produces radicals near these CF₃ substituted carbons. It is interesting to note that, in a recent study of stretched polypropylene, an angle of 39° between the main chain direction and g_3 was deduced.²² This conclusion is remarkably similar to conclusions presented in this study.

The energy barrier between the two-jump dynamic process can be deduced by assuming an Arrhenius type dependence of the rotational correlation time, τ , on the temperature, T, and comparison of simulated spectra as a function of τ with experimental spectra as a function of temperature. The results are shown in Figure 8 for the temperature range 138 K ($\tau = 0.3 \ \mu s$) to 268 K ($\tau = 0.003 \ \mu s$). The activation energy is 10.6 kJ mol⁻¹. This

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value is about half the activation energy for the chain axis rotation of the same radical in PTFE. In NMR studies, it was suggested that the effect of CF₃ substitution is to lower the temperature at which chain axis rotation is observed in the crystalline phase. Our results for the activation energy are in agreement with these conclusions and strengthen our assumption that the mid-chain peroxy radicals are located in the crystalline phase of FEP.

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Ethylene Dimerization on Pd-Ca-X Zeolite: Gas Chromatographic and Electron Spin **Resonance Studies**

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The conversion of ethylene over Pd-Ca-X zeolite was investigated in the temperature range 280-403 K. The observed reversed temperature dependence of the rate of this reaction is accounted for by the migration of Pd^{2+} cations to inaccessible sites in the β -cages at higher temperatures. The influence of various cocations, such as Ca²⁺, Mg²⁺, Na⁺, and K⁺, on the activity of palladium X zeolite also has been studied. It is found that the presence of divalent cocations promotes dimerization of C_2H_4 over Pd-X at low concentrations of Pd²⁺ (2 Pd²⁺ per unit cell) at relatively low temperatures. Under the same conditions palladium X zeolites with monovalent cocations are completely inactive for ethylene dimerization. Divalent palladium cations are proposed as the catalytically active metal species on the basis of combined gas chromatographic and electron spin resonance results.

Introduction

Palladium compounds are well-known for their homogeneous catalytic activity for a variety of reactions with olefins.¹⁻³ In a few papers the results of ethylene dimerization over palladium loaded zeolites have been discussed.⁴⁻⁶ In general the selectivity to form *n*-butenes has been found to be rather poor even at relatively low ethylene conversion.

There is no doubt that palladium ions directly participate in the formation of a catalytically active site.⁵ However, the valence state of the palladium cation and its location in the zeolite structure still remain open questions.

In the present work the formation of *n*-butenes in the course of ethylene dimerization over Pd-Ca-X zeolite is correlated with ESR measurements of monovalent palladium complexes in the zeolite. The effect of reaction temperature on ethylene conversion has also been studied.

Experimental Section

Ca-X zeolite was prepared from Na-X (Linde 13X) by ion exchange with 0.1 M CaCl₂ solutions at 353 K for 1 week. Palladium was introduced into zeolite as $Pd(NH_3)_4^{2+}$ cation by ion exchange with various amounts of 0.01 M palladium tetraamine chloride (Alfa) solution at room temperature overnight $(\sim 12 \text{ h})$. Commercial atomic absorption was used to determine the palladium content. Most experiments were done with low Pd²⁺ content zeolite, $\sim 4\%$ of Ca²⁺ cations exchanged, designated as Pd-Ca-X(4). Other zeolites, Pd-Ca-X(30), Pd-Na-X(30), Pd-K-X(30), Pd-Mg-X(4), and Pd-Ba-X(4), have been also studied.

A zeolite sample of 0.5 g was placed on a sintered glass disk inside a glass reactor of diameter 12 mm and total reaction volume of 91 cm³. The zeolite was heated under vacuum at slowly rising temperatures up to 773 K for 1 day. Next the sample was treated with 200 torr of oxygen at 773 K for 3 h and then evacuated at the same temperature overnight (\sim 12 h). Ethylene was adsorbed on the zeolite, activated as described above, at a given temperature at 350 torr. The gas over the zeolite was analyzed periodically with a Varian 1400 gas chromatograph with thermal conductivity detection using a 6-in. column of 0.19 wt % picric acid on 80/100 mesh Graphac-GC support at 25 °C.

ESR experiments were carried out palladium zeolite placed into 2-mm-o.d. Spectrosil quartz tubes. ESR spectra were recorded at 77 K with a Varian E-4 spectrometer.

Results

Catalytic Activity of Palladium X Zeolites. Ca-X zeolite treated in the same way as zeolites loaded with palladium shows no appreciable activity for dimerization of C₂H₄ in the temperature range of 293-363 K. Similarly, Pd-Na-X(4) and Pd-K-X(4) are also inactive in the same temperature range. The isomerization of 1-butene over Ca-X, however, is very fast and at 323 K is completed during 1 h. Pd-Ca-X(4) unlike Pd-Na-X(4) or Pd-K-X(4) efficiently promotes dimerization of ethylene. As shown

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Figure 1. Ethylene dimerization over Pd-Ca-X(4) zeolite at 323 K.

in Figure 1 the conversion of ethylene at 323 K after a 20-min induction period is reasonably fast, reaching 90% after 3 h of reaction. During the first 2 h of reaction only the peaks of the butene isomers, 1-butene, cis-2-butene, and trans-2-butene, appear in the gas chromatogram. For longer times a broad unresolved peak at longer retention times is also recorded indicating the formation of higher oligomers. In this work we studied only the formation of butenes over Pd-X zeolites, and all data presented here are calculated assuming that the samples of gases from the reactor consist only of ethylene and butenes. The isomeric composition of butenes does not change very much during the course of the reaction as is shown in Figure 1. The ratio 1-butene: trans-2-butene: cis-2-butene varies only from 2:26:9 after 0.5 h of reaction to 2:32:10 after 2 h. We studied the isomerization of 1-butene over Pd–Ca–X(4) under the same conditions, and it turned out that the isomerization rate of 1-butene is much faster than the ethylene dimerization rate. The equilibrium composition of isomers (5% of 1-butene, 72% of cis-2-butene, and 25% of trans-2-butene) was reached 1 h after 1-butene admission whereas only 30% of C_2H_4 was converted during the first reaction hour. 1-Butene isomerizes also over Ca-X zeolite at 323 K reaching the same isomer composition after 2 h.

An observed induction period strongly depends on the reaction temperature: the lower the temperature the longer the induction period. At 280 K dimerization starts only 9 h after ethylene admission, but once started it proceeds with a rate not very different from the rate at higher temperatures and during the next 3 h the conversion exceeds 80% (Figure 2). At 363 K the reaction starts after 5 min but after a fast initial period it quickly slows down reaching only 22% of ethylene conversion during 3 h.

The effect of reaction temperature on ethylene conversion is shown in Figure 3. The conversion of ethylene after 1 h of reaction increases with temperature in the range of 293-343 K reaching a maximum of 43% at 343 K. At higher temperatures the conversion dramatically decreases, and reaction is completely stopped at 402 K. The yield of dimerization after 2 h of reaction is strongly dependent on temperature. The maximum conversion of ~95% was obtained at room temperature in the range of 313-343 K the conversion is lower (~63%) and is independent of temperature. At higher temperatures the yield of dimerization decreases very fast. A different temperature effect for ethylene dimerization after 1- and 2-h reaction periods is due to a changing induction period which much influences the conversion yield at the early reaction stage.

Pd-Na-X zeolites are catalytically active only when the palladium concentration in the zeolite is much higher than in Pd-Ca-X zeolite. The comparison of the ethylene conversion rates over Pd-Na-X(30) with a high concentration of palladium cation and over two Pd-Ca-X zeolites with different Pd²⁺ contents is



Figure 2. Ethylene conversion over Pd-Ca-X(4) zeolite at various temperatures.



Figure 3. Effect of reaction temperature on the activity of Pd-Ca-X(4) zeolite: conversion of ethylene after 1 h (\bullet) and after 2 h (Δ) of reaction.

presented in Figure 4. The temperature of 363 K was chosen because the induction period of Pd-Na-X(30) at lower temperatures is too long. Even at 363 K ethylene dimerization over Pd-Na-X(30) does not start until 1 h after ethylene admission whereas 5 min is enough to observe butene formation over Pd-Ca-X(30). It is interesting to note that despite the much longer induction period the conversion of ethylene over Pd-Na-X(30) after 3 h of reaction is higher than over Pd-Ca-X(30). The activity of Pd-K-X is very similar to that of Pd-Na-X. Pd-Na-X(4) is completely inactive, but Pd-K-X(30) at 363 K after a 1-h induction period starts converting ethylene with reasonable efficiency. The presence of divalent cocations other than Ca²⁺ also increases the activity of X zeolites loaded with a low concentration of Pd^{2+} . It was found that Pd-Mg-X(4) and Pd-Ba-X(4) convert ethylene to butenes at 323 K, although the conversion yield is lower in comparison to Pd-Ca-X(4). After 2 h of reaction at 323 K, ethylene conversion over Pd-Ca-X(4) reaches ~65%, over Pd-Mg-X(4) ~31%, and over Pd-Ba-X(4) only $\sim 3\%$.

In a few cases we studied the dimerization of C_2H_4 over Pd-Ca-X zeolites reduced by hydrogen at room temperature which produces Pd⁺ and we found that C_2H_4 conversion decreases about



Figure 4. Comparison of ethylene dimerization at 363 K over various Pd-X zeolites.



Figure 5. ESR spectra of Pd-Ca-X(4) zeolite recorded at 77 K during the induction period of ethylene dimerization at 323 K.

threefold for hydrogen-reduced samples. For example, ethylene conversion over hydrogen-reduced Pd-Ca(30) zeolite does not exceed 10% after 3 h at 363 K whereas for activated Pd-Ca-X it reaches 45%

To study the deactivation of zeolite in the course of ethylene dimerization at 323 K the same sample of Pd-Ca-X(4) zeolite was exposed to ethylene several times. Every time the dimerization reaction was carried out for 3 h. Then the reactor was evacuated for 2 h at 323 K and fresh ethylene was admitted. The activity of Pd-Ca-X, defined as the percentage of ethylene converted during 3 h, decreases about 15% after the first three runs and an additional 10% after the next five runs, indicating that deactivation of Pd-Ca-X(4) zeolite under these conditions occurs to only a minor extent.

ESR Studies. The activation of Ca-X zeolite loaded with $Pd-(NH_3)_4^{2+}$ cations leads to the formation of Pd^+ ions. An ESR signal A with $g_{\parallel} = 3.10$ and $g_{\perp} = 2.103$ representing Pd⁺ in activated zeolite is shown in Figure 5a. After admission of 350 torr of C₂H₄ at 323 K signal A disappears nearly completely in 2 min and four new signals each with a lower g_{\perp} value and a smaller anisotropy of the g tensor are observed (Figure 5b). These signals decay during the next few minutes but the intensity of the remaining signal A does not change at the same time. In the period between 0.5 and 3 h of reaction three new ESR signals appear: first signal B with $g_{\parallel} = 2.37$ and $g_{\perp} = 2.109$, then signals C with $g_{\parallel} = 2.41$ and $g_{\perp} = 2.109$ and D with $g_{\parallel} = 2.81$ and $g_{\perp} = 2.109$ (Figure 6). They all have the same g value for the



Figure 6. ESR spectra of Pd-Ca-X(4) zeolite recorded at 77 K during the "reactive" period of ethylene dimerization at 323 K.

perpendicular component, $g_{\perp} = 2.109$, and the intensity of this ESR line distinctly increases over the same time where ethylene conversion is fast. When 1-butene is adsorbed on Pd-Ca-X(4)at 323 K only signals C and D are seen. This allows us to assign signal B to a $Pd^+-C_2H_4$ complex. The disappearance of signal B during the final stage of dimerization when the ethylene pressure becomes very low additionally confirms this assignment. Most probably signal C, which appears when dimer formation is already for advanced, represents a $Pd^+-C_4H_8$ complex. Signal D with g values not very different from signal A can be assigned to Pd⁺ cations located in sodalite cage of the zeolite structure and coordinated by framework oxygens.

Discussion

It has already been shown that the first product of ethylene dimerization over NiY, RhY, and RuY is 1-butene that then isomerizes to produce an equilibrium composition of *n*-butenes.⁷ As a result the ratio of butene isomers changes distinctly during the course of reaction. Similar changes have been reported for ethylene dimerization over Ni-Ca-X zeolite.8 In the case of Pd-Ca-X zeolite, regardless of the palladium concentration and reaction temperature, the ratio of butenes even at very early reaction stages does not differ very much from the equilibrium composition. The results of 1-butene isomerization over Pd-Ca-X(4) show that the isomerization rate is much faster than the ethylene dimerization rate and does not differ much from the isomerization rate over Ca-X zeolite, indicating that palladium is not an active site for isomerization. The acidic hydroxyl groups polarized by calcium ions have been proposed as catalytically active sites for 1-butene isomerization over Ca-X.9-11 The exchange of sodium by calcium ions, which have a stronger polarization effect, results in an increase of the acid strength of the hydroxyl group and increases the zeolite activity for isomerization. Because Ca-X is inactive for ethylene dimerization we postulate that dimerization of ethylene over Pd-Ca-X zeolite consists of two stages. The primary product 1-butene is formed at a palladium site in the zeolite supercages. The later isomerization of 1-butene is proposed to proceed immediately as a result of its interaction with Ca^{2+} polarized acidic hydroxyl groups in the close vicinity. Because there are about 20 Ca^{2+} cations for every Pd^{2+} cation in the Pd-Ca-X(4) unit cell the probability of a polarized OH group in close vicinity to Pd²⁺ seems rather high; this can explain

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why the isomerization of 1-butene is so fast. The overall kinetics is controlled by 1-butene formation and because of that the composition of butenes is close to the equilibrium ratio even at early reaction stages.

The valence state and location of the active palladium site cannot be directly determined from the present studies. However, the correlation of ESR and gas chromatography leads us to conclude that divalent palladium cations are the catalytically active species for ethylene dimerization. It is known from our earlier studies¹² that the concentration of Pd⁺ cations in Pd-Ca-X(30) zeolite reduced by H₂ at room temperature is significantly higher than in thermally reduced zeolite during sample heating and evacuation. However, the ethylene conversion over hydrogen reduced Pd-Ca-X zeolite is less efficient than over oxidized and evacuated zeolite clearly indicating that Pd⁺ cations do not play the active role in ethylene dimerization. On the other hand the observed increase of the concentration of monovalent palladium cations represented by an ESR signal with $g_{\perp} = 2.109$ (Figure 6) during the "reactive period" of dimerization over Pd-Ca-X(4)at 323 K suggests an active role for Pd²⁺ cations.

The formation of Pd⁺ cations can be explained by the following reaction:

$$Pd^{2+} + CH_2 = CH_2 \rightarrow Pd^+ - CH_2 - \dot{C}H_2^+$$
(1)

As a result of electron transfer an ESR signal B with $g_{\parallel} = 2.36$ and $g_{\perp} = 2.109$ is observed. In further reaction stages a complex of monovalent palladium with butene can be also formed by the same mechanisms. This complex is represented by signal C with $g_{\parallel} = 2.41$ and $g_{\perp} = 2.109$ in Figure 6. Signal D with $g_{\parallel} = 2.81$ and $g_{\perp} = 2.109$ has g values quite similar to the original signal A and probably represents Pd⁺ which after electron transfer and complex decomposition migrates back to the sodalite units.

Because of the high affinity of Ca^{2+} ions for the SI' sites in the β -cage of the zeolite, it is anticipated that Pd^{2+} cations will be forced to occupy more accessible sites like SII' or SII in the β -cages. The ethylene molecule is too bulky to enter the β -cages so the formation of a palladium-ethylene complex needs a migration of Pd^{2+} into supercages. We assume that the induction period for ethylene dimerization is due to Pd^{2+} migration toward ethylene molecules in the supercages. At higher temperature the migration of exchangeable cations in the zeolite structure is faster which explains a shortening of the induction period.

The dimerization yield also decreases with increasing temperature. To explain this we postulate that the percentage of Pd^{2+} cations which migrate to the supercages decreases with increasing temperature as a result of a greater tendency for Pd^{2+} to also occupy sites inside the β -cages. Such a tendency has been already shown in Pd-NaH-Y zeolite by X-ray studies¹³ which revealed that at 473 K all Pd²⁺ migrate to SI' sites. Although in Pd-Ca-X the SI' sites are occupied by Ca²⁺ cations, we think that there is a general trend which induces Pd²⁺ to migrate inwards to the β -cages at higher temperature. The higher the temperature the

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less Pd^{2+} migrates to accessible sites for ethylene and above 403 K ethylene dimerization does not occur. It should be mentioned that the original Pd⁺ cations stabilized in Pd–Ca–X after oxidation and evacuation have to occupy accessible sites because their ESR signal (A) disappears immediately after C₂H₄ adsorption (Figure 5).

The presence of a divalent cocation in the X zeolite makes it very active for ethylene dimerization even if the concentration of Pd^{2+} is as low as ~4% exchangeable cations. On the other hand, X zeolite with monovalent cocations has to be loaded with a much higher amount of Pd^{2+} (~30%) to show the catalytic activity. This interesting dependence between palladium zeolite activity and the valence state of the cocation is due to the location of Pd^{2+} . Since Ca²⁺ cations have a strong affinity for SI' sites, Pd²⁺ cations are forced to occupy more accessible sites as was observed for Cu^{2+,14} In Pd-Na-X(4) and Pd-K-X(4) with low Pd^{2+} concentration, the palladium cations occupy inaccessible SI' sites. There is a critical value of the degree of exchange above which palladium ions start occupying the more accessible sites SII' and SII. As a result Pd-Na-X zeolite becomes catalytically active. In general the dimerization of ethylene over Pd-Na-X is less advantageous in comparison to Pd-Ca-X because of (1) the higher concentration of Pd^{2+} needed for the same degree of ethylene conversion and (2) the higher reaction temperature needed to shorten the induction time.

Conclusions

The results of this work clearly show that Pd-Ca-X(4) with a low content of Pd^{2+} can effectively promote the dimerization of ethylene at relatively low temperatures (313-343 K). Pd-Na-X(4) is completely inactive under the same conditions. This is due to the different locations of Pd^{2+} cations in both zeolites. In Pd-Na-X(4) palladium cations occupy inaccessible SI' sites whereas in Pd-Ca-X(4), because of the strong affinity of Ca²⁺ for SI' sites, Pd^{2+} is located in more accessible SII' or SII sites.

The observed time correlation between the formation of butenes and the increase of Pd⁺ concentration enabled us to conclude that divalent palladium cations are responsible for the catalytic activity of Pd–Ca–X zeolite in ethylene dimerization. The reverse temperature dependence for ethylene conversion was interpreted in terms of increasing affinity of Pd²⁺ for the less accessible sites inside the β -cages at higher temperatures. As a result less Pd²⁺ cations are able to migrate to the sites accessible for ethylene.

The detailed mechanism of ethylene dimerization over Pd-Ca-X still remains unclear and further studies are needed on the structure of the active complex and its transformations.

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