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REVIEW ARTICLE

Features of heterogeneous catalytic transformations of strained carbocyclic compounds of the norbornene series

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Abstract

Objectives. *Catalytic processes involving norbornene (NBN) and norbornadiene (NBD) offer exceptional opportunities for the synthesis of a wide range of hard-to-reach polycyclic hydrocarbons. The problems of selectivity and manufacturability of these reactions are fundamentally important for their practical implementation. The aim of this review is to summarize the latest advances in the field of designing heterogeneous catalysts for the preparation and transformation of promising NBN- and NBD-derivatives with the maintenance of a strained carbocyclic framework in isomerization and dimerization reactions of these compounds.*

Results. *Various strategies for the selection of catalysts and prospects for the development of heterogeneous catalysis for syntheses based on NBN and NBD derivatives were considered. The possibility of selective cyclic dimerization and isomerization of NBN and NBD was shown. The factors that affect the direction of the reactions and make it possible to maintain the strained norbornane structure were discussed.*

Conclusions. *An analysis of the current state of this problem showed that at present, the technological parameters of the conversion of NBD and NBN derivatives with the participation of heterogeneous catalysts are significantly inferior to homogeneous systems. In order to improve the productivity of these processes and design catalyst regeneration, further investigations are required. However, some progress in these areas has already been made. In a number of processes, it is possible not only to maintain the strained carbocyclic framework, but also to* *establish ways to control regio- and stereo-selectivity. In some cases, the use of heterogeneous catalysts allows the process to be direct into a completely new path, which has no analogues for homogeneous systems.*

Keywords: *norbornene, norbornadiene, heterogeneous catalysis, dimerization, isomerization, transition metals, zeolites, strained carbocyclic compounds*

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ОБЗОРНАЯ СТАТЬЯ

Особенности гетерогенно-каталитических превращений напряженных карбоциклических соединений норборненового ряда

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Аннотация

Цели. *Каталитические процессы с участием норборнена (НБН) и норборнадиена (НБД) открывают исключительные возможности для синтеза широкого круга труднодоступных полициклических углеводородов. Проблемы избирательности и технологичности этих реакций принципиально важны для их практической реализации. Целью обзора является обобщение последних достижений в области создания гетерогенных катализаторов для получения и превращений перспективных НБН- и НБД-производных с сохранением напряженного карбоциклического каркаса в реакциях их изомеризации и димеризации.*
Результаты. *Рассмотрены различные стратегии подбора катализаторов и перспективы развития гетерогенного катализа для синтезов на основе НБН и НБД производных. Показана возможность селективного проведения циклической димеризации и изомеризации НБН и НБД. Обсуждены факторы, влияющие на направление реакций и позволяющие сохранять напряженную норборнановую структуру.*
Выводы. *Анализ современного состояния данной проблемы показывает, что в настоящее время технологические показатели процессов превращения НБД и НБН-производных с участием гетерогенных катализаторов существенно уступают гомогенным системам. Их оптимизация, увеличение производительности и регенерация катализатора требует дальнейшего изучения и совершенствования. Тем не менее, на данном этапе достигнуты определенные успехи. В ряде процессов удается не только сохранить напряженный карбоциклический каркас, но и установить пути управления регио- и стерео-селективностью. В некоторых случаях применение гетерогенных катализаторов позволяет направить процесс в совершенно новое русло, не имеющее аналогов для гомогенных систем.*

Ключевые слова: *норборнен, норборнадиен, гетерогенный катализ, димеризация, изомеризация, переходные металлы, цеолиты, напряженные карбоциклические соединения*

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INTRODUCTION

Norbornadiene (NBD), norbornene (NBN), and their derivatives hold an important place in organic and petrochemical synthesis [1]. Over a 70-year history, these compounds have found application in the perfume industry [2–5], medicine [6–9], agriculture [10–12], in the production of polymeric materials with unique properties [13–22], microelectronics, and photonics [23–27], as solar energy converters [28–34], fuels with different properties [35–47], and so on. The number of publications and patents related to the preparation and use of NBN and NBD derivatives exceeded 35000 in 2022. Due to their unique structure, these compounds are coming to the fore in modern chemistry and chemical technology (Fig. 1).

NBN, NBD, and some of their simplest derivatives have a reliable raw material base, since they are formed from large-scale products of oil or coal processing: dicyclopentadiene (DCPD), 1,3-cyclopentadiene (CPD), acetylene, alkenes, and alkadienes of various structures [46, 48–50]. The production of CPD can be easily combined with the production of other products, in particular, ethylene and isoprene [46, 51, 52]. Currently, not all CPD finds a qualified application, so the search for new promising ways to use it is very relevant. At the same time, the CPD itself can already now be obtained not only during the processing of oil fractions or the technology of indirect liquefaction of coal raw materials, but also by synthesis from natural products (Fig. 2) [53, 54].

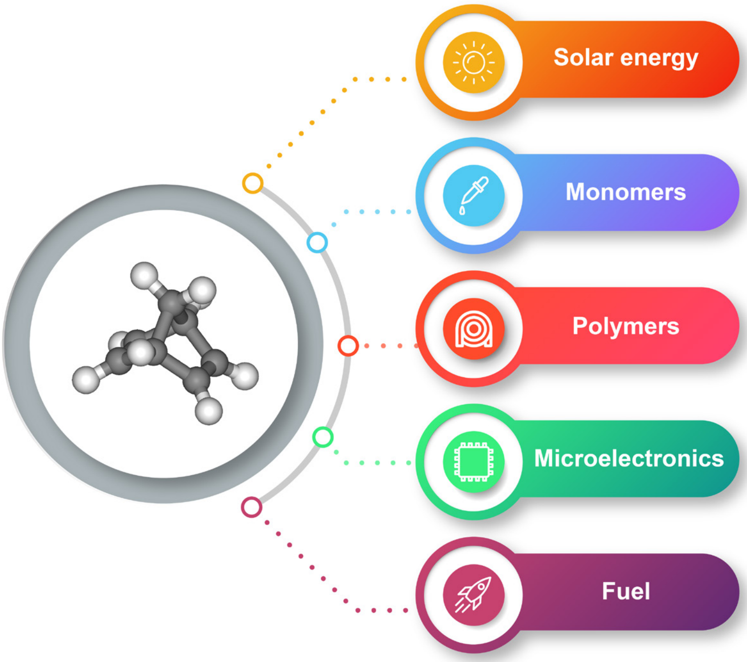

Fig. 1. Application areas of norbornene and norbornadiene derivatives.

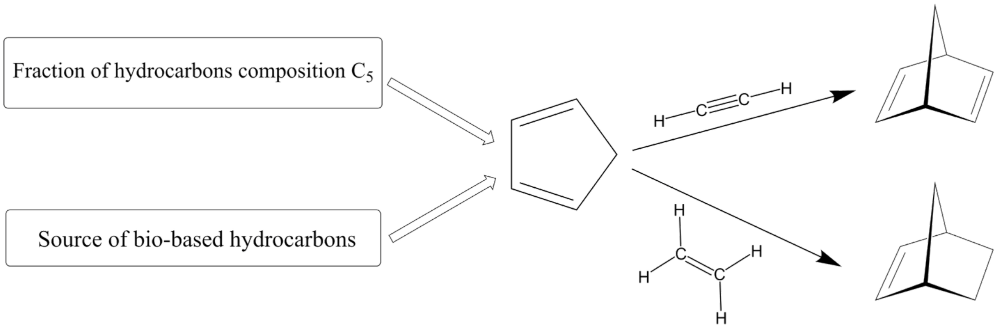

Fig. 2. Scheme of obtaining NBD and NBN.

Despite the extremely rich synthetic possibilities, the use of NBN and NBD derivatives as universal substrates is currently quite limited. The structural features of the norbornane carbocyclic skeleton suggest that such compounds have all types of isomerism: skeletal, regio-, stereo-, and enantio-isomerism. In real syntheses, this leads to the formation of mixtures of isomers. Difficulties in the separation of isomeric products with similar properties, their analysis, including the establishment of the structure of isomers, as well as modern problems of the rational use of reagents, largely limit the large-scale use of NBN and NBD. On the other hand, cycloaddition reactions (Fig. 3) involving NBD have unlimited possibilities for studying and implementing various directions and levels of isomerism. These circumstances can be very productive for developing new methods and approaches that solve the problems of manufacturability and selectivity of various levels in such processes.

At present, the vast majority of works on the synthesis of carbocyclic compounds based on NBN and NBD are associated with the use of homogeneous metal complex catalysis. The application of its methods and approaches through the targeted selection of the metal, ligand environment and reaction conditions made it possible to determine the strategic directions for improving these processes.

Great progress has been made in the last 15–20 years, when systematic studies of the kinetics and mechanisms of reactions involving NBN and NBD began [55–59], and quantum chemistry methods began to be applied to such objects and processes [60–65]. The synergy of these intensively developing areas allows targeted developing and optimizing reaction conditions in order to obtain individual products and materials with special properties based on them. Further development of a strategy associated with a close combination of theoretical and experimental approaches will not only reduce labor intensity and optimize experimental studies, but will also allow a better understanding of the mechanisms of the investigating processes to create highly efficient catalysts.

In the same period, studies began on the development of heterogeneous catalytic systems,

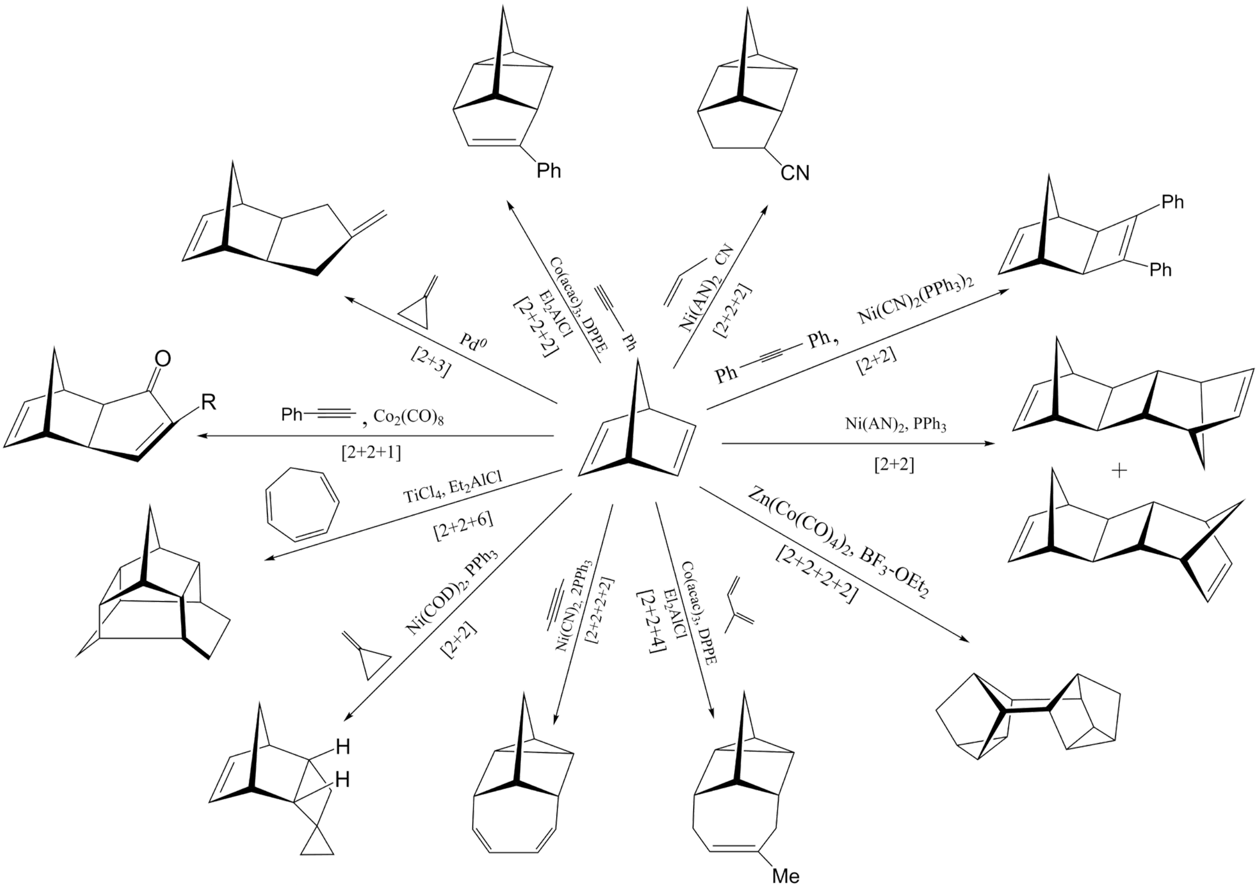

Fig. 3. Some catalytic codimerization reactions involving NBD.

which have undoubted technological advantages over homogeneous ones. The possibility of simple separation of the catalyst from the reaction products and the use of flow type reactors in the case of heterogeneous catalysis significantly increases the economic efficiency of such processes [66–68]. However, it should be emphasized here that the main and fundamental problem in the use of heterogeneous systems is the maintenance of the strained norbornane structure in the products. Heterogeneous catalysts exhibit activity under more severe conditions than homogeneous ones, which can lead to the destruction of the strained framework of NBN and NBD derivatives. In addition, the inhomogeneity of the surface and composition of the active centers of catalysts of this type leads to a significant decrease in their activity and selectivity compared to homogeneous systems [69].

Considering that the number of works in the field of catalytic chemistry of NBN- and NBD-derivatives is extremely large and synthetic aspects have been shown in a significant number of fundamental reviews and monographs [1, 29, 44, 70–76], in this work, emphasis is placed on the application and development of heterogeneous catalysis predominantly to the starting reagents. Consideration of the processes for obtaining polymeric materials based on NBN and NBD, as well as the catalytic transformations of quadricyclane (QC) and its derivatives obtained as a result of photochemical isomerization or decomposition of NBD, is beyond the scope of this work. If necessary, this and additional information can be obtained from [1, 20, 77, 78]. This review mainly considers the current state of heterogeneous catalytic transformations involving NBN, NBD and their derivatives, aimed at obtaining important monomers and intermediates that maintain the original norbornane structure and, if possible, an active double bond in the norbornene ring.

ISOMERIZATION OF NORBORNADIENE

Reversible valence isomerization of NBD to energy-rich QC is a promising solar energy storage reaction. It is known that during one hour the Sun gives more energy to the Earth's surface than people consume in a whole year, while most of it is simply inefficiently dissipated on the surface. In this regard, the ability to draw on this huge potential is an important stage in the development of the energy sector, and the creation of efficient technologies in this area is critically needed. In the NBD→QC system, solar energy is accumulated and converted into a stored form at the molecular level, since as a result of the NBD→QC photoreaction, a metastable structure is formed containing highly stressed fragments: two cyclopropane and cyclobutane rings. In the future, the accumulated energy can be quickly released in the form of heat (110 kJ/mol) by the reverse catalytic reaction QC→NBD. Additional advantages of systems based on this reaction are that they bypass the problems associated with the batch type of energy production by solar panels, and the low molecular weight of NBD provides high efficiency and energy storage capacity (Fig. 4)

Despite the fact that several fundamental reviews have been devoted to the NBD↔QC system [28–31, 79], it is constantly being improved in terms of optimizing the conditions for both the direct photoreaction and the reverse catalytic process.

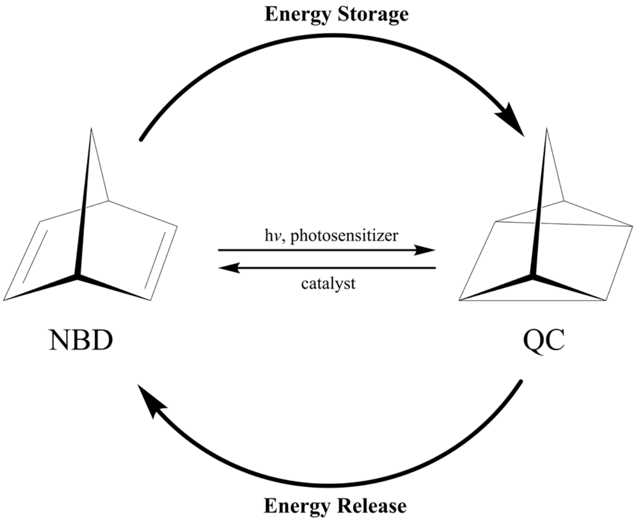

Fig. 4. Scheme of isomerization in the NBD⇄QC system.

Direct isomerization of NBD→QC

NBD isomerization in QC occurs upon irradiation, but NBD molecules cannot directly absorb solar energy. This isomerization is facilitated by sensitizers or photocatalysts. In this regard, to implement this process, scientists used Michler's ketones, benzophenone, as well as $CuCl_2$ and Ru compounds in this reaction [78, 80, 81]. Despite the fact that these sensitizers exhibit high activity and selectivity, they have a number of disadvantages, in particular, they are unstable under irradiation and prone to decomposition. Homogeneous sensitizers are soluble in the solution of the reagent itself, which makes it difficult to recycle and purify the product. From the point of view of practical application, heterogeneous photocatalysts are more advantageous. Initially, it was reported that semiconductors, including ZnO, ZnS, and CdS, can catalyze NBD → QC isomerization [82] with yields up to 90–100%; however, during their operation, sulfur is washed out into the reaction mass. Subsequently, it was reported that Y zeolites substituted with K^+, Cs^+, and Tl^+ ions also sensitize the process due to the heavy atom effect [83]. In this case, the reagent is pre-adsorbed in the micropores of the support. Attempts have been made to use Y zeolites with the exchange of La, Cs, Zn and K for the photoisomerization of NBD in the liquid phase. It was found that LaY exhibits a relatively high activity [84], which is explained by the heavy atom effect and the presence of Brønsted acid sites.

These approaches to the heterogenization of catalysts for the direct reaction were significantly improved in [85–88], where titanium-containing materials were synthesized in the pores of MCM-41[1] silica gel in order to replace homogeneous analogues. Initially, chemical grafting of titanium dioxide led to the formation of fine quantum size TiO_2 crystallites in the pores of MCM-41. Isomorphic substitution leads to inclusion of Ti into the framework, which disrupts the ordered porous structure of MCM-41; however, with an increase in the Ti content, some non-framework Ti particles are formed. It has been found that Ti-containing materials based on MCM-41 silica gel exhibit a significantly higher photocatalytic activity than bulk TiO_2, and framework Ti particles are more active than surface-dispersed particles. For the photocatalytic reaction, the yield of the NBD→QC reaction exceeds 90%, but with an increase in the amount of Ti particles in the system in the series: Ti–MCM-41(30) > Ti–MCM-41(50) > TiO_2–MCM-41 > Ti–MCM-41(70) > TiO_2, a decrease in the yield to 30% is observed, since it is the isolated Ti framework particles that are the most active. Doping of this system with ions of various metals (V, Fe, Ce, Cu, Cr) makes it possible to increase the activity of the catalytic system by an order of magnitude in the photomeasurement of NBD in QC. At the same time, the efficiency of the systems decreases in the series: Fe–TiO_2 > V–TiO_2 > Cr–TiO_2 > Ce–TiO_2 > TiO_2 > Cu–TiO_2. It is assumed that the local structure and type of dopant are critical, since photoreactivity correlates with the amount of oxygen on the lattice surface.

Reverse isomerization of QC→NBD

To realize the main advantage of the NBD↔QC system, namely, the release of stored energy on demand, an efficient method for the reverse isomerization of QC to NBD derivatives is required. Thermal initiation is possible for this process, but it is not favorable for energy reasons. From a practical point of view, an induced catalytic back reaction is more desirable. Previously, most approaches used catalysis using unsaturated coordination complexes of transition metals and metal oxides, such as MoO_3, WO_3, V_2O_5, and copper(II) sulfate [29, 89–91]. In these cases, the reverse reaction usually proceeds through the oxidized form of QC, which is why only a few of these types of catalysts meet the most important technological requirements, such as the absence of side reactions, high turnover rates and long-term stability. The most promising results were obtained for square planar Co(II) complexes [92, 93], which became the starting point for creating heterogeneous catalysts based on them. Using approaches to immobilization of homogeneous catalysts, Co(II) compounds were grafted onto various oxide and carbon supports [94–97]. Among them, cobalt phthalocyanine complexes covalently bonded to silica gel showed the highest efficiency in combination with stability to immobilization. The valence isomerization of quadricyclane to norbornadiene in the presence of such a catalyst proceeds at a temperature of 0–60°C both in an indifferent solvent and in a bulk of QC with conversions up to 100% and reaction selectivity up to 99.9%. The number of catalytic cycles varies in the range from 10000 to 40000 depending on the composition of the catalyst. However, in addition to the aspect of purification of the reaction mass from the catalyst, it is also necessary to take into account the activity of the immobilized catalyst, because, depending on the material of the solid support, access to the active centers of the catalyst can be difficult. The technical application of systems of the NBD↔QC type requires the development of simple, reliable, inexpensive and efficient methods for each stage of the reversible isomerization of the NBD–QC system along with easy purification. In this regard, in recent years, interest has increased in metal

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[1] MCM-41 (Mobil Composition of Matter No. 41) is a mesoporous material with a hierarchical structure with a hexagonal array of unidirectional and non-communicating pores from a family of silicate and aluminosilicate solids, which were first developed by researchers at *Mobil Oil Corporation* (USA) and can be used as catalysts or catalyst carriers.

oxide nanoparticles, which are an excellent platform for solving this problem due to the high surface-to-volume ratio compared to bulk material [98], the possibility of tuning their surface properties [99], and the simplicity of their synthesis. Systems of the Fe_3O_4–CoCat type synthesized in this way, which are complexes of cobalt (Co) with salphene and phthalocyanine ligands (Cat) immobilized on iron oxide nanoparticles (Fe_3O_4), turned out to be able to catalyze the reverse reaction of QC isomerization in NBD, showing excellent characteristics with high the initial turnover frequency of the catalyst is up to 3.64 s^{-1} and the turnover number is more than 3305 [100, 101]. However, a solvent dependent catalyst performance was observed, whereby a more polar and coordinating solvent degraded the catalyst performance. A comparison of all currently available heterogeneous catalytic systems for the isomerization reaction of QC derivatives in NBD is presented in Table 1.

Analyzing the achievements in direct and reverse isomerization in the NBD↔QC system, we can say that significant progress has been made in both directions in recent years. Efficient ways of photosensitization have been developed using metal complexes or various photosensitizers, while the activity of catalytic systems is maintained over a large number of cycles. Undoubtedly, systems using 2,3-disubstituted NBD derivatives, which can absorb solar energy not in the ultraviolet, but in the visible light range ($\lambda > 400$ nm), come to the fore in the issue of solar energy absorption. However, due to the importance of the NBD↔QC system in other areas: as molecular switches, optical waveguides, chemosensors, photo-switchable materials and fuels, a number of more technologically advanced heterogeneous catalysts have recently been developed that can achieve 100% selectivity and conversion for the direct as well as the reverse reaction. However, despite the undeniable advantage of using heterogeneous catalysts and the statements of researchers about the absence of negative side processes, there is usually practically no information in publications about the technological parameters of such catalytic systems: the turnover number of catalyst, conversion, selectivity, etc.

DIMERIZATION OF NBN AND NBD

Depending on the number of active bonds and the type of substituents in the molecule, NBN- and NBD-derivatives can participate in various [2π+2π], [2π+4π], and [4π+4π] type cycloaddition reactions, which leads to the diversity and complexity of the resulting dimers. Figure 5 shows the structures of the main possible dimers of NBN and NBD [72, 74, 102]. However, it should be noted that although the formation of NBD **4**, **5**, and **6** isomers, as well as NBN **26**, **27**, and **28** isomers is purely theoretically possible, these isomers have not yet been obtained in practice, since their formation is energetically less favorable [1].

Dimerization of NBN, NBD and their derivatives is usually widely used in the field of fuel technology [43]. In particular, some NBD dimers have high densities and high volumetric net calorific values, making them good candidates for high density fuels. High-density hydrocarbon fuels are key materials for increasing range and payload for aircraft with limited fuel tank capacity. However, in addition to the wide use of norbornyl polycyclic compounds as various fuels, dimerization products of NBN and NBD derivatives are already being used in biology [103] and in the development of new multifunctional materials [104–106]. Thus, studies of the dimerization of NBD and its derivatives are of great academic and industrial importance, especially for the purpose of highly selective production of individual stereoisomers. In recent decades, research in this area has developed greatly. At the moment, the amount of literature on the dimerization of NBN, NBD, and their derivatives is extremely large, and relative synthetic aspects have already been systematically developed in many reviews and articles, in particular, in the recently published review [44]. Nevertheless, the synthetic possibilities of such processes are insufficiently realized. This is equally related to both the low selectivity of obtaining individual isomers and the difficulties of separating their mixtures and the need to remove the catalyst from the reaction mass. In this regard, in this review, we have focused in detail on the problem of creating heterogeneous catalysts for reactions of this type.

Dimerization of NBD

Cyclodimerization of NBN and NBD derivatives always proceeds in the presence of a catalyst. As in the case of NBD valence isomerization in QC, the first and best studied catalysts are systems based on transition metal complexes [1, 2, 74, 102, 107]. As a rule, these are complex compounds of Ni, Co, Fe, and Rh in the lowest oxidation states. Separate examples of the use of Cr, Ti, Pd and Ir compounds

Table 1. Isomerization catalysts of the NBD⇄QC system

Isomerization NBD⟶QC						
Catalyst	**Conversion, %**	**Selectivity, %**	**TON***	***T*, °C****	**Reaction time, h**	**Link**
ZnO, ZnS, CdS, Ge	90–100	–	–	30	28–32	[82]
LaY (t) > LaY > CsY > ZnY > KY	35–83	100	–	–	7.0	[84]
Ti-MCM-41(30)> Ti-MCM-41(50)> TiO_2-MCM-41> Ti-MCM-41(70)>TiO_2	35–91	~100	–	25	12.0	[85]
Fe-TiO_2 > V-TiO_2 > Cr-TiO_2 > Ce-TiO_2 > TiO_2 > Cu-TiO_2	63–83	~100	–	–	4.0	[86, 87]
Isomerization QC⟶NBD						
Catalyst	**Conversion, %**	**Selectivity, %**	**TON***	***T*, °C****	**Reaction time, h**	**Link**
$CuSO_4$	75	–	–	70	24.0	[91]
MoO_3, WO_3, V_2O_5, and other oxides	100	~100	–	28	24.0	[89]
$CoPc(C_2NEt_2)_7/SiO_2$ [2]	up to 100	99.9	up to 40000	0–60	0.5–1.0	[96]
Fe_3O_4-CoSalphen [3]	100	100	more than 3305	25–110	1.0	[100]
Fe_3O_4-Cat3	100	100	more than 3305	25	0.5–1.0	[101]

* TON – Turnover number.
** Temperature of the process.

are also known. Depending on the type of metal used and its ligand environment, it is already quite selective to obtain paired mixtures of substances or individual isomers with a high substrate conversion (Table 2).

In order to improve the manufacturability of the process of cyclodimerization of NBN- and NBD-derivatives, various heterogeneous catalysts have been created and tested in recent years. The first among them were catalysts in the form of rhodium on a carbon support [108, 109]. The result of catalytic dimerization of NBD in the presence of 5% Rh/C catalyst is a mixture containing 57% *endo-endo* **7** and 8%

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[2] Pc – phthalocyanine.

[3] Salphen – *N*,*N′*-phenylenebis(salicylideneimine).

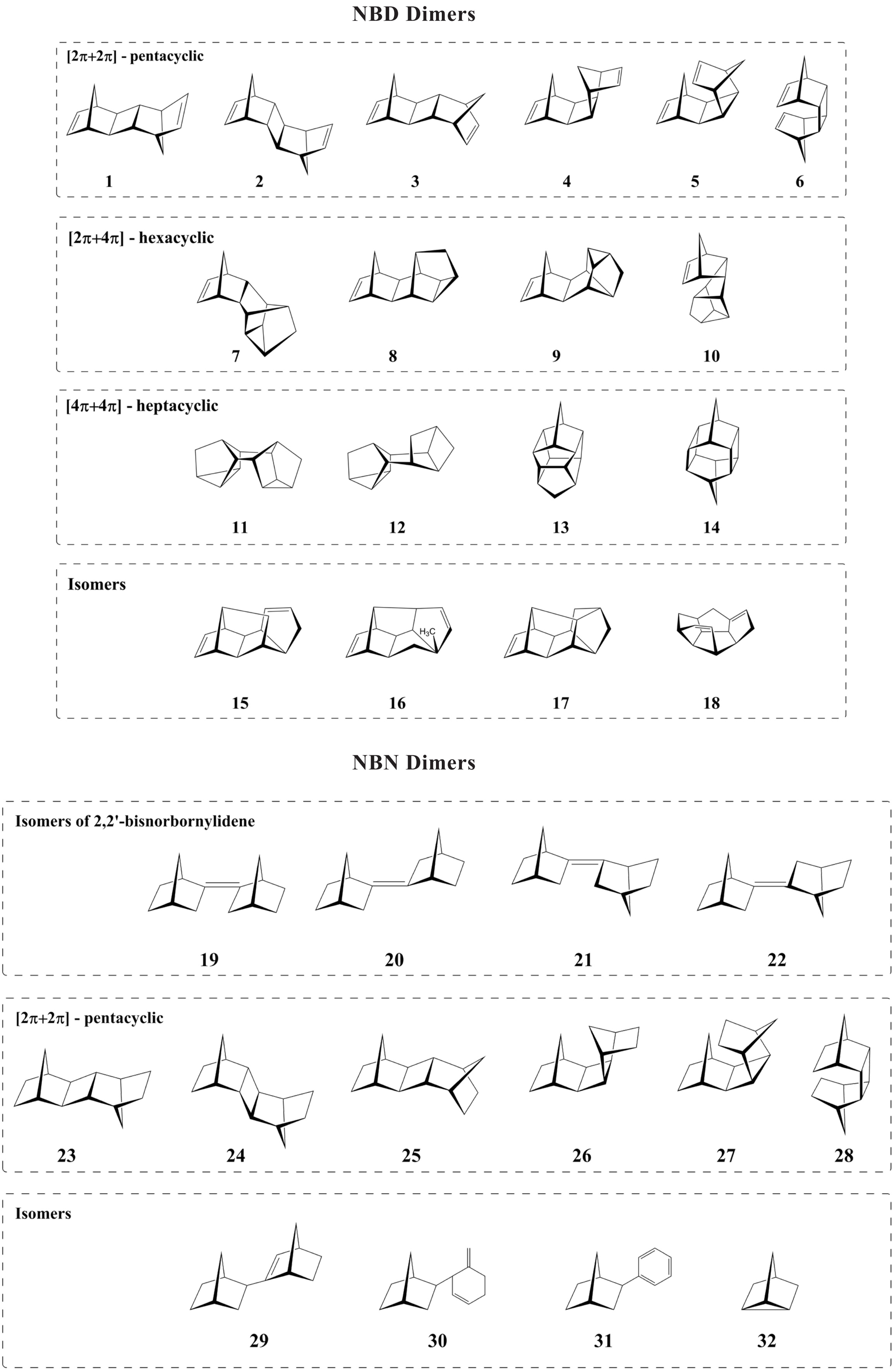
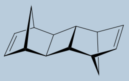
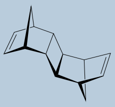
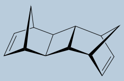
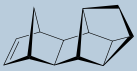
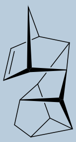
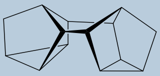


Fig. 5. Structures of NBN and NBD dimers.

exo-endo **9** dimers and 25% trimers as main products. Further development of this direction occurred more than 20 years later, when it was reported on the use of transition metals supported on zeolite as NBD dimerization catalysts [110]. Transition metals were introduced into the zeolite by ion exchange and impregnation using $Ni(NO_3)_2$, $[Rh(NH_3)_5Cl]Cl_2$, $RhCl_3$, and $PdCl_2$ as precursors. The main reaction product in this case is *exo-endo* dimer **9**, together with a small amount of *endo-endo* (**7**) and *exo-trans-exo* (**1**) dimers. Alcohols and ethers are also formed in trace amounts. The effect of the precursor structure, preparation methods, and pretreatment temperature on activity and selectivity was studied. Various types of zeolites were used as carriers for the main component of the catalysts. On a 0.3% Rh/Na–TsVM[4] catalyst prepared by ion exchange using $RhCl_3$ as a precursor, the highest selectivity for the formation of NBD dimers (97%) was achieved: 82% of dimer **9** and 15% of dimer **7**. However, the conversion of NBD did not exceed 50% after 3 h reaction at 130°C. In the presence of Rh ions or acid sites, the dimerization of NBD leads to side reactions—the formation of alcohols and esters. Most likely, this is due to the hydration of NBD with water on the acid sites of the zeolite. The temperature of catalyst pretreatment and reaction also affects its selectivity. An important effect can be exerted by water, which participates in the NBD hydration reaction and changes the adsorption behavior of the zeolite. With an increase in the pretreatment temperature, the yield of dimers increases, while the yield of alcohols and ethers decreases significantly. Changes in the activity of the catalyst during its treatment with hydrogen over a wide temperature range allowed the authors to suggest that the main active species in the dimerization of NBD are centers in which Rh is in the +1 oxidation state. When bulky ligands, such as triphenylphosphine (TPP), which cannot penetrate the zeolite channel, are added to the catalytic system, the reactivity is significantly reduced. Taking into account the strong coordination ability of TPP with rhodium atoms, it was concluded that the dimerization reaction occurred on the surface of the zeolite. In addition, in the presence of TPP, heptacyclic dimer **11** appeared among the reaction products, which is also formed during NBD dimerization using the $[Rh(NBD)CF_3COO]_2$–TPP catalytic system [111]. It was suggested that TPP in the Rh–zeolite catalytic system can change the type of cycloaddition from [2π+4π] to [4π+4π], as occurs during catalysis by the $[Rh(NBD)CF_3COO]_2$ complex. The Rh-containing zeolite probably catalyzes the process similarly to the homogeneous Rh(I) complex. Thus, at the initial stage, much

Table 2. Achievements of homogeneous catalysis in NBD dimerization

Conditions for obtaining	**Dimer**					
	 **1**	 **2**	 **3**	 **8**	 **10**	 **11**
Catalyst active site	[Ni]	[Ni]	[Ni]	[Fe]	[Fe], [Co]	[Co–Zn]
Maximum isomer yield, %	95	20	90	60–75	50–75	95
Selectivity, %	98	25	95	75	75	98
TON*	8000	5000	5000	5000	5000	3500

* TON – Turnover number.

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[4] Na-pentasil, analog of pentasil ZSM-5 (see below), synthesized without an organic matrix, ratio $SiO_2/A1_2O_3$ = 33.3.

attention was paid to the development of Rh-containing heterogeneous catalysts, such as Rh/C, Rh/zeolites. Heterogeneous catalysts based on Rh have good selectivity for *endo-endo* (**7**) and *exo-endo* (**9**) dimers (65% and 82%, respectively). However, their activity is much lower than that of homogeneous catalytic systems. It should be noted separately that Rh complexes can catalyze NBD dimerization with the selective formation of *exo-endo* dimer **9**, which is not formed in the presence of other transition metal catalysts.

Further development of this direction led to the creation of heterogeneous catalysts based on nickel. As expected, the catalysts obtained by impregnating polystyrene with Ni salts followed by their high-temperature reduction with heavy paraffins [112] show rather high activity and selectivity with respect to pentacyclic dimers [113, 114].

By applying bis(η^3-allyl)nickel onto phosphinated polystyrene containing a different number of coordinating centers, a catalyst similar to the homogeneous $Ni(NBD)_2$–phosphine system was obtained in terms of specific activity and selectivity of action with respect to individual isomers. Its productivity was 120–150 g/h of dimers per liter of solution. The catalyst itself is regenerated with molecular hydrogen followed by washing with toluene. The time of continuous operation of the catalyst without regeneration reaches 40–50 h. The catalyst showed a rather high productivity, however, it was still lower than that typical for homogeneous systems by a factor of 1.8–2.5.

Further development of the direction of heterogenization of homogeneous metal complexes led to the creation of a catalyst in which Pd(0) was heterogeneously supported on a silica support with the content of polyethylene glycol (PEG) controlled to increase its stability and the possibility of reuse with a limited decrease in the activity and selectivity of dimers. The structure of the silica support was tuned to achieve proper interaction with PEG and the Pd(0) complex. Chain length and PEG concentration were adjusted to further optimize the state of the Pd(0) complex on silica. The developed heterogeneous Pd(0) complex deposited on PEG2000[5] controlled dendritic mesoporous silica nanospheres demonstrated excellent performance for the production of high energy density fuels through the selective codimerization of NBD with QC, with an 80% yield in a nitrogen atmosphere at a temperature of 110°C, dimer **8** was obtained [115]. However, even though the authors of this work managed not only to reduce the proportion of inactive Pd(II) catalyst particles and the aggregation of active Pd(0) particles in this reaction due to PEG, the time stability of heterogenized catalysts for dimerization processes continues to be a stumbling block. when creating effective technologies based on them.

Recently, there has been an active interest in the use of various zeolites as catalysts for the dimerization of NBN, NBD, and their derivatives.

The use of zeolites HY[6], Hβ[7], HZSM-5[8], Al-MCM-41[9], KIT-6[10], and Co/HY[11] [116–120] in the dimerization of NBD leads not to the formation of traditional products **23**–**28**, but to the formation of 4 stereoisomers 2,2'-binorbornylidene **19**–**22** and, in some cases, to isomers **29**–**31**. The activity of zeolites largely depends on the reaction temperature, and as it increases from 100 to 250°C, the NBD conversion increases from 2% to 42%. Among zeolite catalysts, HY shows the highest yield of NBD dimers. This is probably due to the combination of the high concentration of Brønsted acid sites and the suitable pore structure of the HY zeolite. When HY zeolite is impregnated with cobalt salts, the concentration of Brønsted acid sites decreases, while that of Lewis sites, on the contrary, increases. The conversion of NBD

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[5] PEG 2000 is a high-quality ethylene glycol polymer with a molecular weight close to 2000 a.u.

[6] HY is a hydrogen-type molecular zeolite catalyst with a Y-type crystal structure, is a faujasite molecular sieve with a pore diameter of 7.4 Å and a three-dimensional pore structure, which is directly calcined by the ammonium exchange of the NaY synthetic molecular sieve. The basic structural units of Y zeolites are sodalite cells, which are arranged in such a way that they form supercells large enough to accommodate spheres with a diameter of 1.2 nm.

[7] Hβ is a hydrogen-type molecular zeolite catalyst with the β-crystal structure, which is a microporous crystalline aluminosilicate with a three-dimensional system of pores, the intersecting channels of which are formed by 12-membered rings with a diameter of 0.67 nm.

[8] H-ZSM-5 is the H-form or proton type of ZSM-5 zeolite (see below).

[9] Al-MCM-41 belongs to the ExxonMobil M41S family of mesoporous molecular sieves.

[10] KIT-6 is a high quality mesoporous silica molecular sieve available from *ACS Material* (USA). KIT-6 has a bicontinuous cubic mesostructure with Ia3d symmetry and an interpenetrating cylindrical pore system.

[11] Co/HY is a cobalt catalyst supported on a hydrogen-type molecular zeolite catalyst with a Y-type crystal structure.

and the yield of dimers on Co/HY were higher than on the HY catalyst, which was explained by the presence of a high concentration of Lewis acid sites [118].

In [119], the efficiency of mesoporous aluminosilicate Al-KIT-6[12] containing both Lewis and Brønsted acid sites for NBD dimerization was studied. The influence of the nature of acid sites and the structure of pores on the activity of the catalyst and selectivity for dimers is described. The catalyst can be reused, but the yield of NBD dimers turned out to be low (<40%).

By applying the Co–Ni metals by the impregnation method on Al–MCM-41, MCM-48[13], and γ-alumina, it was possible to carry out the dimerization of NBD with yields up to 85%. The activity of the supported Ni/Al–MCM-41 catalyst turned out to be much higher than that of MCM-48 and γ-Al_2O_3. The catalyst itself can be easily reduced and regenerated by filtration and calcination [121].

The advantages of zeolite catalysts are their low cost, reproducibility and reusability. But their disadvantages are also obvious. Not only the conversion of NBD, but also the selectivity of dimers on such catalysts is much lower than in the case of homogeneous catalysis with transition metals. The highest yield achieved on HY or Co/HY is 40–50%. In addition, the distribution of NBD isomeric dimers is complex, not all of them have been fully identified.

When a Cr/SiO_2 catalyst is used, the indicators are slightly higher: *exo-trans-exo* isomer **1** is formed [122]. The conversion reaches 85% and the selectivity is about 76%. The performance of this zeolite catalyst is also somewhat higher.

Dimerization of NBN

The number of published data on the dimerization of NBN itself is currently much less. This process has been well studied only for porous materials: zeolites and supported SiO_2/Cr catalysts [109, 122–127].

Patent [122] describes a method for obtaining reduced CrO_3 on large-pore silica gel, which allows NBN dimerization according to the [2π+2π] type to obtain a saturated *exo-trans-exo* isomer **23**, while a 71% yield of NBN dimers was achieved, among of which the content of dimer **23** is 85%. In the presence of zeolites of the ZSM family (Zeolite Socony Mobil), including MSM-22[14], PSH-3[15], SSZ-25[16], and Hβ zeolites, compounds **19**–**22** are the main products [123]. The NBN conversion in the presence of ZSM-5 zeolite reaches 81% at room temperature in a nitrogen atmosphere. The selectivity of the oligomers exceeds 95%, of which 79% are NBN dimers and 21% are trimers. Under similar conditions for zeolite Hβ, the selectivity for NBN dimers decreases to 70%.

In [125], the influence of the porous structure of zeolites and reaction conditions on the selectivity of NBN dimerization was studied. It has been shown that in chloroalkanes in argon, the NBN conversion reaches 100%, and the dimer selectivity is 90% in the presence of HZSM-12[17] and Hβ zeolites.

When using ZSM-5[18], the NBN conversion was 5%, which is explained by the lower concentration of “strong” acidic sites and the narrow pore size of the zeolite. The direct channel diameter in HZSM-12 is 0.56–0.67 nm, while for ZSM-5 this value is 0.51–0.56 nm. Therefore, bulky NBN dimers are practically not formed on ZSM-5; only smaller isomerization products are formed on them, in particular, QC, however, the mechanism of its production has not been described.

The possibility of using amorphous mesoporous aluminosilicates ASM-40[19] in this

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[12] Al-KIT-6 is an aluminum-substituted mesoporous material KIT-6.

[13] MCM-48 (Mobil Composition of Matter No. 48) is a mesoporous material with a hierarchical structure with a three-dimensional cubic pore structure from the family of silicate and aluminosilicate solids, which were first developed by researchers at *Mobil Oil Corporation* (USA) and can be used as catalysts or catalyst carriers.

[14] MCM-22 is a type of MWW zeolite with a pore size of 10-MR and a layered structure with two independent pore channels. One consists of two-dimensional sinusoidal slightly elliptical 10-MR channels, and the other has a supercylindrical 12-MR cage between the layers.

[15] PSH-3 is a zeolite with the chemical formula $M_2/nO\cdot Al_2O_3\cdot(20–150)SiO_2$, where M is an *n*-valent cation.

[16] SSZ-25 is a zeolite with the chemical formula (from 0.1 to 2.0) $(Q_2O\cdot(0.1–2.0)M_2O\cdot W_2O_3\cdot(20–200)YO_2$, where M is an alkali metal cation, W is aluminum, gallium, iron, boron and/or mixtures thereof, Y is silicon, germanium and/or mixtures thereof, and Q is the quaternary ammonium ion adamantane.

[17] HZSM-12 is a hydrogen-type molecular zeolite catalyst, which is a silica-rich zeolite with a one-dimensional 12-member system of annular channels and a pore opening of 5.7 × 6.1 Å, which is slightly larger than that of ZSM-5 (see below).

[18] ZSM-5—Zeolite Socony Mobil-5, patented by Mobil in 1975 with the chemical formula $Na_nAl_nSi_{96}–nO_{192}\cdot 16H_2O$ $(0 < n < 27)$.

[19] ASM-40 is a mesoporous aluminosilicate with an atomic ratio of Si/Al = 40.

reaction was also reported [126]. NBN is selectively converted to dimers **19**–**22**, QC, and part of trimers in 40%, 24%, and 31% yields, respectively. On heterogeneous catalysts such as zeolite and amorphous mesoporous aluminosilicate, dimers **19**–**22** are the main components of the products. The possibility of reuse, stability and catalytic activity of zeolite catalysts is higher than that of metal complexes. In particular, under the conditions of catalysis with ZSM-12[20] and Hβ zeolites, the yield of NBN dimers exceeds 90% within one hour, which meets the requirements of green chemistry and industrial economy. However, these heterogeneous catalysts are sensitive to water and oxygenated compounds. An urgent task at the moment is to increase their resistance to oxygen.

In [127], the authors performed dimerization of NBN on zeolites with acid sites. The influence of the structure of the acidic properties of zeolites on the catalytic properties and selectivity of dimeric products was studied. The results indicate that, at the first stage, NBN isomerization occurs to give isomeric product **32** (nortricyclene), which then turns into dimers **19**–**22**.

Among acid zeolites, Hβ-25[21] shows the best performance in NBN conversion and dimer selectivity due to the synergistic effect of the appropriate ratio of Brønsted and Lewis acid sites (B/L) and suitable pore size. Under optimal reaction conditions (140°C, 8 h, Hβ-25), an NBN conversion of 99.5% was achieved, and the dimer selectivity was 72.9%.

It should be noted that it is difficult to selectively synthesize [2+2]-cyclodimers using NBN dimerization. On the other hand, NBN dimerization in the presence of tungsten complexes or H-type zeolites can lead to four stereoisomers **19**–**22** containing the bis-2,2'-norbornylidene structure, which can also be used as an additive for fuels with high energy density. Thus, we can conclude that the currently available modified acid zeolite systems make it possible to maintain the norbornene structure during the heterogeneous catalytic dimerization of NBN.

Heterogeneous catalytic systems for the dimerization reactions of NBN and NBD derivatives, as well as their comparative characteristics, are presented in Table 3.

Analyzing the data in Tables 2 and 3, it can be seen from Fig. 3 that only a part of the structural dimers can be efficiently synthesized at present. Given the significant differences in the properties of various stereoisomers, the controlled synthesis of purer spatial dimers based on a combination of experimental and theoretical methods has broad research prospects. With a view to a more industrially oriented practical application, studies of catalytic systems for these processes have gradually moved from homogeneous metal complexes to heterogeneous catalysts. For NBD dimerization, the catalytic performance of heterogeneous catalysts is significantly lower than that of metal complex systems that have already become classical. On the other hand, the use of Hβ and HZSM-12 zeolites in NBN dimerization has already shown great success. Interestingly, the tiny difference in structure between NBD and NBN leads to a completely different course of the dimerization process. It is worth noting the progress in the field of creating heterogenized catalytic systems, which makes it possible to obtain dimers with a selectivity close to homogeneous systems. However, most works on the heterogeneous dimerization of NBN and NBD do not describe such important parameters as [67]: the real structure of the catalyst, its technological parameters, the possibility of its recycling, turnover frequency, as well as an important aspect in the immobilization of metal complexes—the problem of leaching of active particles, often changing the mechanism process, as well as contamination of products with metal particles [128–131]. In the future, the development of a new type of efficient heterogeneous catalyst or improvement of the recycling characteristics of metal complexes for dimerization of NBD is an urgent task, while it is important not to forget to investigate the exact mechanism of the catalyst.

CONCLUSIONS

In recent years, interest in compounds containing norbornene and norbornadiene fragments has grown significantly. The spheres of their use in the areas of obtaining both strained low molecular weight reactive substrates and new polymeric materials are constantly expanding. For the optimal and large-scale solution of the tasks set, accessible, reliable, and technological methods for the selective synthesis of norbornene monomers using heterogeneous catalysts are required, which allow the processes to be carried out with the maintenance of the strained norbornene structure.

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[20] ZSM-12 is a silica-rich zeolite with a one-dimensional 12-member system of annular channels and a pore opening of 5.7 × 6.1 Å, which is slightly larger than that of ZSM-5.

[21] Hβ-25 is a hydrogen-type molecular zeolite catalyst Hβ with a frame ratio Si/Al = 25.

Table 3. Heterogeneous catalysts of NBN and NBD dimerization

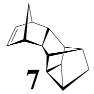
NBD dimerization							
Catalyst	**Conversion, %**	**Main product**	**TON***	**Selectivity, %**	***T*, °C****	**Reaction time, h**	**Link**
5% Rh/C	90	 **7**	–	65	90	23	[108]
0.3% Rh/Na-pentasil (33.3)	16.8	 **9**	–	82	130	1	[110]
0.3% Rh/Na-TsVM	16.9	 **9**	–	82.5	130	1	[110]
Ni/$(C_8H_{10}P)_n$	99	–	1500	95/10	–	40–50	[113, 114]
Pd-0.5PEG2000/DMSNs	95–100	 **8**	–	90–93.6	110	3	[115]
HY	~68	 **8**	–	~42	250	12	[116, 117, 1205
Hβ	~70	 **8**	–	~36	250	12	[116, 117, 120]

Table 3. Continued

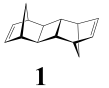
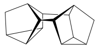
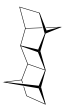
NBD dimerization							
Catalyst	**Conversion, %**	**Main product**	**TON***	**Selectivity, %**	***T*, °C****	**Reaction time, h**	**Link**
HZSM-5	~63	 **8**	–	~33	250	12	[116, 117, 120]
Al-MCM-41	~69	 **8**	–	~30	250	12	[116, 117, 120]
HY	~38	 **1**	–	~58	250	8	[118]
Co/HY	~59	 **1**	–	~50	250	8	[118]
Al-KIT-6	44.7	 **1**	–	58	250	6	[119]
Co-Ni/Al-MCM-41	~92	 **11**	–	~90	200	9	[121]
Cr/SiO$_2$	85	 **1**	2000	~76	60	3	[122]

Table 3. Continued

Catalyst	Conversion, %	Main product	TON*	Selectivity, %	*T*, °C**	Reaction time, h	Link
NBN dimerization							
CrO_3/SiO_2	85	 **23**	100	90	95	14	[122]
ZSM, MCM-22, PSH-3, SSZ-25	81	**19–25**	–	7	75–250	19.1–25.9	[122]
Hβ HZSM-12	97–100	**19–22**	–	~57 89–93	80	1	[124, 125]
ASM-40	98	**19–22**	–	41	60	5	[126]
Hβ-25	99.5	**19–22**	–	72.9	140	8	[127]

* TON – Turnover number
** Temperature of the process

An analysis of the current state of this problem shows that only the first steps have been taken in this direction, and researchers will have to overcome many problems, both theoretical and experimental. However, some progress has already been made along this path. In a number of processes, it is possible not only to maintain the strained carbocyclic framework, but also to find ways to control the regio- and stereo-selectivity of the reaction. Sometimes the use of heterogeneous catalysts even gives a unique effect, allowing you to direct the process in a completely new direction.

The activity and selectivity of heterogeneous catalysts in reactions involving NBD are still significantly lower than in homogeneous systems. Catalyst performance improvement and recycling still require further study. The design and development of new types of heterogeneous catalysts, the immobilization of transition metal complexes, the use of new types of supports and surface modifiers for the qualitative fixation of active centers can become strategic directions. It will be necessary to study and use the phenomenon of synergy, which makes it possible to consistently predict and select optimal conditions for substrates and products of a given structure. This includes taking into account the possibility of leaching of active components from the surface of carriers during the reaction and other technologically unfavorable transformations of catalysts during their operation in order to optimize the reaction in continuous flow reactors.

Authors' contributions

Sergey A. Durakov – analysis of literary sources, conceptualization of the review idea, systematization of scientific publications, and writing the text of the review;

Alexey A. Kolobov – search for publications on the review topic, technical and bibliography editing, and design of illustrative materials;

Vitaly R. Flid – conceptualization of review materials, scientific editing, critical revision with the addition of valuable intellectual content.

The authors declare no conflicts of interest.

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