Cyclodimerization of bicyclo[2.2.1]hepta-2,5-diene in the presence of rhodium-containing zeolite catalysts

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It has been shown that norbornadiene is dimerized in the presence of rhodium-containing zeolite catalysts, forming hexacyclic [4+2]dimers preferentially. The effect of the structure and the method of preparation and pretreatment of the catalysts on their activity and selectivity in norbornadiene cycloaddition was studied. The influence of the above parameters on the change in the electronic state of rhodium in the course of the reaction was also investigated.

Key words: norbornadiene, cyclodimerization, rhodium, zeolite, catalysis, XPS.

Bicyclo[2.2.1]hepta-2,5-diene (norbornadiene, NBD) is a useful intermediate for production of various valuable organic substances such as polycyclic hydrocarbons, ingredients of highly energetic mixtures.[1,2] Norbornadiene is a homodiene. The synchronous process of [4+2]cycloaddition of NBD takes place only with strong dienophiles, *e.g.*, with tetracyanoethylene.[2] In the absence of the catalyst homo[4+2]dimers are not obtained. Cyclodimerization of NBD can be carried out in solution in the presence of catalysts, such as complexes of low-valence cobalt,[3] iron,[4] rhodium,[5,6] and other transition metals.[7] A heterogeneous catalyst, 5 % Rh/C,[8] was demonstrated to be efficient in this reaction. Four different compounds were obtained; however, the selectivity with respect to NBD hexacyclic dimers approached 70 %.

The development of efficient 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 of interest to elucidate the possibility of the use of the molecular-sieve properties of crystalline aluminosilicates (zeolites) for the preparation of products with a certain structure. In addition to shape selectivity, zeolites are able to stabilize unusual oxidation states of transition metals. For this reason, zeolites attract considerable interest as catalysts and components of various catalytic systems.[9,10]

The present work presents the results of the first study on the effect of the preparation method and pretreatment of zeolite catalysts on their activity and selectivity in cyclodimerization of NBD and the change in the electronic state of rhodium in the course of the reaction.

Experimental

Norbornadiene was distilled over sodium and stored in an evacuated ampoule at 5 °C. Freshly distilled norbornadiene was used in all the experiments. 3-Hydroxynortricyclane and its ethers were prepared as described in Refs. 11, 12.

The catalysts used were prepared using the following zeolites: NaY (molar ratio SiO_2/Al_2O_3 = 4.4), Na—TsVM (Na-pentasil, an analog of pentasil ZSM-5 synthesized without an organic template, SiO_2/Al_2O_3 = 33.3), and Na-ultrasil (an analog of pentasil ZSM-8 synthesized in the presence of tetraethylammonium bromide as a structure-forming agent, SiO_2/Al_2O_3 = 46). Decationized modifications of parent zeolites were obtained from their NH_4-forms by drying and heating in air at 500 °C for 5 h. The degree of exchange of Na^+ for H^+ is denoted by a number before H in the zeolite code. Transition metals were introduced into zeolites either by ion exchange (IE) or by impregnation (IM) of dehydrated zeolites using aqueous solutions of $Ni(NO_3)_2$, $RhCl_3$, $PdCl_2$, $[Rh(NH_3)_5Cl]Cl_2$. Ion-exchanged samples containing rhodium were prepared by a method described earlier.[13] Other catalysts were obtained by impregnation of powdery Na—TsVM, H—NaY, and alumosilicate beads filled with 16 % LnHY zeolite (AShNTs-6) calcined at 500°C with a calculated amount of aqueous solutions of $RhCl_3$ or $[Rh(NH_3)_5Cl]Cl_2$.

The samples were activated in a stream of dry air before use. When the effect of the preliminary reduction of catalysts by H_2 was studied, the respective samples were heated at 500 °C, cleared with argon at 200°C, and then treated with H_2 for 5 h. The samples to be studied by X-ray photoelectron spectroscopy (XPS) were pressed into pellets at 100 atm.

The catalysts prepared were transferred without contact with air into the ampoules, then NBD was refrozen (catalyst : NBD = 5 : 1, w/w), and the ampoules were evacuated, sealed, and heated. The reaction mixture was analyzed by GLC on a "Biochrom-1" chromatograph (5-m×3-mm column with 15 % Silicone E-301 on Chromatone N-AW-DMCS,

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200 °C, gas-carrier was nitrogen). The samples intended for XPS study were washed with NBD under anaerobic conditions and evacuated.

XPS-spectra were obtained on an ES-200B spectrometer in accordance with Ref.14. The pressed samples of rhodium-containing zeolites were either heated or treated under reaction conditions and then transferred into the XPS-spectrometer without exposure to air. The binding energies were corrected using C1s (E_b = 285 eV) and Si2p (E_b =103.8 eV) photoelectron lines. The atomic ratios 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 Rh3d level for Rh-containing zeolites was carried out on a PDP II/03L minicomputer using a program for the synthesis of Gaussian peaks. The intensity ratio $Rh3d_{5/2}/Rh3d_{3/2}$, the spin-orbit splitting, and the halfwidth on halfheight (HWHH) of the $3d_{5/2}$ and $3d_{3/2}$ components upon deconvolution were kept the same as in Rh 3d spin doublets of individual rhodium compounds.[15] The accuracy of the determination of E_b was ±0.2 eV; the accuracy of the atomic ratios and the parameters of the unresolved lines was 10—20 %.

Results and Discussion

1. Some regularities of norbornadiene cyclodimerization in the presence of zeolite catalysts

Investigation of NBD conversion with different zeolites obtained either in Na- or in H-form and then modified with transition elements such as Rh, Pd, or Ni, showed that in the absence of reducing agents only Rh-containing samples acted as catalysts in NBD cyclodimerization within a wide temperature range (30—200 °C) both in neat norbornadiene and in the presence of various solvents. As seen from Table 1, NBD dimers 1—3 are formed in this reaction (Scheme 1): products of [4+2]cycloaddition of NBD are mainly observed, viz., hexacyclic dimers, exo-endo- and endo-endo-hexacyclo[9.2.1.0^{4,6}.0^{3,8}.0^{2,10}.0^{5,9}]tetradec-12-enes **1** and **2**, respectively.

Scheme 1

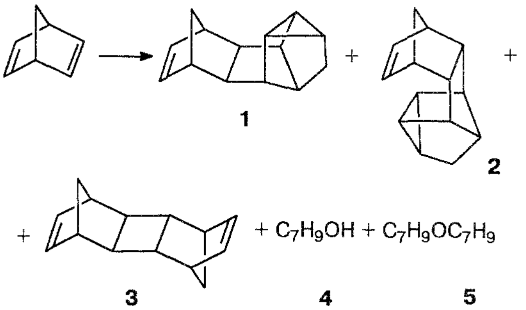

Table 1. Catalytic properties of rhodium-containing zeolites in norbornadiene cyclodimerization

Entrie	Catalyst (SiO_2/Al_2O_3 mol/mol)	Method of preparation	K_{NBD} (%)	A	Distribution of products (%)					S(%)
					1	2	3	4	5	
1	0.3%Rh/Na-pentasil (33.3)	IE	16.8	127.0	83.0	13.0	1.0	1.0	2.0	96.0
2	0.7%Rh/Na-pentasil (33.3)	IE	7.0	23.0	75.0	8.9	2.1	5.7	8.3	84.0
3	0.7%Rh/Na-pentasil* (33.3)	IM	4.0	30.0	82.0	17.0	1.0	Traces		99.0
4	2%Rh/Na-pentasil (33.3)	IM	9.0	11.6	87.2	12.5	0.2	Traces		99.0
5	0.5%Rh/H-pentasil (33.3)	IE	6.8	35.8	77.0	12.0	1.5	5.7	2.8	90.0
6	0,5%Rh/0.63HNa-ultrasil(46)	IE	3.5	17.0	76.0	10.0	4.0	5.0	5.0	86.0
7	0.5%Rh/HNaY** (4.4)	IM	2.4	10.0	28.5	6.8	2.7	37.0	25.0	34.0
8	0.5%Rh/AShNTs-6	IM	2.9	8.0	83.4	11.6	1.3	Traces		95.0
9	0.5%Rh/H-pentasil*** (33.3)	IE	6.4	22.0	44.0	8.6	1.4	36.0	10.0	52.0

Note. K is the total conversion of NBD; A is the catalyst activity (mol dimers/g-atom Rh h); S is the selectivity calculated from hexacyclic dimers **1** and **2**; IE is ion exchange; IM is impregnation. Pretreatment conditions: air, 500 °C, 5 h; reaction conditions: evacuated ampoule, 130 °C, 1 h.

* Catalyst was pressed into a pellet.

** Catalyst was prepared by impregnation of zeolite with $[Rh(NH_3)_5Cl]Cl_2$, all other samples were prepared by using $RhCl_3$.

*** Pretreatment temperature is 300 °C.

Effect of the structure and composition of the zeolite. The distribution of the NBD conversion products and their yields depend on the structure and chemical composition of the zeolite (Table 1). The highest yields of cyclodimers were observed in the presence of samples prepared from the sodium form of pentasil. If samples containing both rhodium and acid sites were used, the formation of dimers **1**—**3** was accompanied by formation of the oxygen-containing products alcohols **4** (3-hydroxynortricyclane and 3-hydroxynorborneol) and ethers **5** (3-(tricyclo[2.2.1.0^{2,6}]heptyloxy-3')bicyclo[2.2.1]hept-5-ene and 3.3'-oxydinortricyclane). These compounds can be obtained as a result of norbornadiene hydration with water retained in zeolite after its pretreatment. Subsequent addition of the alcohols formed to NBD or dehydration of the alcohols gives rise to ethers. Interaction of NBD with acid forms of the parent zeolites that contain no rhodium, among them pentasil, was previously shown to result in the formation of alcohols and ethers only.[16] Rhodium introduced into H-pentasil suppresses acid-catalyzed reactions of norbornadiene; norbornadiene cyclodimerization becomes the main reaction pathway. However, 0.5%Rh/H-pentasil catalyst exhibits significantly lower activity in cyclodimerization of NBD than 0.3%Rh/Na-pentasil. The preferential formation of oxygen-containing compounds in the presence of 0.5%Rh/HNaY is likely to be due to a higher concentration of acidic sites in the zeolite and a large quantity of adsorbed water retained by the samples after their pretreatment. This is not the case with pentasil, which is known to be a rather hydrophobic zeolite. The effect of adsorbed water on the acid-catalyzed conversion of NBD was confirmed by an experiment in which the temperature of 0.5%Rh/H-pentasil pretreatment was decreased from 500 °C to 300 °C. In this case the selectivity with respect to hexacyclic dimers decreased from 90 % to 52 % (Table 1, entries 5 and 9, respectively).

Effect of rhodium content. With increase in the rhodium content in the catalysts obtained *via* both ion exchange and impregnation the catalytic activity decreases (Table 1). It should be noted that oxygen-containing products were almost absent if cation-exchanged 0.3%Rh/Na-pentasil and impregnated samples of various compositions were used. At the same time, detectable amounts of alcohols and ethers appear in the presence of ion-exchanged 0.7%Rh/Na—TsVM. In this case the decrease in the selectivity toward hexacyclic dimers of NBD could be attributed to the formation of acidic sites as a result of decomposition of water molecules on rhodium ions during zeolite catalyst activation.

Effect of pretreatment temperature. The influence of the conditions of pretreatment of a catalyst on the distribution of products of NBD conversion and the yield of hexacyclic dimers **1** and **2** were investigated using 0.3%Rh/Na-pentasil as an example (Table 2). At a low temperature of sample pretreatment (T_{pr}) the concentration of dimers in the reaction mixture is not high. In this case, the selectivity toward hexacyclic dimers **1** and **2** amounts to 60 % and the reaction mixture contains a large quantity of oxygenated compounds. As T_{pr} increases, the yield of dimers grows, whereas that of alcohols and ethers decreases. Similar data were also obtained in the case of 0.5%Rh/Na—TsVM catalyst (Table 1, entries 5 and 9). At 500° C, which is the optimum T_{pr} for 0.3%Rh/Na—TsVM catalyst, the latter was found to exhibit high activity and selectivity in norbornadiene cyclodimerization. The extreme dependence of the catalyst activity on T_{pr} is probably associated with a change in the content and state of water, which not only can be involved in a side reaction of norbornadiene hydration but also influences the state of rhodium and the adsorption capability of the catalyst. Deactivation of the catalyst at T_{pr} = 900 °C is associated with a change in the state of rhodium and its localization at zeolite crystal sites not accessible by NBD rather than with pentasil structure destruction.

Effect of solvents. It was shown that some solvents such as acetone, acetonitrile, DMSO, and morpholine completely inhibit cyclodimerization of NBD catalyzed by 0.3%Rh/Na-pentasil. On the contrary, the catalyst activity increases somewhat in ethanol and approaches a

Table 2. Effect of the pretreatment temperature for 0.3%Rh/Na—TsVM catalyst prepared by ion-exchange on the distribution of the products of norbornadiene conversion

T_{pr} /°C	K_{NBD} (%)	[**1** + **2**] mol L^{-1}	A*	Products (%)					S (%)
				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	Traces	—	—	—	Traces		—	—	—

Note. Pretreatment conditions: catalyst was heated in a stream of dry air for 2 h at the temperature indicated; reaction conditions: evacuated ampoule, 130 °C, 1 h.

* A/(mol dimers/g-atom Rh h).

Table 3. Effect of solvents on cyclodimerization of norbornadiene in the presence of 0.3% Rh/Na—TsVM

Solvent	K_{NBD} (%)	A*	Products (%)		
			1	2	3—5
Ethanol	16.5	140.0	83.0	15.0	2.0
Ethanol**	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

Note. Pretreatment conditions: air, 500 °C, 5 h; reaction conditions: evacuated ampoule, 130 °C, 1 h, [NBD] = 3.3 mol/L. No rhodium was detected using atomic absorption spectroscopy.
* A/(mol of dimer/g-atom Rh h).
** Reaction time is 3 h.

maximum conversion of about 50 % in 3 h, the selectivity by hexacyclic dimers being about 97 % (Table 3). C_3—C_4 alcohols exhibited the same effect. For comparison, ethanol and acetone were the best solvents for norbornadiene dimerization in the presence of $[Rh(O_2CCF_3)NBD)]_2$ or $Rh_2(O_2CCF_3)_4$ complexes[6,17] (in this case, the catalytically active mononuclear Rh(I) complex was formed; morpholine also inhibited cyclodimerization of NBD). The effect of the solvent properties on the yield and distribution of NBD cyclodimers was associated with the change in the structure of the catalytically active form of Rh(I): formation of the cationic, mono- or binuclear Rh(I) complex.

In the case of zeolite catalysis, the solvent, *e.g.*, acetone, may not only participate in the formation of the active form of rhodium, but also be competitive with NBD for the adsorption sites at the aluminosilicate crystal for the zeolite catalyst. The retention of high catalytic activity of the samples in ethanol is probably associated with the formation and stabilization of the mononuclear Rh(I) complex attached to the zeolite matrix, which is similar to the complex formed in the reaction in solution.

Effect of pretreatment of the catalyst with hydrogen. Complexes of Rh(I) are catalytically active species in cyclodimerization of NBD in solution. Norbornadiene reduces Rh(II), initially present, to Rh(I), thus participating in the formation of the catalyst.[18] On the other hand, 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] Because of this, it was of interest to study the effect of reduction of the 0.3%Rh/Na-pentasil catalyst by H_2 on its catalytic activity and selectivity in norbornadiene cyclodimerization.

The activity of the catalyst that was reduced by H_2 at 150 °C prior to the cyclodimerization reaction was to 260 mol dimers/g-atom Rh h, which was twice that of the catalyst heated in a flow of air and in argon only (127 mol dimers/g-atom Rh h). The catalyst activity decreases as the temperature of H_2 pretreatment increases to 500 °C and can be as low as 100 mol dimers/g-atom Rh h. Therefore, one can assume that at a low temperature the initial Rh^{3+} ions are mainly reduced to the Rh^{1+} state, which is probably catalytically active. At a higher reduction temperature (500 °C), Rh species could be reduced to Rh, and the concentration of the active sites decreases. Stepwise reduction of Rh^{3+} by H_2 was previously observed for the samples of Rh/SiO_2.[20]

$$Rh^{3+} \xrightarrow[55\ ^{\circ}C]{H_2} Rh^{2+} \xrightarrow[150\ ^{\circ}C]{H_2} Rh^{1+} \xrightarrow[500\ ^{\circ}C]{H_2} Rh^{0}$$

Effect of the coordinating ligands. It is known that the selectivity of cyclodimerization of NBD catalyzed by the homogeneous Rh(I) complex is regulated by the ligand environment of the rhodium atoms.[18] We studied the influence of various modifiers on the properties of the heterogeneous catalyst 0.3%Rh/Na-pentasil. By addition of complex-forming ligands to the reaction mixture we wanted not only to modify the catalyst to change its selectivity toward norbornadiene cyclodimers but also to elucidate whether the reaction took place on the outside surface of the catalyst or within the zeolite channels. Both 4-methylquinoline (4-MeQ) and PPh_3, which were used as the modifiers, have an effective molecular size that inhibits their easy penetration into the catalyst channels.

It was found that addition of 4-MeQ to the reaction mixture in the molar ratio 4-MeQ : Rh = 1 : 1 (calculated to all of the rhodium) reduced the catalyst activity by one-half. When the amount of 4-MeQ was increased, further, cyclodimerization of NBD was suppressed completely. It is known that $[Rh(NBD)L_2]ClO_4$ (L is a heteroaromatic amine) does not show any activity in NBD cycloaddition.[21] Therefore, it is reasonable to assume that the deactivation of the heterogeneous catalyst 0.3%Rh/Na-pentasil is associated with binding of the surface rhodium into stable complexes with 4-MeQ, and rhodium located within zeolite channels is not accessible for NBD molecules.

Modification of Rh/Na—TsVM catalyst with PPh_3 also confirmed our conclusion that the rhodium species on the surface of the zeolite crystals are the only catalytically active sites. Addition of PPh_3 to the reaction mixture (Rh : PPh_3 = 1 : 1 or 1 : 2) results in the formation of a heptacyclodimer ("binor-S"), which was also obtained in the presence of $[Rh(NBD)CF_3COO]_2$ and PPh_3, instead of hexacyclic dimers **1** and **2**. Thus, norbornadiene cyclodimerization in the presence of rhodium on the zeolite surface is similar to that in the presence of the homogeneous Rh(I) complex[18]: the addition of PPh_3 leads to a change in the reaction from $[4\pi+2\pi]$- to $[4\pi+4\pi]$cycloaddition in both cases.

2. XPS of the catalysts

The interaction of NBD with Rh-containing Na-pentasil prepared both by ion exchange and impregnation was studied by means of the XPS technique. The results obtained are presented in Fig. 1 and Table 4. In all initial samples, rhodium is present as Rh^{3+} ions with an $Rh3d_{5/2}$ binding energy of about 310 eV. As seen from the atomic ratio Rh/Si, ion exchange facilitates greater penetration of Rh^{3+} aquacomplexes into the pentasil channels (in comparison with impregnation).[14] Thermal treatment of cation-exchanged samples at 500 °C leads to a considerable decrease in the Rh/Si ratio, which indicates further Rh^{3+} cation migration into the zeolite crystals. Analysis of the values of the binding energy of $Rh3d_{5/2}$ leads to the conclusion that rhodium exists as isolated Rh^{3+} cations in ion-exchanged zeolites and that aggregates of $>Rh^{3+}-O-Rh^{3+}<$ type are present in samples obtained by impregnation.[14]

Norbornadiene reduces Rh^{3+} in pentasil efficiently. Interaction of NBD with sample 9 at 130 °C for 15 min (Table 4) results in complete conversion of Rh^{3+} to an oxidation state with an $Rh3d_{5/2}$ binding energy of 308.8 eV, characterictic of Rh(I) in individual compounds of Rh(I), particularly in the $[Rh(NBD)CF_3COO]_2$ complex (Table 4). This form of Rh also constitutes a large proportion in samples 2 and 6, NBD being a milder reducing agent than H_2. Upon prolonged treatment (1 h) of Rh-zeolites with NBD, in addition to Rh^{1+} Rh^0 is formed (30—50 %) (Fig. 1).

Reduction of rhodium with NBD is accompanied by an increase in the Rh/Si ratio and a decrease in that of Na/Si and Na/Al. This indicates reverse migration of Rh out of the cavities of aluminosilicate crystals onto the outside surface under the action of NBD. Selective formation of the Rh(I) complex stabilized by NBD and oxygen of the zeolite framework, *i.e.*, $(NBD)Rh(I)-O_{zeol}$, which is evidently located at the point of intersection of the zeolite channels, can apparently be achieved by changing the reduction conditions. Convincing evidence for Rh reduction and the formation of Rh(I) complexes attached to the zeolite is preparation of a heptacyclic NBD dimer, "binor-S," on Rh/Na-pentasil samples in the presence of PPh_3, as was observed for $[Rh(NBD)CF_3COO]_2$.[18]

On the basis of the data obtained, we may suggest the following scheme for modification of the surface layer of Rh-zeolites under the action of NBD:

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

$$Rh^{3+} + OZ^- \xrightarrow{NBD} [Rh(NBD)]^+OZ^-$$

The coordinating properties of NBD are well known.[23] By virtue of its π-acceptor properties, NBD stabilizes metals in their low-valence oxidation state and acts as a bidentate ligand in Rh(I) complexes. However, monodentate coordination of NBD can be assumed for

Table 4. State of rhodium in Rh-containing zeolites and individual complexes

No.	Sample	Method of preparation	Pretreatment	$E_b(Rh3d_{5/2})$			Atom ratios		
				Rh^{3+}	$Rh^{\delta+}$	Rh^0	Na/Si	Na/Al	Rh/Si
1	0.7%Rh/Na-pentasil	IE	Initial, hydrated	309.8	—	—	0.08	1.00	0.12
2	0.7%Rh/Na-pentasil	IE	500° C, air	310.0	—	—	0.07	1.2	0.005
3	0.7%Rh/Na-pentasil	IE	The same+NBD, 130 °C, 15 min	310.0	309.2	—	0.064	1.31	0.0043
4	0.7%Rh/Na-pentasil	IE	The same+H_2, 150 °C	310.1	308.5	307.5	—	—	0.0058
5	0.7%Rh/Na-pentasil	IM	Initial, hydrated	310.0	—	—	0.11	1.66	0.024
6	0.7%Rh/Na-pentasil	IM	500 °C, air	309.3	—	—	0.09	2.03	0.015
7	0.7%Rh/Na-pentasil		The same+NBD, 130 °C, 15 min	309.8	308.4	—	0.054	0.97	0.043
8	2%Rh/Na-pentasil	IM	Initial, hydrated	310.4	—	—	0.13	1.5	0.059
9	2%Rh/Na-pentasil	IM	500 °C, air	309.0	—	—	0.08	1.6	0.023
10	2%Rh/Na-pentasil	IM	The same+NBD, 130 °C, 15 min	—	308.8	—	0.07	1.1	0.039
11	$RhCl_3$	—	—	310.2	—	—	—	—	—
12	$Rh_2(CF_3COO)_4$	—	—	310.3	—	—	—	—	—
13	$[Rh(NBD)CF_3COO]_2$	—	—		308.8	—	—	—	—
14	Rh(metal)[14]	—	—		—	307.4	—	—	—

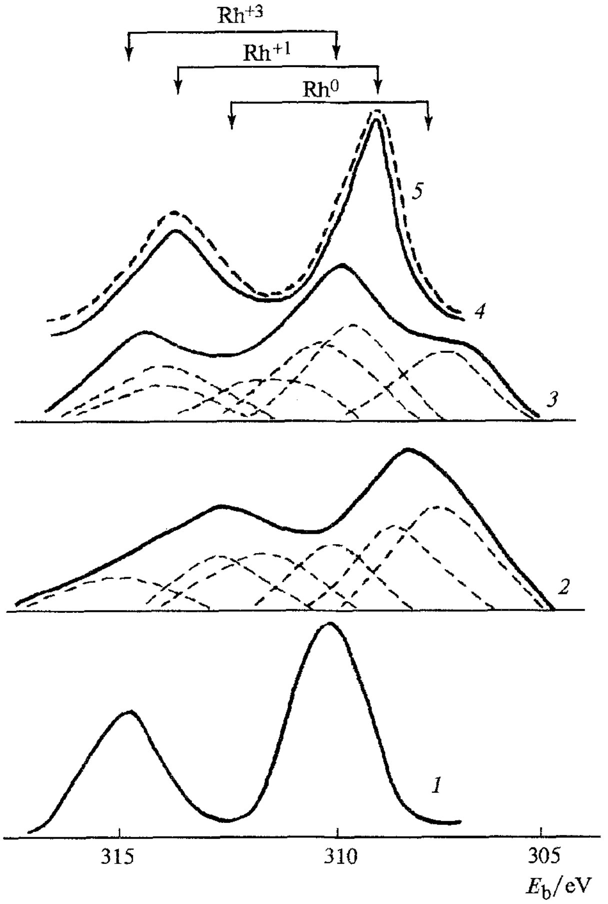

Fig. 1. XPS-spectra of the Rh 3d level for Rh-containing zeolites [ion-exchanged 0.7%Rh/Na—TsVM (*1—3*)] and impregnated 2%Rh/Na—TsVM (*4*) after respective treatment: *1*, 500 °C, air; *2*, 500 °C, air + 150 °C, H_2; *3*, 500 °C, air + 130 °C, NBD, 60 min; *4*, 500 °C, air + 130 °C, NBD, 15 min; *5*, $[Rh(NBD)CF_3COO]_2$. The dashed lines are attributed to the components obtained by simulation of spectra using PDP11/03L minicomputer.

rhodium located in the zeolite surface layer, which is possibly one of the reasons for the lower stability of the complex formed.

2. Formation of Rh^0 is a result of reduction of rhodium-zeolite by a hydrocarbon or disproportionation of rhodium cations. Zero-valence rhodium obtained by such means should apparently have high dispersion, since this is most likely to occur for samples with a low content of Rh upon low-temperature treatment.[9,19]

3. Comparison of XPS-data and catalytic activity of samples

Data on the catalytic activity of Rh(I) complexes and Rh-containing zeolites and on the concentration of Rh^{1+} in various samples are presented in Table 5. Analysis of the correlation between the concentration of rhodium in the intermediate oxidation state (extimated from the XPS spectra) and the catalytic activity of Rh-zeolite samples shows that Rh^{1+}ions in zeolite seem to be involved in the reaction just like Rh complexes. However, the merely qualitative character of this correlation indicates that it also depends on other factors. Dimer formation catalyzed by samples pretreated with H_2 at 500 °C, in which the degree of reduction of rhodium to metal approaches 100 %,[14] indicates that highly dispersed Rh^0 clusters might also form catalytically active sites. The key feature of this process might be the ability of Rh^0 to be oxidized to Rh^{1+} under the reaction conditions. In this oxidation water and non-framework oxygen might also be involved. This scenario can be realized in the formation of highly dispersed Rh particles in the course of the reaction. This is particularly likely for catalysts of low Rh content treated at a low temperature. Based on these considerations, one can explain the observed extremal dependence of the

Table 5. Comparison of the data on the concentration of Rh(I) and the catalytic activity of zeolite catalysts in cyclodimerization of norbornadiene

Catalyst	Method of preparation	Treatment of catalysts	Reaction time/h	K_{NBD} (%)	A*	$[Rh^{+1}]$**	Products (%)				
							1	2	3	4	5
0.7%Rh/Na-pentasil	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-pentasil	IM	Air, 500 °C, 5 h	0.5	4.0	30.0	51.0	82.0	17.0	1.0	Traces	
0.3%Rh/Na-pentasil	IE		0.5	8.0	64.0	36.0	84.0	14.0	1.0	Traces	
$[Rh(NBD)CF_3COO]_2$***	—		1.0	29.0	14.5	100.0	83.8	15.7	0.5	—	—

* A/(mol dimers/g-atom Rh h).

** Fraction of Rh(I) according to XPS data.

*** Reaction conditions: solvent is ethanol, [NBD] = 2.3 mol/L, [Rh] = $2.3 \cdot 10^{-2}$ mol/L, 100 °C. In the other experiments: 130 °C, 1 h, NBD : zeolite = 5 : 1 (w/w).

catalytic activity of rhodium-containing zeolites on the temperature of reduction with H_2 as well as the higher activity of 0.3%Rh/Na-pentasil catalyst compared to other samples.

It is seen from Tables 1 and 5 that catalysts with a low rhodium content produced from Na-pentasil both by ion exchange and impregnation exhibit the highest selectivity toward cyclodimers of norbornadiene. This is consistent with a higher Na/Al ratio and a less pronounced decrease in the Na^+ concentration in the surface layer of the catalyst in the course of the reaction (see Table 4). As a result, more efficient neutralization of acidic sites is possible. These acidic sites can be formed either due to decomposition of water molecules on rhodium ions or by reduction of rhodium. Consequently, the yields of products 4 and 5 decrease.

The high mobility of rhodium in the zeolite matrix, the concomitant enrichment of the surface layer with rhodium (Table 4) due to migration of Rh from the framework channels and its coordination with NBD followed by cyclodimerization of NBD on the outer surface of the zeolites did not allow the molecular sieve properties of the zeolites to change the selectivity of the rhodium zeolite catalysts studied in norbornadiene cyclodimerization.

Thus, active intermediate states of rhodium can be obtained for the zeolite-containing catalysts by their reduction with bicyclo[2.2.1]hepta-2.5-diene just as for rhodium complexes in solution. These oxidation states of rhodium are stabilized in the zeolite catalyst not only due to coordination with NBD but also as a result of interaction of rhodium with the zeolite matrix acting as an additional stabilizing ligand. That is the reason why rhodium-containing zeolites, namely Rh/Na-pentasil, are active and selective catalysts of norbornadiene cyclodimerization either in neat norbornadiene or in the presence of solvents.

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