4

^a In addition to Zr.

^b Based on total cation.

^c Percent of stoichiometric amount needed for complete precipitation of cations.

^d $K_p C_m C_1^*/(K_p C_m C_1^* + K_p C_m C_2^*)$.

^e $K_p C_m C_2^*/(K_p C_m C_1^* + K_p C_m C_2^*)$.

All catalysts with these supports were prepared at the same reaction conditions (105°C, 3 h) and with the same concentration of TiCl_4 solution (40 vol %) in heptane. Typically, 1 g of the support reacted with 10 mL of TiCl_4 in 15 mL of heptane. The catalysts were filtered, washed with $3 \times 25\text{-mL}$ portions of heptane, and dried under vacuum for several hours.

Specific surface areas of all supports and the catalysts evaluated by the Brunauer–Emmett–Teller (BET) method and Ti content in the catalysts are shown in Table I.

These catalysts were tested for ethylene polymerization under identical conditions: temperature = 70°C, ethylene pressure = 14.6 atm, solid catalyst loading in the reactor 0.100 g, $\text{Al}(\text{C}_2\text{H}_5)_3$ —2 mL of 25% solution in heptane, and polymerization medium—200 mL of heptane. The reaction was carried out in an Autoclave Engineers 0.5-L autoclave fed at constant reaction pressure by purified ethylene from a high-pressure reservoir.

Kinetics of ethylene consumption in the polymerization reaction were studied by measuring ethylene pressure decrease in the ethylene reservoir. Taken into account was substantial deviation of the ethylene pressure–density dependence from ideal behavior.

Preliminary experiments showed that the supported catalysts used in this work are not kinetically stable at 70°C. Usually they exhibit the highest polymerization rate at the beginning of the reaction, then the reaction rate decreases to some significantly lower level, after which it can be regarded as constant to a first approximation.

Such behavior is very typical for many Ziegler–Natta catalysts including most of the supported catalysts for ethylene polymerization.^{1,5} Traditionally, this kinetic behavior was described assuming that all polymerization centers on the catalyst surface are divided into two groups: kinetically stable centers (amount C_1^* , providing a stable rate of ethylene polymerization in the final stages of the polymerization reaction) and kinetically unstable centers (amount C_2^*). These unstable centers decay in the first-order reaction with a decay rate constant K_d .

In this case the total amount of polymerization centers in a catalyst at time t is

$$C^* = C_1^* + C_2^* \exp(-K_d t) \quad (1)$$

If one assumes that the value of the propagation rate constant K_p for ethylene polymerization is the same for both types of polymerization centers, the expression for the rate of polymerization is

$$R(t) = K_p C_m C^* = K_p C_m [C_1^* + C_2^* \exp(-K_d t)] \quad (2)$$

where C_m is the monomer concentration in solution.

The expression for polymer yield $Q(t)$ can be obtained by integration of eq. (2):

$$Q(t) = K_p C_m \left\{ C_1^* t + (C_2^*/K_d) [1 - \exp(-K_d t)] \right\} \quad (3)$$

This expression describes reasonably well experimental $Q(t) - t$ dependencies for ethylene polymerization with all studied catalysts. It was used for the comparison of experimental curves in coordinates $Q(t) - t$ and the kinetic model. This comparison allows one to estimate kinetic parameters of the models by adjustment of Eq. (3) to experimental data. Three parameters were adjusted: $K_p C_m C_1^*$, $K_p C_m C_2^*$, and K_d . The adjustment was carried out with the help of SAS nonlinear regression program NLIN.

RESULTS AND DISCUSSION

Preliminary evaluation of catalyst performance was based on polyethylene yields after 3 h of polymerization. The catalyst prepared by treating ZnAlZr phosphate with $TiCl_4$ gave the highest polymer yield (937 g/g). It was followed by the catalysts based on CoZr phosphate (880 g/g), and two AlZr phosphates (768 g/g and 701 g/g). The third AlZr phosphate, CuAlZr phosphate, TiAlZr phosphate, and CuMgAlZr phosphates resulted in yields of 520–600 g polymer/g catalyst. The remainder of the phosphate supports gave polymer yields of less than 500 g/g, with Zr phosphates being the poorest. It appears that the highest yields of polyethylene are obtained with those materials which contain both Al and Zr and another cation. The lone exception is the catalyst prepared from CoZr phosphate. It should be noted that five catalysts based on mixed metal phosphates gave yields higher than that for the $TiCl_4/Al_2O_3$ catalyst (558 g/g cat).

One example of the treatment of the kinetic data used for the evaluation of supported Ziegler–Natta catalysts is shown in Figure 1 [experimental data in coordinates yield time, their description by eq. (3), and the rate-time dependence calculated with eq. (2)]. This procedure was used for the processing of experimental data for all tested catalytic systems. Table I lists

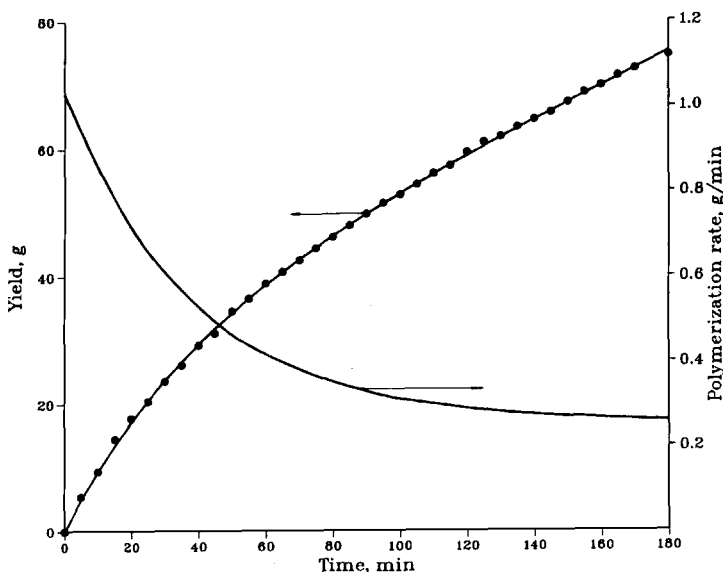


Fig. 1. Kinetics of ethylene polymerization with catalyst No. 7 (see table). (●) Experimental data on yield versus time.

all apparent kinetic information—the values of $K_p C_m C_1^*$ (proportional to the amount of stable polymerization centers), $K_p C_m C_2^*$ (proportional to the amount of unstable polymerization centers), and the deactivation rate constant K_d . Also included are the value of $K_p C_m (C_1^* + C_2^*)$ proportional to the total initial activity of the catalysts, the fractions of stable and unstable centers in the catalysts, and polyethylene yields for 1 h.

Information about properties of supports, the catalysts, and kinetic parameters characterizing the catalysts in ethylene polymerization was processed by application of the statistical linear correlation program in SAS.

It can be seen from Table I that deposition of $TiCl_4$ on these supports results in some decrease in surface area, and the correlation between these two parameters is good (correlation coefficient 0.95).

On the other hand, no meaningful correlation was found between any of the surface areas measured and the titanium content in the catalysts. Approximate calculations of surface coverage with $TiCl_4$ (in our case carried out under the assumption that the area occupied by one $TiCl_4$ molecule is ca. 40 \AA^2) showed that the measured Ti content roughly corresponds to a monomolecular layer of $TiCl_4$ ($\pm 50\%$).

Performance of the catalysts can be characterized either by initial activity, $K_p C_m (C_1^* + C_2^*)$, or polyethylene yield for 1 h. The correlation between these two parameters is good (correlation coefficient 0.90) thus indicating that initial activity of these catalysts and their productivity for 1 h are approximately proportional, both reflecting catalyst behavior.

Statistical analysis showed that the amounts of stable and unstable centers, as well as total initial activity, are roughly proportional to the total activity, i.e., the higher the catalyst activity the higher the number of both stable and unstable centers it has. This correlation is better for unstable centers but only because unstable centers constitute the largest part of all centers, as is evident from Table I.

Figure 2 shows the dependence between the fraction of stable centers and total initial activity of the catalysts. There is an obvious tendency for the fraction of stable centers to decrease (and the fraction of unstable centers to increase) when the initial activity increases. This trend is typical for many supported Ziegler–Natta catalysts—the higher their initial activity the less stable they are.

As to the rate constant of catalyst deactivation, K_d , statistical analysis showed no meaningful correlation between it and initial catalyst activity.

The following catalyst parameters were used for correlation between catalytic activity and catalyst characteristics: S_0 of the support, S_0 of the catalyst, and Ti content in the catalyst.

Figure 3 shows the dependence between polyethylene yield for 1 h and the specific surface area of the catalyst. Excluded from the correlation are catalysts based on zirconium phosphates of various anionic compositions which exhibit the lowest activity and the highest stability compared with other catalysts. A dependence similar to that shown in Figure 3 was found also between the initial activity $K_p C_m (C_1^* + C_2^*)$ and the surface area. It can be seen from Figure 3 that reasonable correlations exist between catalyst performance and its surface area (statistical correlation coefficients for yield and initial activity versus surface area of the catalysts are 0.79 and 0.81)

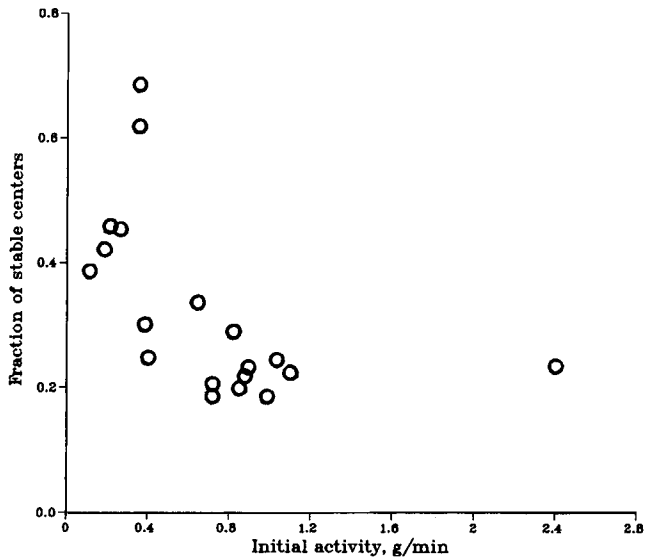


Fig. 2. Correlation between fraction of stable centers and total initial activity of the catalysts.

which, to a first approximation, hold irrespective of the type of metal present in the supports. Thus, the number of polymerization centers developed in the catalysts depends primarily on the specific surface area of the supports rather than on their chemical composition.

It is significant that the data for alumina follow the same correlations. It emphasizes the absence of any noticeable promotional effect of several transition and nontransition metals also present in the catalyst and supports the assumption of a predominantly monometallic nature of polymer-

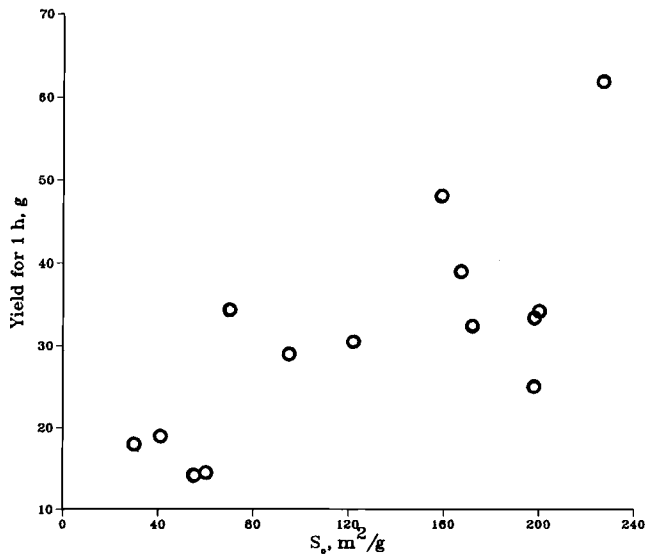


Fig. 3. Correlation between yield after 1 h and specific surface area of the catalysts.

ization species in Ziegler–Natta catalysts.^{1,5} However, decreased activity and increased stability of the catalysts based on zirconium phosphates shows that the presence of aluminum in the supports is an important factor determining their activity. Such an influence can be paralleled with the well-known effect of $MgCl_2$ support on the performance of catalysts for propylene polymerization.¹

The discovered dependence of the activity of supported Ziegler–Natta catalysts on their specific surface area in a wide range of S_0 , although approximate, is very important. Attempts to establish such dependence for solid $TiCl_3$ -based catalysts⁶ showed that the composition and crystal structure of the solids, as well as the method of their preparation, influence catalyst activity and mask the effect of S_0 .

No obvious correlation was found for the rate constant of catalyst deactivation K_d or the fraction of stable centers. It can be seen from Table I that for catalysts with S_0 higher than 60 m^2/g the fractions of stable and unstable centers no longer depend on S_0 and constitute 20–25 and 75–80% of the active centers, respectively.

No correlation was found between parameters determining catalyst performance and their titanium loading—correlation coefficients in all cases are of the order 0.4. Apparently only a small part of all Ti species present in the catalysts constitutes polymerization centers, the rest of them forming an inert addition to the supports. It is significant in this respect that the support-containing Ti (Table I, support 11) produced the catalyst indistinguishable in behavior from catalysts containing other metals. This finding stresses the importance of Ti-Cl bonds rather than merely the presence of Ti atoms for the formation of polymerization centers.

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