

CATALYTIC PROPERTIES OF Pd-ZEOLITES IN ETHYLENE OLIGOMERIZATION

By

A. L. LAPIDUS, V. V. MAL'TSEV, M. I. MAGANYA, V. I. GARANIN
and Kh. M. MINACHEV

N. D. Zelinski Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow

(Received 14th February, 1978)

Pd-zeolite catalysts display activity in C_2H_4 conversions under atmospheric pressure, the principal reaction products being dimers, trimers and other oligomers of C_2H_4 . On the [3% Pd] 0.75 CaNaY zeolite, the conversion of C_2H_4 at 50–100 °C equals 29–34%, while on [0.1% Pd] 0.4 CaNaY at 200° the yield of C_4 hydrocarbons is as high as 70% based on converted C_2H_4 . The conversion of C_2H_4 on the PdCaNaY ion-exchanged zeolite grows as the content of Pd increases and the extent of Na^+ exchange with Ca^{2+} becomes greater. Zeolite pretreatment with various gases, in combination with the XPS technique, made it possible to establish that in C_2H_4 conversions the catalytic activity is displayed by Pd in the cationic form, while Pd metal is inactive. Pd on amorphous silica-alumina behaves similarly. It is concluded that the presence of Pd in the cationic form, in conjunction with proton acidic sites, is essential for obtaining an active C_2H_4 oligomerization catalyst.

Introduction

Pd-containing zeolites are active in ethylene oligomerization [1–3]. However, the nature of catalytic effect of these catalysts and also the structure of the oligomerization active site have not been studied in sufficient detail. We investigated the properties of Pd-zeolites in this reaction and also the nature of their catalytic activity.

Experimental part

Runs were carried out in a flow system under atmospheric pressure [3]. The ion-exchanged catalysts were prepared by introducing 0.01–3.0 wt.% Pd in zeolites: Na-mordenite ($SiO_2/Al_2O_3 = x = 10$), NaY, CaNaY ($x = 4.3$), CaNaX ($x = 2.5$) using an aqueous solution of $[Pd(NH_3)_4]Cl_2$. The extent of Na^+ exchange with Ca^{2+} in CaNaY and CaNaX zeolites was 20–75 and 48 eq. % respectively. A number of catalysts were prepared by impregnating carriers with aqueous solutions of H_2PdCl_4 and $[Pd(NH_3)_4]Cl_2$. The catalysts prepared by ion exchange are designated as [Pd] zeolites, and those by impregnation as Pd-zeolites.

The X-ray photoelectron spectra (XPS) of catalysts discharged from the reactor in Ar were recorded by an ES-100 spectrometer [4].

Prior to each run, the catalysts were heated in an air stream (450°, 8 hrs, space velocity $800 h^{-1}$). Run duration was generally 30 min, the time of C_2H_4 contact being 2 s (space velocity $900 h^{-1}$).

Discussion

The effect exerted by the technique of Pd incorporation and the temperature on C_2H_4 conversions was studied in the 50—200 °C temperature range (Table I). Ethylene conversion (A) of ~30% was obtained on the type Y ion-exchanged zeolite at 100°, and at 150° in the case of impregnated specimen containing the same amount of Pd. The yield of C_4H_8 based on C_2H_4 converted was higher (20—30%) for the impregnated catalyst than for the ion-exchanged one, the overall yield of C_4 hydrocarbons (Y_b) on both catalysts at 100—200° being ~30%, and that of $i-C_4H_8$, 0.1—0.5%.

Table I
Effect of method of preparation and zeolite type on ethylene oligomerization

Catalyst	T °C	C_2H_4 conversion (A), %	Yield based on converted ethylene, %						K = $\frac{2\text{-butenes}}{1\text{-butene}}$
			C_2H_6	$C_3H_8 + C_3H_6$	C_4H_{10}	C_4H_8	C_5-C_8	ad-sorbed hydrocarbons	
[1% Pd] 0.75 CaNaY	50	15.0	3.1	0.4	9.3	10.3	38.2	38.7	11.7
	100	31.9	5.3	1.1	15.3	16.8	31.2	30.3	7.6
	150	38.3	6.5	1.2	14.4	11.7	29.5	36.7	6.5
	200	31.4	8.4	2.2	22.4	8.0	25.3	33.7	5.6
1% Pd -0.75 CaNaY	50	10.5	2.8	0.5	12.4	30.3	54.0		13.7
	100	22.3	3.8	0.3	8.6	20.0	36.5	30.8	8.9
	150	31.8	4.6	0.5	7.9	19.8	39.0	28.2	6.6
	200	31.6	4.3	0.7	8.7	22.4	40.1	23.8	5.5
[1% Pd] 0.48 CaNaX	200	21.9	—	0.9	3.4	35.0	33.3	27.4	5.3
1% Pd -0.48 CaNaX	200	14.6	—	2.3	7.9	60.4	1.8	27.6	5.4

As the temperature increases from 50 to 200°, A grows, while on the ion-exchanged zeolite the yields of C_4H_8 decrease, but C_4H_{10} yields increase, Y_b remaining practically unchanged. As the temperature increases, $K = \beta - C_4H_8/\alpha - C_4H_8$ diminishes.

Pd-containing X zeolites are less active than type Y zeolites, but display higher selectivity as regards C_2H_4 dimerization.

The 0.01% Pd-containing catalyst at 100° is inactive in C_2H_4 oligomerization, but on the 3% Pd-containing zeolite A equals 28.9% even at 50° (Table II). With respect to T_{min} required for obtaining A equal to 28—31%, the [Pd] 0.75 CaNaY catalysts are arranged in the order: 0.01% Pd > 0.1% Pd > 1% Pd > 3% Pd.

The degree of Na^+ exchange with Ca^{2+} (α) in zeolites affects C_2H_4 oligomerization (Table II). On the 0.1% Pd-containing catalysts, the growth of α from 0 to 75 eq. % results at 200° in a 41-fold increase of A and a 2.5-fold decrease of Y_b , the yield of higher hydrocarbons being simultaneously increased. Process selectivity as regards C_2H_4 dimerization experiences diminution.

With respect to the growth of A at 200°, the catalysts containing 0.1% Pd are arranged in the order [Pd]NaY \cong [Pd] 0.2 CaNaY < [Pd] 0.4 CaNaY < [Pd] 0.75 CaNaY

Table II

Effect of palladium content and the degree of Na⁺ exchange with Ca²⁺ on ethylene oligomerization

Catalyst	T, °C	C ₂ H ₄ conversion (A), %	Yield based on converted C ₂ H ₄ , %					Ad-sorbed hydrocarbons	K = $\frac{2\text{-butenes}}{1\text{-butene}}$
			C ₂ H ₆	C ₃ H ₈ + C ₃ H ₆	C ₄ H ₁₀	C ₄ H ₈	C ₅ -C ₈		
[0.01 % Pd] 0.75 CaNaY	100	0.8	not analyzed						
	200	18.5	1.5	1.4	16.3	10.0	41.5	29.3	6.4
	250	28.1	3.1	2.4	16.9	14.5	38.8	24.3	4.8
[0.1 % Pd] 0.75 CaNaY	100	9.4	2.0	1.4	13.7	31.9	51.0		10.3
	200	28.8	6.9	1.7	11.7	16.0	31.4	32.3	5.2
[3% Pd] 0.75 CaNaY	50	28.9	8.5	0.5	8.6	8.8	39.8	33.8	13.7
	100	34.4	10.4	0.5	6.0	8.3	41.2	33.6	7.3
[0.1 % Pd] NaY	200	0.7	0.7	Not analyzed					
[0.1 % Pd] 0.2 CaNaY	200	1.0	1.0	Not analyzed					
[0.1 % Pd] 0.4 CaNaY	200	9.6	1.8	0.8	10.6	59.5	7.0	20.3	6.0

the order of selectivity of these catalysts for C₄ hydrocarbon formation being reversed. The maximum values of Y_b (70%) and C₄H₈ yield (59.5%) were observed at 200° for the [0.1 % Pd] 0.4 CaNaY zeolite.

Hence, in type Y zeolites the growth of acidity as the value of α increases [5, 6] results in A rise, Y_b diminution and hydrogen redistribution enhancement which manifests itself in greater yields of some paraffins.

The role played by the acidity of Pd-zeolites is also seen from the fact that practically nonacidic Na-forms of mordenite containing 0.1 and 1% Pd are devoid of activity for C₂H₄ oligomerization, while Y zeolites are more active than X zeolites (Table I).

On all Pd-zeolites, A maximum is observed, in accordance with [3], after pretreatment with air (450 or 380°). The ion-exchanged and impregnated zeolites dried in the air at 100—120° after 1% Pd incorporation and next treated with H₂ are inactive for C₂H₄ conversions. The ion-exchanged zeolite is also inactive on being treated with Ar due to complex ion [Pd(NH₃)₄]²⁺ decomposition to form Pd metal [7].

The results of heat treating the catalysts with diverse gases, in combination with XPS data, showed A to depend on the Pd cationic form share in the catalysts [8].

The spectrum of Pd3d_{5/2} electrons of the starting zeolite is close to the spectrum of [Pd(NH₃)₄]Cl₂, the bond energy of Pd3d_{5/2} electrons (E_b) being 338.2 eV. After treatment with the air (at 380 or 450°), E_b declines by ~1 eV. An analogous shift in the spectrum due to [Pd(NH₃)₄]²⁺ decomposition and partial Pd²⁺ reduction to Pd⁺, as well as due to Pd²⁺ clustering to form PdO was observed for the PdX zeolite [4, 9].

The maximum value of A is observed for zeolites that contain all Pd in the cationic form. Treating the starting sample with H₂ or Ar at 380° results in reducing the palladium in [Pd(NH₃)₄]²⁺ to Pd⁰, as shown in [4, 9], the value of A being 0.2%. After treating the [3% Pd] CaY zeolite with Ar or H₂, followed by treatment in the air, there appears in XPS a signal analogous to that observed for the zeolite treated with the air alone and containing all the palladium in the cationic form. Here, the value of A is maximal (33—37%).

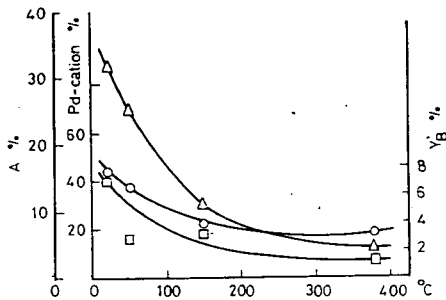


Fig. 1. Effect of temperature of hydrogen treatment of [3% Pd] 0.75 CaNaY zeolite preheated in air stream on the state of Pd in zeolite and ethylene conversions. Δ — C₂H₄ conversion (A), %; \circ — share of palladium in cationic form, %; \square — yield of C₄ hydrocarbons based on C₂H₄ feed (Y_b), %.

containing [Pd(NH₃)₄]²⁺ exclusively, increases after treatment with either air or argon to 0.4 and 0.58, respectively, presumably because of Pd⁰ migration into the surface layer and oxidation.

Ethylene, like CO and H₂ [12], reduces Pd²⁺ to Pd⁰ in zeolite. In the course of experiments, A and the share of cationic palladium decreases.

Palladium supported on active carbon, SiO₂ or Al₂O₃, in contrast to Pd-zeolites, is inactive for C₂H₄ oligomerization under the investigated conditions after treatment with both air and H₂. The Pd-impregnated amorphous synthetic silica-alumina (Pd-ASA) displays maximum activity after treatment with air and is devoid of activity after H₂ treatment. The catalyst obtained by impregnating ASA with an aqueous solution of [Pd(NH₃)₄]Cl₂ displays greater selectivity for C₂H₄ dimerization and higher stability than does the catalyst prepared using H₂PdCl₄. In the 20—250° temperature range the C₂H₄ conversion and C₄H₈ yield pass through a maximum (Fig. 2), the yield of C₄H₈ being up to 97.6% based on converted C₂H₄.

Fig. 2. Effect of temperature on C₂H₄ dimerization in the presence of 4%-ASA catalyst. Δ — C₂H₄ conversion (A), %, \circ — yield of C₄H₈, %

In C₂H₄ oligomerization on zeolites treated with the air (4 hrs, 380°) and then with H₂ (2 hrs at different temperatures), zeolite activity and C₄ hydrocarbon yield based on the C₂H₄ feed (Y_b) experience symbatic variation with the cationic Pd share (Fig. 1). The data on the degree of Pd reduction are in agreement with [10].

ESR data show the catalytically active [3% Pd] CaY zeolite treated with the air and then with H₂ at room temperature to contain Pd⁺, this being in agreement with [11].

The ratio of intensities of Pd3d_{5/2} and Si2s, which equals 0.24 in the stock zeolite

containing [Pd(NH₃)₄]²⁺ exclusively, increases after treatment with either air or argon to 0.4 and 0.58, respectively, presumably because of Pd⁰ migration into the surface layer and oxidation.

Ethylene, like CO and H₂ [12], reduces Pd²⁺ to Pd⁰ in zeolite. In the course of experiments, A and the share of cationic palladium decreases.

Palladium supported on active carbon, SiO₂ or Al₂O₃, in contrast to Pd-zeolites,

is inactive for C₂H₄ oligomerization under the investigated conditions after treatment with both air and H₂. The Pd-impregnated amorphous synthetic silica-alumina (Pd-ASA) displays maximum activity after treatment with air and is devoid of activity after H₂ treatment. The catalyst obtained by impregnating ASA with an aqueous solution of [Pd(NH₃)₄]Cl₂ displays greater selectivity for C₂H₄ dimerization and higher stability than does the catalyst prepared using H₂PdCl₄. In the 20—250° temperature range the C₂H₄ conversion and C₄H₈ yield pass through a maximum (Fig. 2), the yield of C₄H₈ being up to 97.6% based on converted C₂H₄.

Hence, in C₂H₄ oligomerization, palladium is active in the cationic form. Rela-

tion of the yield of C₄H₈ to the C₂H₄ conversion is shown in Fig. 2.

The yield of C₄H₈ is shown in Fig. 2 as a function of temperature. The yield of C₄H₈ is up to 97.6% based on converted C₂H₄.

The yield of C₄H₈ is shown in Fig. 2 as a function of temperature. The yield of C₄H₈ is up to 97.6% based on converted C₂H₄.

The yield of C₄H₈ is shown in Fig. 2 as a function of temperature. The yield of C₄H₈ is up to 97.6% based on converted C₂H₄.

The yield of C₄H₈ is shown in Fig. 2 as a function of temperature. The yield of C₄H₈ is up to 97.6% based on converted C₂H₄.

The yield of C₄H₈ is shown in Fig. 2 as a function of temperature. The yield of C₄H₈ is up to 97.6% based on converted C₂H₄.

The yield of C₄H₈ is shown in Fig. 2 as a function of temperature. The yield of C₄H₈ is up to 97.6% based on converted C₂H₄.

tionships between the activity of Pd-zeolites, the degree of Na^+ exchange with Ca^{2+} and also the zeolite type, and absence of activity of palladium supported on carbon, SiO_2 or Al_2O_3 make it possible to conclude that, in the same way as in Ni-silica-aluminas [13, 14], in Pd-silica-aluminas in the formation of an oligomerization active site there participate acidic sites, apart from palladium in the cationic form. Proton sites are, presumably, essential for the formation of Pd^{2+} cation from PdO according to the scheme: $\text{PdO} + 2 \text{H}^+ \rightarrow \text{Pd}^{2+} + \text{H}_2\text{O}$ analogous to the scheme suggested for Ni-zeolite catalysts [15].

* *

The authors wish to express their appreciation to G. V. ANTOSHIN, E. S. SHPIRO AND V. A. SHVETZ for participation in physico-chemical examinations of catalysts.

References

- [1] US Pat. 3644565 (1972). C. A. 76, 154450c (1972).
- [2] US Pat. 3738977 (1973), C. A. 79, 54080a (1973).
- [3] Lapidus, A. L., V. V. Mal'tsev, V. I. Garanin, Kh. M. Minachev, Ya. T. Eidus: *Izv. AN SSSR, Ser. Khim.* 1975, 2819.
- [4] Minachev, Kh. M., G. V. Antoshin, E. S. Shpiro: *Izv. AN SSSR, Ser. Khim.* 1974, 1012.
- [5] Sharf, V. Z., M. A. Piontkovskaya, L. Kh. Freidlin, I. E. Neimark, M. N. Rastorgueva, G. S. Shameka: *Izv. AN SSSR, Ser. Khim.* 1971, 2196.
- [6] Tanabe, K.: *Solid Acids and Bases*. Academic Press, N. Y.-L., 1970.
- [7] Kerr, G. T., A. W. Chester: *Thermochimica Acta*, 3, 113 (1971).
- [8] Lapidus, A. L., V. V. Mal'tsev, E. S. Shpiro, G. V. Antoshin, V. I. Garanin, Kh. M. Minachev: *Izv. AN SSSR, Ser. Khim.* 1977, 2454.
- [9] Minachev, Kh. M., G. V. Antoshin, E. S. Shpiro, T. A. Navruzov: *Izv. AN SSSR, Ser. Khim.* 1973, 2134.
- [10] Gallezot, P., B. Imelik: *Adv. Chem. Ser.* 121, 66 (1973).
- [11] Naccache, C., M. Primet, M. V. Mathieu: *Adv. Chem. Ser.* 121, 266 (1973).
- [12] Philips, F. C.: *Amer. Chem. J.*, 16, 255 (1894).
- [13] Lapidus, A. L., R. V. Avetisyan, Ya. I. Isakov, Kh. M. Minachev, Ya. T. Eidus: *Neftekhimiya* 10, 648 (1970).
- [14] Lapidus, A. L., V. V. Mal'tsev, A. A. Slinkin, M. I. Loktev, Ya. T. Eidus: *Izv. AN SSSR, Ser. Khim.* 1976, 1080.
- [15] Minachev, Kh. M.; Ya. I. Isakov, G. V. Antoshin, V. P. Kalinin, E. S. Shpiro: *Izv. AN SSSR, Ser. Khim.* 1973, 2527.