Selective rhodium-containing zeolite catalysts for cyclodimerization of bicyclo[2.2.1]hepta-2,5-diene

Nataliya F. Gol'dshleger [a,*], Boris I. Azbel' [a], Yakov I. Isakov [b,*,1], Efim S. Shpiro [b], Khabib M. Minachev [b]

[a] *Institute of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Russia*
[b] *N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 117913 Moscow, Russia*

Abstract

It has been shown that norbornadiene (NBD) is dimerized in the presence of rhodium zeolite systems forming hexacyclodimers, *exo-endo-* and *endo-endo*-hexacyclo[9.2.1.0$^{4.6}$.0$^{3.8}$.0$^{2.10}$.0$^{5.9}$]tetradec-12-enes preferentially. The effect of the structure, preparation procedure and pretreatment of the catalysts on their activity and selectivity in norbornadiene cyclodimerization and the change in the rhodium electronic state in the course of the reaction have been studied. Alcohols (nortricyclan-3-ol and norbornen-5-ol) and ethers (3-tricyclo[2.2.1.0$^{2.6}$]-heptyloxy-3')bicyclo[2.2.1]hept-5-ene and 3,3'-oxydinortricyclane) as well as norbornadiene cyclodimers were formed when the catalysts containing both the rhodium and acid sites were pretreated with retaining adsorbed water. Interaction of the Rh/Na-ZSM-5 catalyst with H$_2$ or norbornadiene under mild conditions (130–150°C) leads to the stabilization of a significant portion of rhodium in the form of Rh(I), and apparently a complex formed is like that of [NBD–Rh(I)]–O$_{zeol}$. Norbornadiene cyclodimerization takes place with the participation of the active centres localized on the outside surface of the zeolite crystals.

Keywords: Norbornadiene; Rhodium; Zeolite; Cyclodimerization

1. Introduction

Bicyclo[2.2.1]hepta-2,5-diene (norbornadiene, NBD) is a useful intermediate for production of various valuable chemicals such as polycyclic hydrocarbons including norbornadiene dimers, the ingredients of high-energetic mixtures [1,2]. Cyclodimerization of NBD can be carried out in solution in the presence of catalysts, such as the complexes of low-valent cobalt [3], iron [4], rhodium [5,6] and other transition metals [7]. The efficiency of a heterogeneous catalyst has been also demonstrated in this reaction. Four different compounds were obtained over 5% Rh/C, selectivity toward NBD hexacyclic dimers approached 70% [8].

The development of the selective catalysts is of fundamental importance since a great number of dimers and trimers can be obtained in oligomerization of NBD [7]. Therefore, it was interesting to employ the known properties of zeolites, e.g., shape selectivity and capability of

---

* Corresponding author. Fax.(+ 7-096) 515-3588.
[1] Fax. (+ 7-095) 135-5328.

stabilizing an unusual metal oxidation state [9,10] to decide this problem.

This work presents the results of the first study on the influence of the method of preparation and pretreatment of zeolite catalysts on their activity and selectivity in norbornadiene cyclodimerization. The rhodium electronic state in Rh/Na-ZSM-5 was examined by X-ray photoelectron spectroscopy (XPS) in the course of the reaction.

2. Experimental

2.1. Materials

Norbornadiene was purified by two successive rectifications over sodium and stored in evacuated ampoule at 5°C. 3-Hydroxynortricyclane and its ethers were prepared as described in [11,12]. Cyclodimers of NBD used as the standards for GLC analysis were prepared as described elsewhere [4,6,8].

The NaY zeolite used has a SiO_2/Al_2O_3 ratio of 4.4. The Na-ZSM-5 zeolite ($SiO_2/Al_2O_3 = 33.3$) synthesized without an organic template and the Na-ZSM-8 zeolite ($SiO_2/Al_2O_3 = 46$) synthesized in the presence of tetraethylammonium bromide were obtained according to [13]. Decationized modification of zeolites were obtained from the Na parent forms by exchange with ammonium nitrate (2 M) for NaY and ammonium chloride (2 M) for Na-ZSM-5 followed by calcination under a flow of dry air at 500°C during 8 h. The degree of cation exchange was denoted as a number before H in the zeolite symbol.

2.2. Preparation of catalysts

Ion-exchanged samples containing rhodium were prepared by the procedure described for Rh/NaY in [14]. The powdery zeolite Na-ZSM-5 (22.25 g) with a moisture content of 8.9% was stirred with 300 ml of H_2O at room temperature

for 2 h. The suspension was centrifuged and a liquid with pH 8.8 decanted. Zeolite was repeatedly washed with H_2O and then suspended in 250 ml H_2O. At vigorous stirring, 30 ml of 2.2×10^{-2} N aqueous solution of $RhCl_3 \cdot 3H_2O$ (pH 5 on addition of NaO_2CCH_3) were added in small portions to suspension during 30 min. After completing the solution addition, the stirring was continued for 4 h at 50–60°C. Then the exchanged zeolite catalyst was filtered, washed thoroughly with water, followed by drying overnight in air at 80°C. The catalyst contained 0.3% rhodium. Same procedure was used for 0.7% Rh/Na-ZSM-5.

Other catalysts were obtained by impregnation of powder Na-ZSM-5 and 0.85H-NaY zeolites heated at 500°C with a calculated amount of aqueous solutions of $RhCl_3$ or $[Rh(NH_3)_5Cl]Cl_2$.

The catalysts were activated in a dry air flow at 500°C for 5 h before use.

When the effect of the preliminary reduction of catalysts with H_2 was studied, the respective samples were calcined at 500°C, cooled to 150°C in a flow of argon for 2 h, reduced in a pure hydrogen stream (10 ml/min) at 150 or 500°C for 5 h, and then cooled to room temperature in same hydrogen stream and stored in a sealed glass ampoule.

2.3. Procedure for catalytic reaction

The catalyst calcined was transferred without contact with air to glass ampoules (a capacity of 3 ml), NBD refrozen by using of a vacuum line (catalyst:NBD = 1:5, w/w), the ampoules were evacuated, sealed and heated at 130°C during 1 h. At the reaction completion the ampoules contents were extracted repeatedly with hexane, concentrated and analyzed. GLC of reaction mixture was performed on a 'Biochrom-1' chromatograph equipped with a 15% Silicone E-301 on Chromatone N-AW-DMCS column (500 cm 0.3 cm) and a flame ionization detector. N_2 was used as a gas-carrier; a column temperature was 220°C. Diphenyl was used as an internal stan-

Table 1
Catalytic properties of rhodium-containing zeolites in norbornadiene cyclodimerization [a,b]

Run	Catalyst (SiO$_2$/Al$_2$O$_3$)	Method of preparation	K [c]	A [d]	Distribution of products (%)					S [e]
					1	2	3	4	5	
1	0.3% Rh/Na-ZSM-5 (33.3)	ion exchange	16.8	127.0	83.0	13.0	1.0	1.0	2.0	96.0
2	0.7% Rh/Na-ZSM-5 (33.3)	ion exchange	7.0	23.0	75.0	8.9	2.1	5.7	8.3	84.0
3 [f]	0.7% Rh/Na-ZSM-5 (33.3)	impregnation	4.0	30.0	82.0	17.0	1.0	trace	trace	99.0
4	2% Rh/Na-ZSM-5 (33.3)	impregnation	9.0	11.6	87.2	12.5	0.2	trace	trace	99.0
5	0.5% Rh/H-ZSM-5 (33.3)	ion exchange	6.8	35.8	77.0	12.0	1.5	5.7	2.8	90.0
6	0.5% Rh/0.63HNa-ZSM-8 (46)	ion exchange	3.5	17.0	76.0	10.0	4.0	5.0	5.0	86.0
7 [g]	0.5% Rh/0.85HNaY (4.4)	impregnation	2.4	10.0	28.5	6.8	2.7	37.0	25.0	34.0
8 [h]	0.5% Rh/H-ZSM-5 (33.3)	ion exchange	6.4	22.0	44.0	8.6	1.4	36.0	10.0	52.0

[a] Pretreatment conditions: air, 500°C, 5 h.
[b] Reaction conditions: evacuated ampoule, 130°C, 1 h, catalyst:NBD = 1:5.
[c] K is a total conversion of norbornadiene, (%).
[d] A is a catalyst activity calculated as mole dimers/g-at. Rh h.
[e] S is a selectivity calculated from the concentrations of hexacyclic dimers 1 and 2 (%).
[f] Catalyst pressed into a pellet.
[g] Catalyst prepared by the impregnation of zeolite with [Rh(NH$_3$)$_5$Cl]Cl$_2$ aqueous solution; other samples were prepared by using RhCl$_3$.
[h] Pretreatment temperature is 300°C.

dard. Product identification was by GLC using authentic materials.

2.4. XPS measurement

The samples of rhodium-containing zeolites studied by XPS were pressed into pellets, treated (see Table 4) and introduced into XPS spectrometer without exposure to air using a glove box and techniques described elsewhere [15]. XPS spectra were obtained on an ES-200B spectrometer according to [16]. Binding energies (E_b) were corrected by using C 1s (E_b = 285 eV) and Si 2p (E_b = 103.8 eV) photoelectron lines. The atomic ratios of Na/Si, Na/Al and Rh/Si were calculated from integrated photoelectron peak intensities which were corrected for the photoionization cross section and the instrumental sensitivity factors. Deconvolution of the Rh 3d level for Rh-containing zeolites was carried out on a PDP 11/03L minicomputer using a program for the synthesis of Gaussian peaks. The intensity ratio Rh 3d$_{5/2}$/Rh 3d$_{3/2}$, the spin-orbit splitting and the halfwidth on halfheight (HWHH) of the 3d$_{5/2}$ and 3d$_{3/2}$ components upon deconvolutions were kept the same as in Rh 3d spin doublets of

individual rhodium compounds [17]. The accuracy of the determination of E_b was ±0.2 eV; the accuracy of the atomic ratios was 10–20%.

3. Results

Investigation of norbornadiene conversion with zeolites obtained either in Na- or H-form and then modified with the transition elements, e.g. Rh, Pd or Ni, showed that in the absence of reducing agents only Rh-containing zeolites acted as catalysts in cyclodimerization of NBD within a wide temperature range (30–200°C) both in neat norbornadiene and in various solvents [2]. As seen from Table 1, in their presence the reaction proceeded with the preferential formation of *exo-endo-* and *endo-endo-*hexacyclo[9.2.1.0^{4,6}.0^{3,8}.0^{2,10}.0^{5,9}]tetradec-12-enes (compounds 1 and 2), but, depending on the reaction conditions, pentacyclic dimers 3 and oxygen-containing compounds 4 and 5 may be formed (Scheme 1).

---

[2] No Rh was detected in the liquid phase by using atom absorption spectroscopy, and catalyst activity was restored after regeneration.

Scheme 1

Scheme 1.
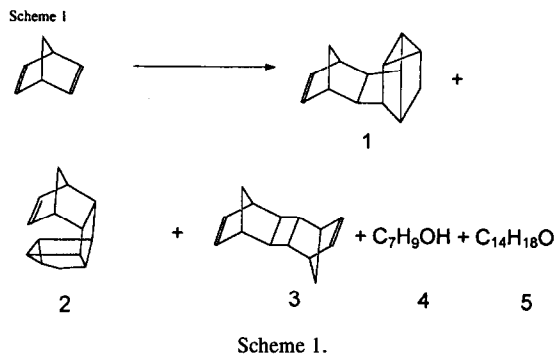
3.1. Effect of the structure and composition of zeolite

Distribution of the NBD conversion products and their yields depend on the structure and the chemical composition of the zeolite (Table 1). Various zeolites including wide-pore faujasites were studied in present paper. The highest yields of cyclodimers were observed in the presence of samples prepared from sodium form of parent pentasil. If the samples containing both rhodium and acid sites were activated with retaining adsorbed water, the formation of dimers 1–3 was accompanied by the formation of oxygen-containing products: alcohols 4 (nortricyclan-3-ol and norbornen-5-ol) and ethers 5 ({3-tricyclo[2.2.1.0$^{2.6}$]-heptyloxy-3'}bicyclo[2.2.1]-hept-5-ene and 3,3'-oxydinortricyclane) (runs 5, 7, 8, Table 1). These compounds might be obtained as a result of norbornadiene hydration with H_2O retained in zeolite after its pretreatment. Subsequent addition of alcohols formed to NBD or dehydration of alcohols give rise to ethers. Interaction of NBD with H_2O in the presence of the H-forms of zeolites, which contain no rhodium, among them H-ZSM-5, was earlier shown to result in the formation of alcohols and ethers only [12]. Rhodium introduced into H-ZSM-5 suppressed the acid-catalyzed reactions of norbornadiene (Table 1). The effect of adsorbed water on the acid-catalyzed NBD conversion was confirmed by the decrease in the selectivity of dimers formation from 90% (run 5) down to 52% (run.8) which was demon-

strated for 0.5% Rh/H-ZSM-5 by the decrease in the temperature of pretreatment from 500°C down to 300°C.

3.2. Effect of rhodium content

With the increase in the rhodium content in the catalysts, obtained both via ion exchange (runs 1, 2, Table 1) and impregnation (runs 3 and 4, Table 1), their activity in the conversion of NBD diminishes. It should be noted that oxygen-containing products were almost absent, if the cation-exchanged 0.3% Rh/Na-ZSM-5 and impregnated samples of various composition were used. At the same time, detectable amounts of alcohols and ethers appear in the presence of ion-exchanged 0.7% Rh/Na-ZSM-5. In this case the decrease in the selectivity toward NBD hexadimers could be assigned to the formation of a greater quantity of acidic sites as a result of the decomposition of water molecules on rhodium ions during preparation and activation of the zeolite catalyst.

3.3. Effect of pretreatment temperature

The effect of the conditions of catalyst pretreatment on distribution of the products of norbornadiene conversion and the yields of hexacyclic dimers 1 and 2 were investigated using as an example 0.3% Rh/Na-ZSM-5 (Fig. 1 and Table 2). At low temperature of sample pre-
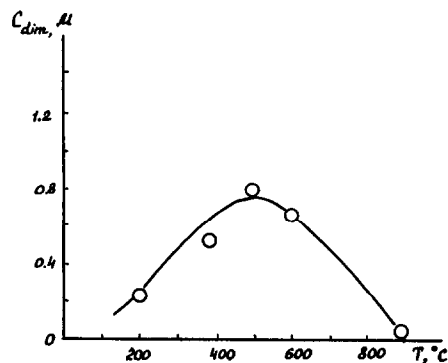

Fig. 1. Effect of the pretreatment temperature of 0.3% Rh/Na-ZSM-5 on the concentration of norbornadiene dimers.

Table 2

Effect of the pretreatment temperature of the 0.3%Rh/Na-ZSM-5 catalyst prepared by ion-exchange on the distribution of the NBD conversion products [a,b]

T_{pr}	K_{NBD}	[1]+[2]	A [c]	Distribution of products (%)					S [d]
°C	(%)	mol/l		1	2	3	4	5	
200	8.4	0.23	39.0	53.0	6.7	3.7	22.0	14.6	59.7
400	10.9	0.44	70.0	71.0	10.1	1.6	10.3	7.0	81.0
500	16.9	0.81	127.0	82.5	13.0	0.9	1.2	2.4	95.5
600	11.6	0.66	90.0	84.5	14.4	1.1	–	–	98.9
900	–	–	...	–	–	–	–	–	–

[a] Catalyst was heated in a stream of dry air at the temperature indicated for 2 h.
[b] Reaction conditions: evacuated ampoule, 130°C, 1 h, catalyst:NBD = 1:5
[c] A /(mol dimers/g-at. Rh h)
[d] Footnote e of Table 1.

treatment (T_{pr}) the concentration of dimers in the mixture is not high. In this case, the selectivity toward hexacyclic dimers amounts to 60% and the reaction mixture contains a large quantity of 4 and 5. As T_{pr} increases, the yield of dimers grows, whereas that of alcohols and ethers decreases. Similar data were obtained in the case of 0.5% Rh/H-ZSM-5 catalyst (runs 5,8, Table 1). At 500°C, the optimum T_{pr}, the catalyst found to exhibit high activity and selectivity in cyclodimerization of NBD (Fig. 1). The effect of calcination on the selectivity of 0.3% Rh/Na-ZSM-5 catalyst (ion exchange) can be associated with the change of the content and the state of water which take part not only in a side reaction of hydration of NBD, but also influences the rhodium state and the adsorption capacity of the catalyst. The relationship between these functions results in the extreme dependence of the catalyst activity in the pretreatment temperature. Deactivation of the catalyst at $T_{pr} = 900$°C is probably associated with the location of the Rh ions in the zeolite sites not accessible by NBD rather than with pentasil structure destruction.

3.4. Effect of solvents

It was shown that some solvents such acetone, acetonitrile, DMSO and morpholine inhib-

ited completely cyclodimerization of NBD with 0.3% Rh/Na-ZSM-5. On the contrary, both in ethanol and C_3–C_4 alcohols, the catalyst exhibited the same activity as in the solvent absence. In this case, the selectivity toward dimers 1 and 2 amounted to 98% (Table 3). Note, that ethanol and acetone were the best solvents for norbornadiene cyclodimerization in the presence of [Rh(O_2CCF_3)NBD]$_2$ [6,18].

3.5. Effect of dihydrogen pretreatment

It is known that the treatment of transition metal-containing zeolites with hydrogen results in the formation of highly dispersed metallic clusters and ions in the intermediate oxidation state [19]. Recently we have also shown that norbornadiene is dimerized with catalytic amounts of $Rh_2(O_2CCF_3)_4$, the Rh(I) complex formed in the system being the catalyst of the process [20]. Therefore it was of interest to study the effect of H_2 pretreatment of the ion-exchanged 0.3% Rh/Na-ZSM-5 catalyst on its catalytic activity and selectivity in cyclodimerization of NBD.

The activity of the catalyst which was reduced by H_2 at 150°C prior to the cyclodimerization reaction was equal to 260 mol dimers/g-at. Rh h which was twice as large as

Table 3

Effect of the solvent on the NBD cyclodimerization in the presence of 0.3%Rh/Na-ZSM-5 [a,b,c]

Solvent	K_{NBD}	A [d]	Products (%)		
	(%)		1	2	3–5
Ethanol	16.5	140.0	83.0	15.0	2.0
Ethanol [e]	46.7	135.0	82.0	15.0	3.0
iso-Propanol	12.0	145.0	83.0	15.4	1.6
iso-Butanol	15.9	141.0	84.0	15.0	1.0
Chloroform	5.0	53.0	79.0	11.0	10.0
Benzene	0.9	10.0	70.0	9.7	20.3

[a] Catalyst pretreatment conditions: air, 500°C, 5 h.
[b] Reaction conditions: evacuated ampoule, 130°C, 1 h, [NBD] = 3.3 mol/l.
[c] No rhodium was detected in the reaction solution by atom absorption spectroscopy.
[d] A /(mol dimers/g-at. Rh h).
[e] Reaction time is 3 h.

that of the catalyst pretreated in a stream of air and then in argon only (127 mol dimers/g-at. Rh h). The catalytic activity decreases down to 100 mol dimers/g-at. Rh h with the increase in the temperature of H_2 pretreatment to 500°C. Therefore, one can assume that at low temperature Rh^{3+} is reduced mainly to the Rh^{1+} state, which is probably a catalytically active site (see also below). At higher temperature, a major portion of Rh species could be reduced to the metallic state and the concentration of the active sites decreased. Stepwise reduction of Rh^{3+} by H_2 previously observed for samples of Rh/SiO$_2$ [21].

3.6. Effect of ligands

We studied the influence of chemical modification on the properties of the 0.3% Rh/Na-ZSM-5 catalyst. Both 4-methylquinoline (4-MeQ) and PPh$_3$ used as modificators have an effective molecular size which inhibits their easy penetration into the catalyst channels [22,23].

It was found that 4-MeQ added to the reaction mixture (in molar ratio 4-MeQ:Rh = 1:1 calculating to all rhodium) reduced the catalyst activity by 50%, but did not affect the selectivity. When the amount of 4-MeQ was further increased, cyclodimerization of NBD was completely suppressed.

Addition of PPh$_3$ to the reaction mixture (in molar ratio Rh:PPh$_3$ = 1:1 or 1:2) results in the formation of $endo$-cis-$endo$-heptacyclo[8.4.0.0$^{1.12}$.0$^{3.8}$.0$^{4.6}$.0$^{5.9}$.0$^{11.15}$]tetradecane ('binor-S') rather than bisnorbornadienes of 1 and 2.

3.7. XPS of the catalysts

Interaction of NBD with Rh/Na-ZSM-5 catalysts prepared both by ion exchange and impregnation was studied by means of XPS technique (see Fig. 2 and Table 4). In all initial samples, rhodium is present as Rh^{3+} ions with Rh 3d$_{5/2}$ binding energy of about 310 eV. As seen from the Rh/Si atomic ratio, the ion ex-

change facilitates the penetration of Rh^{3+} aqua-complexes into the zeolite channels (in comparison with impregnation) [16]. Thermal treatment of cation-exchanged samples (500°C) leads to a considerable decrease in the Rh/Si ratio, which evidences for the further Rh^{3+} cation migration into the zeolite crystals. Analysis of the data on Rh 3d$_{5/2}$ binding energy leads to the conclusion that Rh exists as Rh^{3+} isolated cations in ion-exchanged zeolites and that the aggregates of $\rangle Rh^{3+}-O-Rh^{3+} \langle$ type are present in the samples obtained by the impregnation [16].

Interaction of NBD with sample 9 at 130°C during 15 min (run 10, Table 4) results in complete transition of Rh^{3+} to the oxidation state with Rh 3d$_{5/2}$ binding energy of 308.8 eV characteristic of Rh(I) in individual compounds of Rh(I), particularly in the [Rh(O$_2$CCF$_3$)NBD]$_2$ complex (Table 4). This form of Rh composed also the greater portion in the samples of 3 and 7, NBD being a milder reducing agent as compared with H_2. Upon prolonged (1 h) treatment
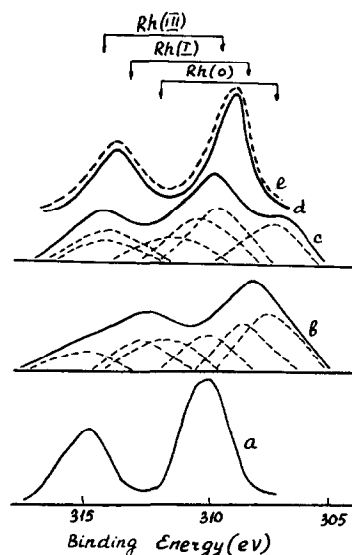

Fig. 2. XPS spectra of Rh 3d level for Rh-containing zeolites [ion-exchanged 0.7% Rh/Na-ZSM-5 (a–c) and impregnated 2% Rh/Na-ZSM-5 (d)] after various treatments and that for Rh(I) complex. (a) 500°C, air; (b) 500°C, air + 150°C, H$_2$; (c) 500°C, air + 130°C, NBD, 60 min; (d) 500°C, air + 130°C, NBD, 15 min; (e) [Rh(O$_2$CCF$_3$)NBD]$_2$. The dashed lines are denoted the components obtained by simulation of spectra using PDP11/03L minicomputer.

Table 4
Binding energy and atomic ratios of elements in rhodium-containing zeolites and complexes

Run	Sample	Method of preparation	Pretreatment	E_b Rh $3d_{5/2}$			Atomic ratios		
				Rh^{3+}	Rh$^{\delta+}$ [a]	Rh^0	Na/Si	Na/Al	Rh/Si
1	0.7% Rh/Na-ZSM-5	ion exchange	initial, hydrated	309.8	–	–	0.08	1.00	012
2	0.7% Rh/Na-ZSM-5	ion exchange	500°C, air	310.0	–	–	0.07	1.2	0.005
3	0.7% Rh/Na-ZSM-5	ion exchange	500°C, air + 130°C, NBD, 15 min	310.0	309.2	–	0.064	1.31	0.0043
4	0.7% Rh/Na-ZSM-5	ion exchange	500°C, air + H$_2$, 150°C	310.1	308.5	307.5	–	–	0.0058
5	0.7% Rh/Na-ZSM-5	impregnation	initial, hydrated	310.0	–	–	0.11	1.66	0.024
6	0.7% Rh/Na-ZSM-5	impregnation	500°C, air	309.3	–	–	0.09	2.03	0.015
7	0.7% Rh/Na-ZSM-5	impregnation	500°C, air + NBD, 130°C, 15 min	309.8	308.4	–	0.054	0.97	0.043
8	2% Rh/Na-ZSM-5	impregnation	initial, hydrated	310.4	–	–	0.13	1.5	0.059
9	2% Rh/Na-ZSM-5	impregnation	500°C, air	309.0	–	–	0.08	1.6	0.023
10	2% Rh/Na-ZSM-5	impregnation	500°C, air + NBD, 130°C, 15 min	–	308.8	–	0.07	1.1	0.039
11	RhCl$_3$	–		310.2	–	–	–	–	–
12	Rh$_2$(O$_2$CCF$_3$)$_4$	–		310.3	–	–	–	–	–
13	[Rh(O$_2$CCF$_3$)NBD]$_2$	–		–	308.8	–	–	–	–
14	Rh(metal) [16]	–	–		–	307.4	–		

[a] Rh ions in the intermediate state of oxidation.

of Rh-zeolites with NBD in addition to Rh^{1+} Rh^0 is formed (30–50%) (Fig. 2). Thus NBD is an efficient reductant of Rh^{3+} in Na-ZSM-5. Stabilization of rhodium in the intermediate oxidation state is a peculiarity of the initial reduction stage. Apparently, the selective formation of Rh(I) complex stabilized by NBD and oxygen of the zeolite framework, i.e., [(NBD)Rh]$^+$–O$^-_{zeol}$, can be achieved by varying the reduction conditions.

Reduction of rhodium with NBD is accompanied by the increase in the Rh/Si ratio and the decrease in that of Na/Si and Na/Al (Table 4). This suggests NBD-induced Rh reserve migration from the zeolite cavities onto the outside surface followed by the opposite migration of sodium ions (runs 3, 7 and 10, Table 4).

4. Discussion

Results presented above show that rhodium-containing zeolites, Rh/Na-ZSM-5, are the active solid catalysts for norbornadiene cyclodimerization. The data on the catalytic activity of the Rh(I) complexes, Rh-containing zeolite and those on the concentration of Rh^{1+} in various samples are presented in Table 5. The

correlation between the concentration of rhodium in the intermediate state of oxidation (estimated from XPS spectra) and the catalytic activity of Rh-zeolite samples suggests that for both Rh complex in solution and solid zeolite systems, coordinatively unsaturated ions of Rh^{1+} are likely to be involved into catalysis. They appear via Rh^{3+} reduction in Rh/Na-ZSM-5 either with hydrocarbon or with dihydrogen under mild conditions at the reduction temperature below 150°C and form [NBD–Rh(I)]–O$_{zeol}$ complexes evidently. This identification is based on the comparison of the E_b values of Rh $3d_{5/2}$ for Rh(I) in the [Rh(O$_2$CCF$_3$)NBD]$_2$ compound and for the Rh in intermediate state of oxidation in the zeolite treated with NBD (Table 4). The E_b Rh $3d_{5/2}$ value equal to 308.6 eV was also found for rhodium supported as [Rh(NBD)S$_2$]$^+$ (S = solvent) onto montmorillonite [24]. This is in a good agreement with the data presented for Rh/Na-ZSM (Table 4).

In the presence of 0.3% Rh/Na-ZSM-5, the solvent effect on the norbornadiene conversion is similar to that observed for Rh(I) complex, i.e. [Rh(O$_2$CCF$_3$)NBD]$_2$ [18,20]. It should be noted that the chemical analysis shows all rhodium to be retained on the zeolite. The sol-

vents with high donor ability (for instance, morpholine) inhibit cyclodimerization of NBD catalyzed with both complex and Rh-containing zeolite. Amine exhibits a similar effect on dimerization of NBD catalyzed by Rh(I) in solution [25]. However, the XPS observation of Rh^0 under the prolonged treatment of Rh/Na-ZSM-5 with NBD indicates that a complex formed and attached to the zeolite matrix is not sufficiently stable. Rhodium solvation can promote its stabilization as $[Rh(NBD)S_2]^+$ species, which are responsible for the catalytic activity as in the case of the homogeneous reaction.

The selectivity in the formation of cyclic norbornadiene dimers in the presence of $[Rh(O_2CCF_3)NBD]_2$ is regulated by the ligand environment of the rhodium atoms [18,20]. Modification of the Rh/Na-ZSM-5 catalyst with 4-MeQ and PPh_3 was carried out to change the selectivity of the cyclodimer formation and to find out whether the reaction proceeded on the external surface or in the intracrystalline space of the zeolite. The catalyst deactivation found with 4-MeQ gave some evidences in favour that rhodium located on the external surface was involved as a catalytically active site. Formation of a stable complex of Rh with 4-MeQ like the

non-active $[Rh(NBD)L_2]ClO_4$ (L = heteroaromatic amine) compound [25] could explain deactivation, provided that rhodium located in the channels is non-accessible for NBD. Modification of the Rh/Na-ZSM-5 catalyst with PPh_3 confirmed our conclusion that the rhodium species on the surface of the zeolite crystals are supposed to be active sites and Rh^{3+} to be reduced under NBD action. There is a total analogy between the cyclodimerization course in the presence of Rh(I) complex and rhodium supported onto the zeolite [20,26]: in the presence of PPh_3 dimerization of NBD proceeded in both cases as cycloaddition of $[4\pi + 4\pi]$-type with the formation of 'binor-S' instead of 1 and 2 dimers (Scheme 2).

At the same time, no strong correlation between the Rh^{1+} content and the catalytic activity of Rh/Na-ZSM-5 was observed (Table 5), thus indicating the contribution of other factors to the catalyst activity. Rhodium was found to be fully reduced in the ion exchanged 0.3% Rh/Na-ZSM-5 at 500°C. Formation of norbornadiene cyclodimers in the presence of this catalyst evidences that highly dispersed Rh^0 species might also form catalytically active sites.

The important role of the effective charge on

Table 5
Comparison of the data on the concentration of Rh^{1+} and catalytic activity of samples in cyclodimerization of norbornadiene

Catalyst [a]	Pretreatment	Reaction time, h	K_{NBD} (%)	A [c]	$[Rh^{1+}]$ [d]	Distribution of products (%)				
						1	2	3	4	5
0.7% Rh/Na-ZSM-5(IE)	Air, 500°C, 5 h	0.25	1.2	12.0	67.0	56.4	7.5	0.8	33.8	1.5
		0.5	2.9	17.9	37.0	59.2	8.6	1.2	27.3	3.7
		1.0	4.9	15.0	39.0	61.6	10.2	1.5	20.4	6.3
	Air, (500°C, 5 h) + argon (200°C, 1 h) +H_2 (150°C, 5 h)	0.5	5.0	33.8	31.0	74.0	13.4	0.6	10.7	1.3
0.7% Rh/Na-ZSM-5(IM)	Air, 500°C, 5 h	0.5	4.0	30.0	51.0	82.0	17.0	1.0	trace	
0.3% Rh/Na-ZSM-5(IE)	Air, 500°C, 5 h	0.5	5.0	40.0	36.0	84.0	14.0	1.0	trace	
$[Rh(O_2CCF_3)NBD]_2$ [b]		1.0	29.0	14.5	100.0	83.8	15.7	0.5	–	–

[a] Ion exchange (IE), impregnation (IM).
[b] Solvent was ethanol, [NBD] = 2.3 mol/l, [Rh] = $2.3 \cdot 10^{-2}$ mol/l, 100°C. In other cases the experiments were done on tablets: 130°C, 1 h, NBD:zeolite = 5:1 (w/w).
[c] A /(mol dimers/g-at. Rh h).
[d] Fraction of Rh^{1+} on the basis of XPS data.

rhodium ions as well as the ability of Rh^0 to be oxidized to Rh^{1+} with water or extra-framework oxygen can be also anticipated. High dispersion of the Rh^0 particles should be considered as a prerequisite to provide its oxidation to the Rh^{1+} in the reaction conditions. Therefore, the low Rh percentage zeolite catalysts, which were reduced at low temperature, seem to be the most appropriate samples to generate the species of this kind. These considerations explain the extreme behaviour of the dependence of the rhodium-zeolites activity on the reduction temperature and a higher activity of 0.3% Rh/Na-ZSM-5 as compared with other samples with a higher metal loading.

The data obtained allow one to propose the following scheme of NBD-induced modification of rhodium in the surface layer of solid catalysts.

1. Interaction of the Rh^{3+} ions with NBD is accompanied by the rhodium migration from the zeolite channels onto the outside of the zeolite crystals and Rh reduction:

$$Rh^{3+} OZ^- \xrightarrow{NBD} [Rh(NBD)]^+ OZ^-$$
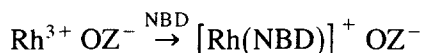
NBD is well known as a ligand with a strong coordinating ability [27]

2. Rh^0 is formed due to the reduction of Rh^{1+} by either hydrocarbon or hydrogen or disproportionation of $Rh^{\delta+}$ and is probably well dispersed, that is characteristic of the samples with the low Rh content, treated at low temperature [19].

As seen from Table 1 and 5, the low content rhodium catalysts prepared by ion exchange of Rh^{3+} with Na-ZSM-5 or by impregnation exhibit the highest selectivity towards cyclodimers. This is in good agreement with a higher Na/Al ratio and a less pronounced decrease in Na^+ concentration in the surface layer of the catalyst in the course of the reaction
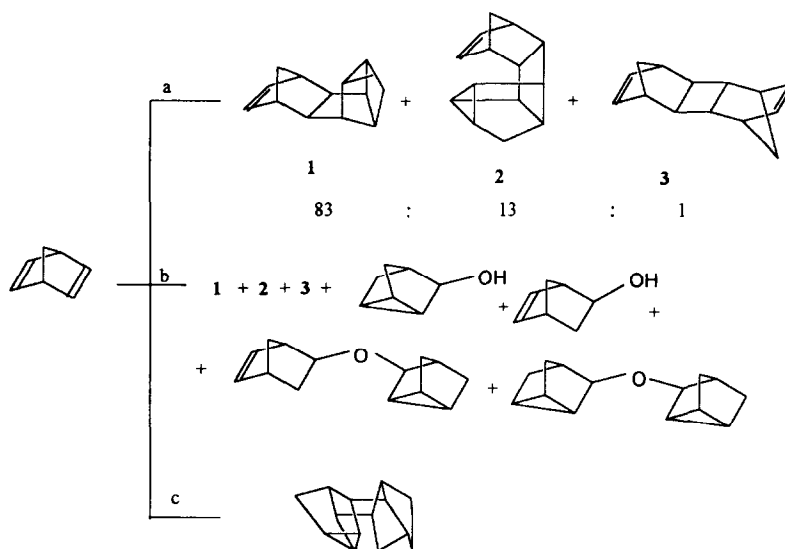
a 0.3% Rh/Na-ZSM-5   (or [(NBD)RhO$_2$CCF$_3$]$_2$, ethanol)

b 0.5% Rh/H-ZSM-5 + H$_2$O

c 0.3% Rh/Na-ZSM-5 + PPh$_3$ (or [(NBD)RhO$_2$CCF$_3$]$_2$ + PPh$_3$, ethanol)

Scheme 2.

(Table 4). Thus the acid sites created by water decomposition on the rhodium ions or during rhodium reduction are better neutralized, which results in the decrease in the yields of products **4** and **5**.

High mobility of rhodium in the zeolite matrix, the concomitant enrichment of the surface layer with rhodium due to migration from the framework channels and its coordination with NBD followed norbornadiene cyclodimerization on the outside surface of the zeolites did not allow the exhibition of molecular sieve properties of the zeolites to change the selectivity of the rhodium-containing zeolite catalysts studied.

5. Conclusion

The variety of the data obtained clearly demonstrates that the active intermediate states of rhodium can be generated in the zeolite catalysts like that it is realized for the rhodium complexes in solution. The most efficient way is the reduction of Rh zeolite with the substrate, bicyclo[2.2.1]hepta-2,5-diene. Stability of Rh^{1+} in the solid catalysts is provided not only due to coordination with NBD, but also as a result of interaction of rhodium with zeolite framework acting as a additional stabilizing ligand. That is the reason why the rhodium-containing zeolites, namely Rh/Na-ZSM-5, possess high activity and selectivity in norbornadiene cyclodimerization either in neat norbornadiene or in the presence of solvents.

References

[1] N.V. Vasil'ev, A.E. Patalakha and A.V. Buzaev. Phizicheskie i khimicheskie svoiystva norbornadiena i ego proizvodnykh (Physical and chemical properties of norbornadiene and its derivatives), Itogi nauki i tekhniki, Ser. Organicheskaya khimiya, T.23, M:VINITI, 1992, p. 149.

[2] A. Greenberg and J.F. Liebmann, Strained Organic Molecules, Academic Press, New York, 1978, p. 187.

[3] G.N. Schrauzer, B.N. Bastian and G.A. Fosselins, J. Am. Chem. Soc., 88 (1966) 4890.

[4] J.R. Thomas, US Pat. 4,094,916; 4,094,917 (1978).

[5] R.R. Schrock and J.A. Osborn, J. Am. Chem. Soc., 93 (1971) 3089.

[6] N.F. Gol'dshleger, B.I. Azbel', A.A. Grigoriev, I.G. Sirotina and M.L. Khidekel, Izv. Acad. Nauk SSSR. Ser. Khim., (1982) 635.

[7] U.M. Dzhemilev, R.I. Khusnutdinov and G.A. Tolstikov, Uspekhi khimii (Russ.), 56 (1987) 65.

[8] J.J. Mrowca and T.J. Katz, J. Am. Chem. Soc., 88 (1966) 4012.

[9] Ya.I. Isakov and Kh.M. Minachev, Sov. Sci. Rev. B. Chem., 17 (1992) 1.

[10] W.F. Hoelderich and H. van Bekkum, Stud. Surf. Sci. Catal., 58 (1991) 631.

[11] L. Scherling, J.P. Luvisi and P.V. Welch, J. Am. Chem. Soc., 78 (1956) 2819.

[12] B.I. Azbel', N.F. Gol'dshleger, Ya.I. Isakov, E.T. Epel'baum, Yu.Yu. Yampol'skii and Kh.M. Minachev, Izv. Acad. Nauk SSSR. Ser. Khim., (1986) 1238.

[13] T.V. Lomova, N.F. Meged', Ya.V. Mirsky and I.E. Neymark, Khimiya i teknologiya topliv i masel, (1982) 11.

[14] T. Yashima, Y. Ushida, M.E. Ebisawa and N. Hara, J. Catal., 36 (1975) 320.

[15] Kh.M. Minachev and E.S. Shpiro, Catalyst Surface: Physical Methods of Studing, Mir, CRC Press, Moscow, Boca Raton, FL, 1990, p. 81.

[16] E.S. Shpiro, O.P. Tkachenko, B.I. Azbel', N.F. Gol'dshleger, Ya.I. Isakov, M.L. Khidekel' and Kh.M. Minachev, Kinet. Katal., 28 (1987) 1248.

[17] J. Okamoto, N. Ishida, T. Iwanaka and S. Teranishi, J. Catal., 58 (1979) 82.

[18] N.F. Gol'shleger, B.I. Azbel' and M.L. Khidekel, Izv. Acad. Nauk SSSR. Ser. Khim., (1983) 1342.

[19] Kh.M. Minachev, E.S. Shpiro, G.V. Antoshin and O.P. Tkachenko, Izv Acad. Nauk SSSR Ser. Khim., (1984) 5.

[20] B.I. Azbel', N.F. Gol'dsheger, M.L. Khidekel, V.I. Sokol and M.A. Porai-Koshits, J. Mol. Catal., 40 (1987) 57.

[21] J. Iwasawa, T. Hayasaka and S. Ogasawara, Chem. Lett., (1983) 1342.

[22] J.R. Anderson and K. Foger, J. Catal., 58 (1979) 114.

[23] A. Rahman, S. Burelle, A. Admot, G. Lemay and S. Kaliaguine, Catal. Today, 6 (1989) 123.

[24] J. Herrero, Blanko, M.A. Esterruelas and L.A. Oro, Appl. Organomet. Chem., 4 (1990) 157.

[25] B. Denise and B. Pannietier, J. Organomet. Chem., 161 (1978) 171.

[26] N.F. Gol'dshleger, B.I. Azbel', Ya.I. Isakov, E.S. Shpiro and Kh.M. Minachev, Dokl. Acad. Nauk SSSR, 314 (1990) 378.

[27] E.W. Abel, M.A. Bennett and G.W. Wilkinson, J. Chem. Soc., (1959) 3178.