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Catalytic synthesis of octadiene-1,7 from ethylene and cyclohexene

L.M. Kustov^{a, b, c, *}, D.B. Furman^a^a N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, Leninsky Prospekt 47, 119991, Russia^b Chemistry Department of Moscow State University, Moscow, Leninskie Gory 1, bldg. 3, 119992 Russia^c National University of Science and Technology MISIS, 119071, Leninsky Prospekt 4, Moscow, Russia

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ABSTRACT

A new method is proposed for the synthesis of octadiene-1,7 by co-metathesis of ethylene and cyclohexene (ethenolysis). The reaction is carried out in a flow setup at elevated pressures using an original $\text{NH}_4\text{ReO}_4/\text{Al}_2\text{O}_3$ heterogeneous catalyst. At the first stage of the reaction, carbenes are formed as intermediates. The optimal conditions of the co-metathesis process were found. The catalyst developed provides the cyclohexene conversion about 25 wt. %, i.e. close to the thermodynamic limit, at the selectivity to octadiene-1,7 close to 100% (99.9%). The catalyst shows good stability in six cycles including 5-h catalytic runs with intermediate regenerative treatments.

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1. Introduction

The synthetic routes to alkenes and α,ω -alkadienes, in particular, olefinic molecules and dienes with a long chain ($>\text{C}_4$) are of considerable industrial interest because presently there are no economically viable processes for producing these valuable products. The following sources of octene-1 are used in industrial processes: (1) catalytic dehydrogenation of paraffins; (2) Fischer-Tropsch synthesis on Co or Fe catalysts, (3) oligomerization of ethene in the presence of metal complex catalysts, all of these processes being non-selective.

Pyrolysis of oil fractions is of low acceptability for octene-1 production because of the poor yield (~1.5%) [1–3] due to formation of large amounts of gases and contamination of the target product with compounds with close boiling points.

The use of heterogeneous catalysts for dehydrogenation of alkanes, such as supported metal-oxide systems allows one to reach the yields of alkenes about 12–18% [1,4] under optimal conditions (reaction temperatures about 450–500 °C) with a selectivity about 90–92%. However, the content of α -alkenes is, as a rule, less than 5%. An increase in the reaction temperature results in non-selective

activation of C–C and C–H bonds. It is practically impossible to produce α,ω -dienes by these methods because the use of rather high reaction temperatures and the presence of acid sites at the catalyst surface favor migration of the double bonds and polymerization as main side processes.

The octene-1 yield in Fischer-Tropsch synthesis is usually not higher than 1–2% even in the case of most effective catalysts [1,5]. Here the main problems are essentially the same as mentioned above.

The methods based on the use of homogeneous catalytic systems for ethene oligomerization, which provide usually high productivity and selectivity to terminal olefins with a low molecular weight (C_4), do not allow the production of individual high-molecular-weight ($>\text{C}_4$) terminal olefins in both low-temperature (–30–+20 °C, $P = 7$ –40 atm) and high-temperature (>100 °C, $P \sim 100$ atm) processes. For example, the yield of octene-1 does not exceed 10–11%. Broad distribution of ethene oligomerization products in their molecular masses creates additional problems related to the isolation of the target product - octene-1. At the same time, the necessity to use Al-organic compounds leads to serious environmental problems and the need to purify waste water from aluminum compounds.

Analysis of the most important sources of terminal olefins leads to two important conclusions. The yield of individual compounds in all methods of production described above is low. This is the main

* Corresponding author. N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, Leninsky prospect 47, 119991, Russia.

E-mail address: lmk@ioc.ac.ru (L.M. Kustov).

drawback of available methods used to produce terminal olefins. In particular, the C₈ olefin fraction in the final products is extremely low and varies from ~1.5 to 10–11%. The further separation of the target product from multi-component reaction mixtures with close boiling points considerably decreases the efficiency of these methods.

The necessity of searching for the new approaches to develop efficient methods suitable for transformation of ethene to C₈ olefins with a high selectivity and productivity is obvious, since octane-1 is widely used in the synthesis of diverse elastomers via copolymerization with ethylene and propylene.

The objective of this research is to develop the catalytic method of synthesis of octadiene-1,7 from commercially available products such as ethene and cyclohexene. The target product is octene-1 produced by successive hydrogenation of octadiene-1,7, but hydrogenation is an easy step and will not be discussed here. The method proposed to achieve the goal is based on the reaction of cyclohexene ethenolysis (co-metathesis) with the formation of octadiene-1,7. The reaction of co-metathesis (ethenolysis) of ethylene and cyclohexene on metal-containing catalysts is a benign approach to develop an effective method of direct activation of the C–C and C–H bonds in hydrocarbon molecules with the purpose to prepare octadiene-1,7 and finally octene-1. This reaction is characterized by a 100% atom efficiency, because no side products are formed.

Currently ethenolysis of olefinic compounds has been studied in detail in the case of homogeneous catalytic systems [6–12]. Rhenium catalysts, including heterogeneous systems are widely used for metathesis reactions [13,14]. However, according to [15], the reaction of co-metathesis of cyclohexene with ethene does not take place due to the difficulties with cyclohexene ring opening. To our surprise and to the best of our knowledge, this is the only publication on the subject, while there are numerous papers on ring-opening metathesis polymerization of cyclohexene derivatives. The reaction of co-metathesis of cyclohexene and ethene has been carried out in Refs. [15,16] using a Mo-Co/Al₂O₃ catalyst under conditions of a batch reactor. No other data on this reaction were found in the literature.

The metathesis reaction usually should proceed at a low temperature (20–100 °C) as many other metathesis reactions, i.e., under mild conditions of metal-complex catalysis. These conditions are favorable for the occurrence of the main reaction but are not favorable for the side processes (double bond migration, polymerization or destruction) related to the transformation of the starting compounds and target products. The information about this reaction is scarce and some data are given in only one patent [16].

2. Experimental

2.1. Chemicals and materials

The following chemicals and materials were used:

Gases:

- (a) ethene (C₂H₄ - 99.5 vol %, O₂ < 0.0001 vol %, H₂O mg/m³);
- (b) argon (Ar - 99.993 vol %, O₂ < 0.0007 vol %);
- (c) nitrogen (N₂ - 99.9 vol %, O₂ < 0.005 vol %, H₂O < 0.0009 vol %, CO₂ - 0.0005 vol %).

Liquids:

- (a) n-hexane, purity ≥ 99.8%, n_D²⁰ = 1.38, H₂O ≤ 0.01%;
- (b) cyclohexene, purity 99.5%, n_D²⁰ = 1.446.

Materials:

- (a) NH₄ReO₄, chemically pure
- (b) (NH₄)₆Mo₇O₂₄ × 4H₂O; reagent pure
- (c) (NH₄)₄W₅O₁₇ × 2.5H₂O, reagent pure.

2.2. Catalysts

The catalysts were prepared by supporting an active component precursor (compounds of Re, Mo and W) onto Al₂O₃ (surface area, S = 196 m²/g; microcrystallite size, 0.5–1.0 mm). Alumina carriers were calcined at 600 °C in air for 3 h before supporting the active phase, then cooled and impregnated with NH₄ReO₄, (NH₄)₆Mo₇O₂₄ × 4H₂O or (NH₄)₄W₅O₁₇ × 2.5H₂O aqueous solutions. The thus prepared catalysts were dried at 150 °C in air for 24 h and activated under flowing dry air (3 ml/s) with a temperature ramping from 20 to 540 °C for 3 h, kept for 6 h at 540 °C in air and cooled with the air flow switched off. The catalyst drying and activation at 540 °C can be done directly in the reactor. The catalysts prepared and tested are listed in Table 1.

2.3. Catalytic equipment and testing

A flow-type catalytic setup with a plug-flow reactor was used for testing. The unit includes the following parts: metal cylinders with gases, Ar, N₂ and ethene, a high pressure reductor, a fine-regulation dosing valve, a glass cylinder (300 cm³ volume) for drying gases with calcined (550 °C) NaX zeolite, manometers, a high-pressure pump for liquid supply, two high-pressure (3–10 mPa) gate valves (upstream), a glass or stainless still vertical cylindrical reactor with the volume 30 ml, a separator for collecting the liquid products, a gas flow meter, a gas-liquid chromatograph, and a loop for taking samples for analysis.

This catalytic unit provided the simultaneous supply into the reactor of gases (through purification columns) and a cyclohexene solution in n-hexane with the help of fine dosing valves. In this case, the liquid was instantaneously supplied onto the catalyst and did not plug the ethene supply line. The catalytic unit allowed us to carry out the experiments under the following conditions: catalyst volume, 0.5–10 cm³; ethylene gas flow rate, V_{ethene} = 0.5–5 nml/sec; liquid flow rate, 1–12 ml/h; P = 0.1–10 mPa; temperature, 50–600 °C. The ethene pressure constancy in the reactor was ensured with the help of both the high-pressure reductor and the regulating gate valve at the inlet to keep the pressure under the critical value and the high-pressure gate valve at the outlet of the unit (back-pressure valve).

The catalysts were activated or regenerated first in a separated unit, which provided the treatment in dry air at a fixed temperature. The activated catalyst was purged at the reaction temperature with Ar or N₂ in the catalytic reactor, after that dry ethene or an Ar-ethene mixture was supplied at a fixed pressure. Then a cyclohexene solution was fed and the flow rate at the outlet was adjusted. The first sample of the reaction products was taken in 15 min after the cyclohexene solution had been fed.

Table 1

Catalysts used for co-metathesis of ethylene and cyclohexene.

No.	Catalyst composition	[Me], wt. % (mol. %)
1	(NH ₄) ₆ Mo ₇ O ₂₄ /Al ₂ O ₃	3.4 (3.5)
2	(NH ₄) ₄ W ₅ O ₁₇ /Al ₂ O ₃	6.0 (3.5)
3	NH ₄ ReO ₄ /Al ₂ O ₃	6.0 (3.5)
4	NH ₄ ReO ₄ /Al ₂ O ₃	0.5 (0.3)
5	NH ₄ ReO ₄ /Al ₂ O ₃	1.0 (0.8)
6	NH ₄ ReO ₄ /Al ₂ O ₃	2.0 (1.2)
7	NH ₄ ReO ₄ /Al ₂ O ₃	3.0 (1.8)
8	NH ₄ ReO ₄ /Al ₂ O ₃	4.0 (2.3)
9	NH ₄ ReO ₄ /Al ₂ O ₃	8.0 (4.7)
10	NH ₄ ReO ₄ /Al ₂ O ₃	10.0 (5.9)
11 ^a	(NH ₄) ₆ Mo ₇ O ₂₄ -Co(NO ₃) ₂ /Al ₂ O ₃	7.3 (7.8) - Mo; 2.4 (4.0) Co

^a Catalyst No. 11 was prepared according to the patent [16] and tested for comparison in the flow setup (although it was tested in a batch reactor in the patent).

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