Chemistry for Sustainable Development **21** (2013) 47–51

UDC 544.478: 547.313: 661.715.3

One-Stage Synthesis of Propylene from Ethylene Using Pd–Re_2O_7/B_2O_3–Al_2O_3 Catalyst

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Abstract

Equilibrium was investigated concerning the sorption of palladium from the H_2PdCl_4 and $Pd(NH_3)_4Cl_2$ solutions onto B_2O_3–Al_2O_3 carrier. It is demonstrated that the sorption equilibrium is described by Langmuir equation. According the results of testing the Pd/B_2O_3–Al_2O_3 samples in the course of oligomerization it has been found that the optimum content of palladium in the catalyst should be equal to 0.5 mass %, whereas the optimum precursor of palladium should be presented by palladium chloride complex. The catalytic properties of Pd–Re_2O_7/B_2O_3–Al_2O_3 system in the one-stage propylene synthesis from ethylene were studied. It has been demonstrated that it is possible to obtain propylene with the yield equal to 77–83 % with respect to the theoretically determined one.

Key words: palladium sorption, ethylene, propylene, oligomerization, metathesis

INTRODUCTION

Currently, more than 60 % of propylene in the world is produced as a by-product in the production of ethylene in the course of the pyrolysis of different petroleum fractions. The main direction of the development of the pyrolysis process at the present stage consists in using cheaper light raw materials, mainly ethane, whereby the proportion of propylene in the pyrolysis products is reduced to a considerable extent [1]. At the same time, the global demand for propylene is growing steadily, and its rate is significantly higher than that for ethylene. As additional sources to cover the deficiency of propylene one generally considers the technologies of deep catalytic cracking and dehydrogenation of propane. To develop methods for producing propylene from ethylene by metathesis reaction is also relevant [2].

Almost all modern industrial technologies the synthesis of propylene *via* metathesis are based on the Triolefins process developed by the Phillips Co. in the 1970s. This process represents an ethenolysis of butenes using a mixture of catalysts intended for metathesis (WO_3/SiO_2) and for the isomerization of butenes (MgO) and it can be used for the production of propylene from ethylene in combination with the process of producing butene *via* ethylene dimerization [2].

The idea of carrying out the reactions of ethylene dimerization, butene-1 isomerization into butene-2 and butene-2 metathesis with ethylene to produce propylene using one catalyst according to Scheme 1 has no principal and thermodynamic limitations being known since 1972 [3]. At the same time, the one-stage process of synthesizing the propylene not only wasn't realized in the industry, but also it is poorly presented in scientific periodical literature. The authors of patents [3–6] propose a catalyst in this process based on bimetallic systems containing Ni [3] or Pd [4] those are responsible for the process of ethylene oligomerization, as well as MoO_3 [3], WO_3 [4] or Re_2O_7 [5], whereon the reactions of metathesis occur. The carrier for these catalysts is generally presented by γ-alumina, on whose surface butene-1

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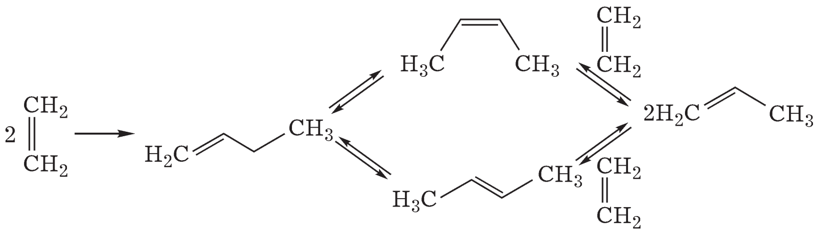

Scheme 1.

can be isomerised into butene-2. It is also known that modifying the carrier with the anions of inorganic acids such as F^- [5] or WO_4^{2-} [6], could lead to a significant increase in catalytic activity.

As a carrier for the efficient catalyst for one-stage synthesis of propylene from ethylene, we proposed to use alumina modified by BO_3^{3-} anions [7]. The authors of [8] demonstrated that in this case on the surface there are formed strongly bound therewith catalytically active nickel species, providing the system of $NiO-Re_2O_7/B_2O_3-Al_2O_3$ to exhibit advantages over other catalysts due to a high rate of butene formation at the stage of oligomerization. In this work, the aluminoborate carrier was used for the preparation of $PdO-Re_2O_7/B_2O_3-Al_2O_3$ system.

This work was purposed at studying an effect exerted by the nature of palladium precursor and by the metal content in the $PdO-Re_2O_7/B_2O_3-Al_2O_3$ system on the catalytic properties thereof.

EXPERIMENTAL

The $B_2O_3-Al_2O_3$ carrier with a boron oxide content of 20 mass % was prepared via a procedure described by the authors of [8]. The sorption isotherms of palladium from solutions H_2PdCl_4 and $Pd(NH_3)_4Cl_2$ onto the carrier was determined using a technique of separate weighed sample portions at pH ≈ 1 and pH ≈ 9, respectively. The palladium content in the solution was analyzed by means of atomic absorption spectroscopy (AA-6300 unit, Shimadzu). The sorption level was calculated basing on the difference in the concentration of palladium in the solution before and after equilibration. The time required to establish equilibrium sorption was determined in a separate experiment to be equal to 2 h.

Palladium and rhenium were the introduced into catalyst sequentially. The introduction of palladium was carried out using a sorption method, whereas the metal content was varied by changing the concentration of the solutions of chloride and amine precursors in accordance with the equilibrium sorption data. Rhenium in an amount of 5.0 mass % was deposited via impregnation by $HReO_4$ solution according to moisture capacity. After applying each of the components the catalyst was dried at 150 °C for 4 h and calcined at 500 °C for 16 h. Reference sample $NiO-Re_2O_7/B_2O_3-Al_2O_3$ was synthesized in a similar manner, NiO in an amount of 2 mass % was introduced *via* sorption from nickel nitrate solution.

Testing the catalysts was carried out using a flow-through reactor with a fixed catalyst bed. The ethylene oligomerization on $PdO/B_2O_3-Al_2O_3$ samples was studied at the temperature values of 100 and 200 °C, at a pressure of 1.0 MPa and at a mass rate of ethylene feeding equal to 1 h^{-1}. The raw material for testing represented a mixture of ethylene (30 mass %) with methane. The process for producing propylene from ethylene using catalyst $PdO-Re_2O_7/B_2O_3-Al_2O_3$ was performed at 40 and 80 °C, at a pressure of 0.1 and 1.0 MPa and at mass rate of feeding raw material equal to 0.3 and 0.5 h^{-1} (as a raw material we used chromatographically pure ethylene). The product composition was analyzed in an online mode using a "Tsvet-800" chromatograph with a DB-1 capillary column (polymethylsiloxane as the liquid phase) and a flame ionization detector.

RESULTS AND DISCUSSION

The sorption of palladium onto $B_2O_3-Al_2O_3$ carrier was observed for both the anionic

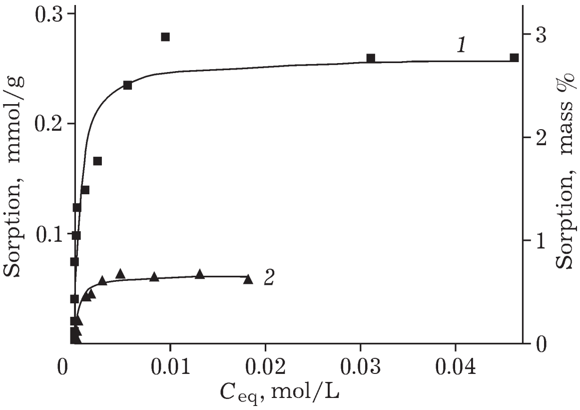

Fig. 1. Palladium sorption isotherms from the solutions of H_2PdCl_4 (*1*) and $Pd(NH_3)_4Cl_2$ (*2*). Points – experimental data, lines – approximation by Langmuir equation.

($[PdCl_4]^{2-}$), and for cationic ($[Pd(NH_3)_4]^{2+}$) complexes of palladium. Taking into account the pH value of precursor solutions, in both cases the surface of the carrier and precursor ions have opposite charges, whereby the mechanism of electrostatic interaction thereof with the surface of the carrier is most likely. The sorption isotherms for both precursors (Fig. 1) can be satisfactorily described by the Langmuir equation. The maximum values of the sorption level are reached at the equilibrium concentration of palladium in solution equal to about 0.006 mol/L to amount to 0.26 and 0.06 mmol/g in the case of using palladium chloride and palladium amino complex, respectively.

In order to determine the optimal type of palladium precursor and its content in the catalyst, the $PdO/B_2O_3{-}Al_2O_3$ samples not containing rhenium in the composition, were tested in the course of ethylene oligomerization. It has been found that in the case of pure $B_2O_3{-}Al_2O_3$ carrier the oligomerization process almost does not proceed. The conversion level of ethylene amounted to about 3 % at 100 °C and less than 5 % at 200 °C. The introduction of palladium in the catalyst in the amount of 0.1 mass % allows increasing the conversion level of ethylene at 100 °C up to 35 % in the case when the metal is applied from the chloride precursor and up to 23 % when applied from the amine precursor (Table 1). The maximum conversion level of ethylene, both at 100, and at 200 °C, regardless of the type of precursor of the active component, is provided by the samples containing 0.5 mass % of palladium. Increasing the levels of palladium content up to 1 mass % (the introduction of such a fraction of palladium *via* the sorption method is possible only from the solution of palladium chloride complex, see Fig. 1) leads to decreasing the catalyst activity. To all appearance, this could be caused by decreasing the dispersity level of the metal and, consequently, by more ready reducing the palladium by the substrate under conversion into zero-valent state inactive with respect to oligomerization.

The nature of the precursor influences upon the activity of the catalysts obtained. As it can be seen from Table 1, at the same content of the metal the samples synthesized from palladium chloride complex provide a slightly higher conversion level of ethylene as to compare with the precursor synthesized from ammine. Possible reasons for this could be presented by

TABLE 1

Parameters of butene oligomerization process on $PdO/B_2O_3{-}Al_2O_3$ catalyst with different content of palladium

Precursors	Mass fraction of Pd, %	T = 100 °C		T = 200 °C	
		X, %	S, %	X, %	S, %
H_2PdCl_4	0.1	35	91	48	60
	0.5	33	94	79	71
	1.0	20	89	43	80
	2.0	12	85	28	83
$Pd(NH_3)_4Cl_2$	0.1	23	96	57	66
	0.2	33	96	69	73
	0.5	34	93	79	71
	0.7	30	96	79	72

Note. Here and in Table 2: X is the conversion level of ethylene, S is the selectivity level with respect to butenes.

TABLE 2

Parameters of propylene synthesis from ethylene at 40 to 80 °C, at ethylene feeding mass rate 0.5 h^{-1} and at a pressure of 0.1 MPa

Precursors	Mass fraction of Pd or Ni, %	T = 40 °C		T = 80 °C	
		X, %	Y, %	X, %	Y, %
H_2PdCl_4	0.1	5.8	5.5	15	10
	0.5	9.3	8.5	22	16
$Pd(NH_3)_4Cl_2$	0.1	7.1	6.7	10	6.9
	0.5	14	13	16	11
$Ni(NO_3)_2$	2.0	5.2	4.9	5.8	5.1

Notes. 1. For designations, see Table 1. 2. Y – propylene yield.

a less strong adsorption of the amino complex onto the carrier as compared with the chloride complex, as well as a partial reduction of palladium by ammonia in the course of the heat treatment of the samples obtained from the palladium amino complex.

As an optimal Pd content in the $PdO-Re_2O_7/B_2O_3-Al_2O_3$ catalyst for the synthesis of propylene from ethylene, we have chosen the palladium content in the catalyst ranging within 0.1–0.5 mass %. The samples containing 5 mass % of rhenium (in the form of Re_2O_7) as well as 0.1 and 0.5 mass % of Pd, applied from both types of precursors, were tested in the course of ethylene conversion into propylene at a pressure of 0.1 MPa, at a mass rate of feeding the raw material equal to 0.5 h^{-1} and the temperature values amounting to 40 and 80 °C. Certain ethylene conversion level (X, %), and propylene yield (Y, %) values for different catalysts are presented in Table 2. As demonstrated, the testing conditions used allow one to differentiate samples with respect to their activity, whose measure in this case is presented by the conversion level of ethylene. Catalysts with the palladium content even equal to 0.1 mass % regardless of the type of precursor, provide a higher conversion level as compared to a nickel-containing reference sample.

Among the samples prepared from the precursors of identical type, just as in the course of the ethylene oligomerization, the samples with palladium content of 0.5 mass % are more active, whereas within the series with the same

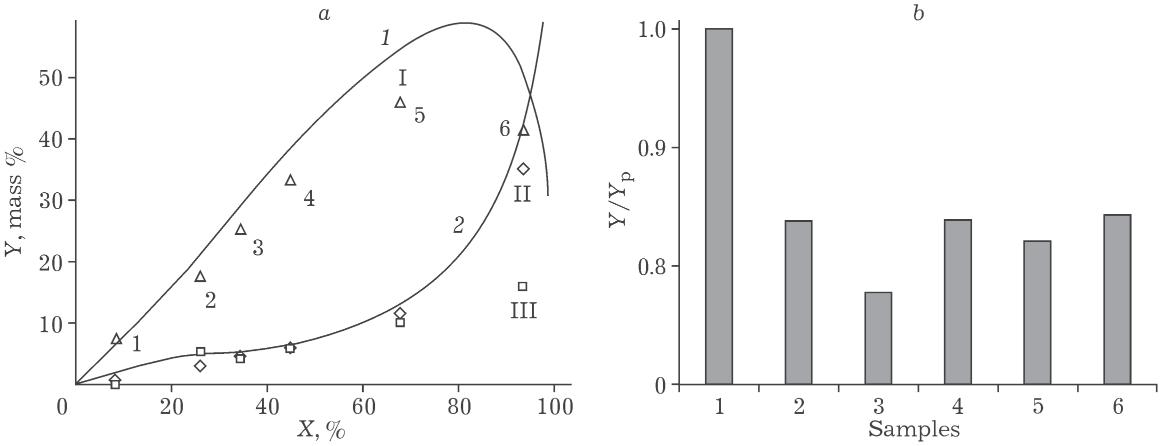

Fig. 2. Results of testing the $PdO-Re_2O_7/B_2O_3-Al_2O_3$ and $NiO-Re_2O_7/B_2O_3-Al_2O_3$ catalysts in the synthesis of propylene from ethylene under different conditions: *a* ? product yield depending on the conversion level of ethylene (I – propylene, II – butenes, III – hydrocarbons C_{5+}); *1* and *2* – the equilibrium yield of propylene and butene, respectively; *b* – effect exerted by the nature of catalyst and process conditions on the ratio between observed propylene yield and the equilibrium one (Y/Y_{eq}); *1*, *4* – $NiO-Re_2O_7/B_2O_3-Al_2O_3$ sample; *2*, *5* – $PdO-Re_2O_7/B_2O_3-Al_2O_3$ sample (Pd amino precursor); *3*, *6* – $PdO-Re_2O_7/B_2O_3-Al_2O_3$ sample (Pd chloride precursor); process conditions: *1–3* – T = 80 °C, P = 0.1 MPa, ethylene feeding rate 0.3 h^{-1}; *4–6* – T = 80 °C, P = 1.0 MPa, ethylene feeding rate 0.5 h^{-1}.

metal content one can observe an effect of the nature of precursor. For both metal content values used, of most activity are the samples synthesized from palladium chloride complex.

Increasing the ethylene conversion level and propylene yield is possible due to changing the process parameters such as raw load and pressure. The results of testing the $PdO-Re_2O_7/B_2O_3-Al_2O_3$ and $NiO-Re_2O_7/B_2O_3-Al_2O_3$ catalysts in the case of mass flow rate of ethylene reduced to 0.3 h^{-1} (at a pressure of 0.1 MPa) and under increased up to 1.0 MPa pressure (at the mass flow rate of ethylene equal to 0.5 h^{-1}) are demonstrated in Fig. 2, *a*. The Fig. 2, *a* also demonstrates the calculated equilibrium yield of propylene and butenes *via* metathesis reaction (Y_{eq}) depending on the conversion level of ethylene. It can be seen that the observed yield of propylene at the ethylene conversion levels greater than 20 % was slightly lower than the equilibrium value. The ratio between the observed and equilibrium propylene yields (Y/Y_{eq}) which in this case is indicative of the selectivity of the process, almost does not depend on the conversion level of the raw material ranging within 0.77–0.83 (see Fig. 2, *b*).

In addition to the target products of the process such as propylene and butenes, there occurs the formation of significant amounts of hydrocarbons C_{5+}. Appearing thereof could be caused by the oligomerization of ethylene and alkenes C_{3+} to occur, as well as by a cross-metathesis of alkenes C_{5+}, being most likely connected with decreasing the reaction rate for the ethenolysis of ethylene oligomers. The latter, in turn, can be attributed to the formation of the film of liquid ethylene oligomers on the surface of the catalyst, whereby the access of this reagent (having limited solubility in the liquid hydrocarbons) to the surface of the catalyst becomes complicated, and its local concentration near the surface decreases.

Basing on the data obtained from thermodynamic calculations (see Fig. 2, curve *1*), the optimal conversion level of ethylene, providing the highest yield of propylene (58 %) should be equal to 80 %. The maximum yield of propylene oxide (46 mass %) registered in the course of testing was exhibited by a palladium-containing sample prepared using an amine precursor of Pd at the conversion level of ethylene amounting to 68 %. A more active sample prepared from H_2PdCl_4, under the same conditions provides achieving the conversion level value of 93 %, exceeding the optimum value. The propylene yield in this case was equal to 42 %, which corresponds to the ratio Y/Y_{eq} = 0.83. Taking into account that the selectivity level of the process within the range of conditions under investigation does not change to any considerable extent, one could predict that at the optimum conversion level of ethylene (80 %) the yield of propylene should amount up to 49 %.

CONCLUSION

Thus, in this work we have demonstrated the possibility of a one-stage synthesis of propylene from ethylene with a selectivity level ranging within 0.77–0.83, proposed an effective catalyst $PdO-Re_2O_7/B_2O_3-Al_2O_3$ for this process, and chosen an optimum precursor the palladium content for the synthesis thereof. The results achieved in the course of laboratory-scale testing could be suitable for the realization of an industrial process of propylene synthesizing from ethylene.

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