Reductive Dimerization and Oligomerization of Alcohols, Ketones, and Aldehydes to Hydrocarbons on a Promoted, Fused Iron Catalyst

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Abstract—A new reductive dimerization and oligomerization reaction of (C_5 and C_6) cycloalkanols and cycloalkanones, benzaldehyde, and benzyl alcohol to hydrocarbons containing as many, or more, carbon atoms as the reactant oxygenated compound on a promoted, fused iron catalyst proceeds at a temperature of 250–350°C, a hydrogen pressure of 0.1–1 MPa, a specific feed rate of oxygenated reagent of 80–320 g $h^{-1}kg^{-1}$Ct, and a hydrogen space velocity of 1×10^3 to 20×10^3 h^{-1}. Possible reaction mechanisms have been considered.

Reduction of carbonyl compounds and alcohols with hydrogen in the presence of various heterogeneous catalysts involves H_2 addition to the C=O bond to form alcohols or hydrogenolysis of the C–OH or C=O bond to form hydrocarbons [1–4]. For preparative synthesis and structural analysis in organic chemistry, the hydrodeoxygenation (HDO) reaction of carbonyl compounds and alcohols to hydrocarbons is used:

$$R-\overset{O}{\overset{\|}{C}}-R^1 \xrightarrow{+H_2} R-\overset{OH}{\overset{|}{C}H}-R^1 \xrightarrow[-H_2O]{+H_2} RCH_2R^1$$
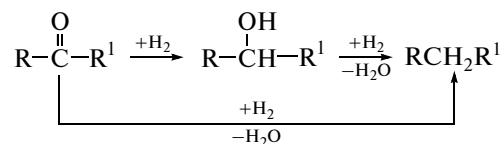
This reaction on an iron catalyst at a temperature above 550°C and a 20 MPa pressure was first observed by Ipatiew [5]. Later, it was found that aliphatic and alicyclic alcohols, aldehydes, and ketones are qualitatively converted to corresponding hydrocarbons, preserving their skeleton, on a reduced promoted, fused iron catalyst (RPFIC) at a temperature of 250–350°C, a hydrogen pressure of 0.1–0.3 MPa, and a hydrogen: substrate ratio of 100 [6, 7].

In some experiments with cyclopentanol and cyclohexanol during a search for optimal conditions of the HDO reaction on the RPFIC, the reaction products along with the anticipated hydrocarbons cyclopentane and cyclohexane were found to contain condensation products, such as cyclopentylcyclopentane and cyclohexylcyclohexane and even heavier hydrocarbons, byproducts of the reductive oligomerization reaction [8–13].

The reductive dehydration of aliphatic alcohols and their mixtures with cyclopentanol yielding saturated hydrocarbons in the presence of polymetallic iron-containing systems was considered in [12–15].

The objective of this work was to study in detail this reaction in the alcohol, aldehyde, and ketone series on reduced promoted, fused iron catalysts.

EXPERIMENTAL

The reaction of the oxygenated compounds with hydrogen was carried out in a catalytic fixed-bed flow reactor with or without hydrogen circulation, wherein the products were recovered with cooled receiver-separators [8]. The RPFIC samples taken for examination were prepared from different kinds of magnetite with various promoters. The reactions were carried out in the temperature range of 250–350°C at a hydrogen pressure of 0.1–1 MPa, a specific oxygenated-reactant feed rate of 80–320 g h^{-1} kg^{-1}Ct, and a hydrogen space velocity of 1×10^3–20×10^3 h^{-1}.

A magnetite mixture (Table 1) with a promoter (V_2O_5 or others) was fused in a water-cooled crucible lined with kaolin and asbestos. Electric-arc melting was conducted using cooled copper electrodes at 1500–1600°C for 60–120 s. The alloy was crushed, and its 2–3-mm fraction was reduced with H_2 at 450°C, 5 MPa for 10–12 h. The degree of catalyst reduction was monitored by measuring the amount of water released. The finished RPFIC contained 90–95 wt % Fe° (the rest was the promoter) and had a specific surface area of 10–15 m^2/g. According to the selective adsorption and X-ray photoelectron spectroscopy data, the major part of the RPFIC surface

Table 1. Magnetites for preparation of PFRICs

Source material for magnetite	Composition, wt %													
	FeO	Fe$_2$O$_3$	Fe^0	Al$_2$O$_3$	CaO	K$_2$O	SiO$_2$	MgO	TiO$_2$	MnO$_2$	CuO	C	S	P
Armco steel	39.3	57.8	0.5	0.13	–	–	0.13	0.03	–	0.11	0.75	–	–	–
Steel 04 ZhR (TU 14-1158-75)	35.7	52.5	0.5	0.10	–	0.30	0.30	–	–	0.10	0.60	–		
Natural magnetite superconcentrate from the Lebedinskii mining and processing works*	99.5		–	0.164	0.092	0.098**	0.085	0.072	0.013	0.059	0.003	0.05	0.003	0.007
Natural magnetite superconcentrate from the Olenegorsk mining and processing works*	99.3		–	0.189	0.046	0.07**	0.154	0.054	0.023	0.062	0.002	0.023	0.003	0.002
Natural magnetite superconcentrate from the Kostomuksha mining and processing works*	99.3		–	0.155	0.055	0.067**	0.143	0.059	0.021	0.059	0.002	0.037	0.025	0.034
Natural magnetite superconcentrate (mixture)	28.7	65.1	–	0.2	<0.1	<0.1**	0.40	0.20	0.021	0.10	<0.10	–	–	–
Carbonyl iron, special purity grade, 13-2 (TU 6-09-3000-78)	57.5	41.7	0.6	<0.1	–	–	<0.1	–	–	–	–	–	–	–

* GOK is the mining and concentration complex. ** K$_2$O + Na$_2$O.

was coated with the promoters and the minor part was occupied by α-Fe° [16, 17, 21]. The catalyst is pyrophoric (spontaneously ignites in air); therefore, its storage and loading/unloading were in a CO$_2$ atmosphere. The RPFIC composition is given in wt % based on the unreduced sample.

Cyclopentanol, cyclohexanol, benzyl alcohol, cyclopentanone, cyclohexanone, and benzaldehyde were of the reagent grade or the analytical grade and had a purity no less than 99% after distillation.

Gaschromatographic/massspectrometric analysis was conducted on an LKB-2091 instrument at ion source and molecular-separator temperatures of 250°C, an ionization energy of 70 eV, and an emission current of 25 µA.

For GLC, a 3000 × 3 mm stainless steel column, packed with 5% Carbowax 20M or 5% SE-30 on 0.25–0.31-mm Chromaton N-AW-DMCS (carrier gas, He; flow rate, 30 mL/min; temperature programming mode from 80 to 220°C at a heating rate of 10°C/min) and a 1200 × 3 mm column packed with 5% SE-30 on 0.15–0.20-mm Chromaton N-AW-DMCS (carrier gas, N$_2$; flow rate, 30 mL/min; temperature programming from 50 to 300°C at a heating rate of 6 °C/min with final holding for 18 min).
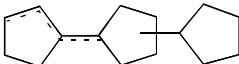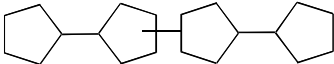
RESULTS AND DISCUSSION
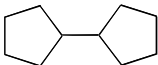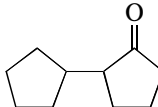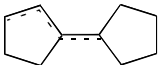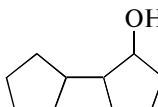
Cyclopentanol and Cyclohexanol

In [8–11, 13], we identified the following hydrocarbons and oxygenated compounds (Table 2) as the products of the reaction of cyclopentanol or cyclopentanone with hydrogen in the presence of the RPFIC.

Preliminarily, it has been found that optimal conditions for the synthesis of bi-, tri-, and polycyclic saturated fused-ring hydrocarbons from cycloalkanols are as follows: a hydrogen pressure (p_{H_2}) of 0.7 MPa, an H$_2$ space velocity of 10^3 h^{-1}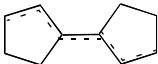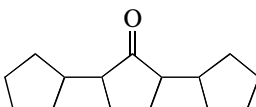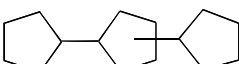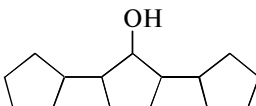, a specific cycloalkanol feed rate of 160–180 g h^{-1}kg^{-1}Ct, and a reaction temperature of 250–270°C for cyclopentanol or 300–350°C for cyclohexanol. Data on the conversion of these alcohols on various RPFICs are given in Table 3 [8–11, 13].

The data in Table 3 (run 7) show that the best results were attained on the RPFIC containing the mixture of oxides 4.7% V$_2$O$_5$ and 1% CuO as promoters. The cyclopentanol conversion on this catalyst was 99.5% and the selectivity for total bi-, tri-, and polycyclic hydrocarbons was 82%. Table 4 lists the hydrocarbons and oxygenated compounds identified among the products of the cycloxexanone reaction with hydrogen on RPFICs [8, 9, 11, 13]. It is seen from Table 5 that the cyclohexanol conversion at 350°C was

Table 2. Products of the reactions of cyclopentanol and cyclopentanone with hydrogen on RPFIC

Product number	Product	Product number	Product
I		VII	with one C=C bond
II		VIII	
III		IX	
IV	with one C=C bond	X	
V	with two C=C bonds	XI	
VI		XII	

99% and the selectivity for total bi-, tri-, and polycyclic hydrocarbons was 43% [9].

We studied the synthesis of bi- and polycyclic hydrocarbons from a cyclopentanol–cyclohexanol mixture [9]. Data on the synthesis products and their yields are given in Tables 6 and 7. It is seen from Table 7 that the alcohol mixture gives fused bi- and tricyclic hydrocarbons containing five- and six-membered rings simultaneously with a total selectivity of 18–31.5%.

Cyclopentanone and Cyclohexanone

Cyclohexanone (XXII) (about 1%) was found among the products of reductive dimerization/oligomerization reaction of cyclohexanol (Table 5). Thermodynamic calculations for the cyclohexanol–H_2 system showed that the equilibrium mixture in the temperature and reactant ratio ranges typical of the synthesis conditions (Tables 3, 5, 7) can contain up to 10% cycloalkanones. These facts suggest that one of the possible routes for the formation of bi-, tri-, and polycyclic hydrocarbons involves the conversion of cycloalkanones. In this connection, the reaction of cyclopentanone or cyclohexanone with hydrogen on various RPFICs was studied under the conditions optimal for the synthesis of fused bi-, tri-, and polycyclic saturated hydrocarbons. The results obtained are given in Tables 8 and 9 [8, 11, 13]. The data in Tables 8 and 9 show that the RPFIC containing the mixture of 4.7% V_2O_5 and 1% CuO as promoters exhibits a high selectivity for fused bi-, tri-, and polycyclic saturated hydrocarbons (conversion was 92% for cyclopentanone or 38% for cyclohexanone).

To reveal the effect of the aforesaid promoters on the selectivity of the cyclopentanone reaction with hydrogen, RPFIC specimens containing 4.7–6.0% V_2O_5 and 0.5–0.25% CuO were studied (Table 8, runs 1–7). It turned out that varying the V_2O_5/CuO ratio from 4.7/0.5 to 4.7/2.5 does not affect within the limits of experimental error the total yield of fused bi-, tri- and polycyclic saturated hydrocarbons, which was 92–95%.

The data in Tables 8 and 9 show that the products include bi- and tricyclic oxygenated compounds whose formation can be attributed to the condensation reactions of cycloalkanones. For example, the overall selectivity for oxygenated compounds on the industrial catalyst SA-1 containing 3.1% Al_2O_3 + 2.2% CaO + 0.7% K_2O as promoters was 56 or 12% in

Table 3. Synthesis of fused bi-, tri-, and polycyclic hydrocarbons from cyclopentanol and hydrogen on RPFICs ($p_{H_2} = 0.7$ MPa, hydrogen space velocity of 10^3 h^{-1}, specific cyclopentanol feed rate of 160 g h^{-1} kg^{-1} Ct)

Run no.	RPFIC promoter*	T, °C	Alcohol conversion, %	Selectivity for products**, %							
				I	II	III	IV	V	VI	VII	Σ(IX–XII)
1	Unpromoted	250	98	35	0	25	13	15	2	0	10
2	9% Al$_2$O$_3$	250	99.5	34	0	35	9	22	0	0	0
3	4.7% V$_2$O$_5$	250	99.5	38	1	40	1	19	1	0	0
4	1% Al$_2$O$_3$ + 1.5% BaO	250	99.5	27	0	12	7	36	6	6	6
5	3.1% Al$_2$O$_3$ + 2.2% CaO + 0.7% K$_2$O***	250	96	23	0	13	13	6	1	4	41
6	4.5% V$_2$O$_5$ + 3.8% BaO	250	99.5	35	3	23	5	31	1	0	2
7	4.7% V$_2$O$_5$ + 1% CuO	250	99.5	18	0	32	2	40	1	7	0
8	4.7% V$_2$O$_5$ + 1% CuO*****	270	99.5	38	0	40	3	0	19****	0	0
9	4.7% V$_2$O$_5$ + 1% CuO*****	290	99.5	47.5	0	30	2.5	0	20	0	0
10	4.7% V$_2$O$_5$ + 1% CuO*****	310	99.5	57.5	0	33	0.5	0	9	0	0

* The RPFIC composition is given on unreduced sample basis, the rest is magnetite to 100%. ** For the product numbers, see Table 2. *** The industrial ammonia synthesis catalyst SA-1, OST (Industry Standard) 6-03-78-80. ****According to ^{13}C NMR data, product VI (dicyclopentylcyclopentane) is a 4 : 1 isomer mixture of 1,2-dicyclopentylcyclopentane and 1,3-dicyclopentylcyclopentane. The spatial configuration of the isomers was not studied because of the difficulty of their chromatographic separation. *****The specific feed rate of cyclopentanol is 80 g h^{-1} kg^{-1} Ct.

the case of cyclopentanone (products IX—XII, Table 2) or cyclohexanone (products XXI and XXIII–XXV, Table 4), respectively. These values indicate enhancement of the condensing activity of RPFIC and weakening of its hydrogenating ability by introducing the promoters K$_2$O, CaO, and Al$_2$O$_3$ into the catalyst. A slight decline in the hydrogenating ability of RPFIC is also caused by addition of BaO.

A comparison of the data in Tables 3, 5, 8 and 9 show that the highest yields of fused hydrocarbons are achieved in the presence of RPFIC of the same composition. Substitution of ketone for alcohol in the reaction only results in an increase in the total yield of bi- and polycyclic hydrocarbons with five-membered (from 82 to 95%) and six-membered (from 10 to 32%) rings. These experimental facts lead to the conclusion that the synthesis of fused hydrocarbons from cycloalkanols includes the step of their dehydrogenation to corresponding cycloalkanones. In this case, the yields of hydrocarbons in the one-step gas-phase process for synthesis from cycloalkanones and hydrogen were an order of magnitude above those in the known process in which Ni/kieselguhr was used as the catalyst [18].

In order to further optimize the preparation of bi- and polycyclic hydrocarbons and completely inhibit the hydrodeoxygenation reaction of cyclopentanone to cyclopentane, the effect of high-temperature heating of RPFIC on its activity and selectivity in the cyclopentanone reaction with hydrogen was studied [8, 19].

The data presented above allow us to hypothesize the following macroscopic mechanism for preparation of fused bi- and polycyclic saturated hydrocarbons,
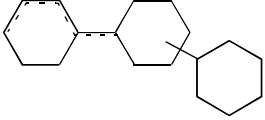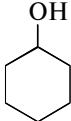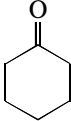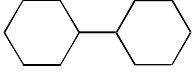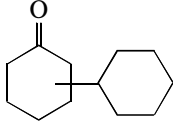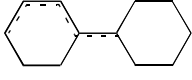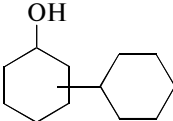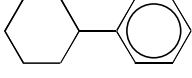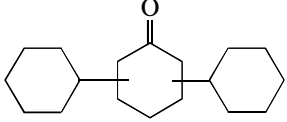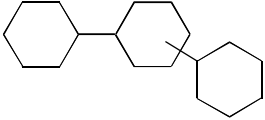
which includes parallel and/or consecutive condensation reactions of the reactant cycloalkanone to bi- and polycyclic oxygenated compounds and the hydrodeoxygenation of the latter to corresponding saturated hydrocarbons. In view of the bifunctional nature of RPFICs, which is due to the hydrogenating/dehydrogenating (metal) and acid–base (oxide promoters) surface properties of these catalysts [20, 21], it may be suggested that ketone condensation proceeds on the acid–base RPFIC sites. This assumption agrees with the published data on cyclopentanone condensation over Al$_2$O$_3$ [22]. The hydrogenation reaction presumably occurs on the hydrogenating/dehydrogenating RPFIC sites.

Along with the mechanism for the formation of fused bi- and polycyclic hydrocarbons, which includes condensation reactions on RPFICs, the alternative scheme of the conversion of aliphatic alcohols to hydrocarbons, including the formation of a carbene complex, was proposed [12, 13].

Regarding the data on the reaction of cyclopentanone with hydrogen (Table 8), it should be noted that a marked portion of the ketone does not manage to condense and undergoes hydrodeoxygenation to yield cyclopentane, a route that is probably due to quite high hydrogenating activity of the RPFIC as compared with its condensing activity.

It was assumed that one of the means by which the hydrogenating activity of RPFIC in the reductive cyclopentanone dimerization/oligomerization reaction can be lowered is the high-temperature heating of the catalyst. This idea also followed from the fact that Al$_2$O$_3$- and K$_2$O-containing RPFICs after heating in

Table 4. Products of the reaction of cyclohexanol and cyclohexanone with hydrogen on RPFIC

Product number	Product	Product number	Product
XIII	(cyclohexane)	XX	(phenyl–cyclohexyl–cyclohexyl) with one C=C bond
XIV	(cyclohexene)	XXI	OH (cyclohexanol)
XV	(benzene)	XXII	O (cyclohexanone)
XVI	(bicyclohexyl)	XXIII	O (2-cyclohexylcyclohexanone)
XVII	(cyclohexenyl-cyclohexyl) with one C=C bond	XXIV	OH (2-cyclohexylcyclohexanol)
XVIII	(cyclohexyl-benzene)	XXV	O (2,6-dicyclohexylcyclohexanone)
XIX	(cyclohexyl-cyclohexyl-cyclohexyl)		

hydrogen at 1000°C markedly decreased their activity in the synthesis from CO and H_2 [23].

Experiments were conducted on the RPFIC promoted with 4.7% V_2O_5 and 0.5% CuO; on this catalyst, the overall selectivity for fused bi- and polycyclic saturated hydrocarbons was 95%, whereas the selectivity for cyclopentane was 4.5% (Table 8, run 5). The heat treatment of the RPFIC was conducted at 600–1000°C for 2–60 min in a hydrogen flow at P_{H_2} = 0.1 MPa. The data in Table 10 clearly show that the high-temperature heating has an extremely strong effect on the RPFIC activity and selectivity [19]. The main products of the cyclopentanone reaction with hydrogen on the heated catalyst are oxygenated compounds' i.e., presumably, the products of the aldol condensation of cyclopentanone. Thus, the high-temperature heating leads to almost complete inhibition of the hydrogenating properties of the RPFIC and to the most pronounced enhancement of its condensing properties. These results indicate that the hydrogenating properties of the RPFIC can be experimentally separated from its condensing (acid–base) properties by varying the conditions of the preliminary heat treatment. It is seen from Table 10 that the high-temperature heating of the catalyst at 600–700°C leads to an increase in the selectivity for monounsaturated (with one C=C bond in molecule) fused bi- and tricyclic hydrocarbons, thereby indicating a significant inhibition of the hydrogenating properties of the catalyst.

By varying temperature of the heat pretreatment of the RPFIC, we failed to find the conditions at which

Table 5. Synthesis of fused bi-, tri-, and polycyclic hydrocarbons from cyclohexanol and hydrogen on RPFIC (p_{H_2} = 1.0 MPa, hydrogen space velocity of 10^3 h^{-1}, RPFIC composition is 4.7% V_2O_5 + magnetite to 100% on unreduced sample basis)

Run no.	T, °C	Specific feed rate of alcohol (g h^{-1} kg^{-1} Ct)	Alcohol conversion, %	Selectivity for products*, %					
				XIII	XIV	XVI	XIX	Σ(XVII, XX)	XXII
1	300	160	99.5	90	0	4	1.5	4.3	0.2
2	350	160	99	26	30	12	0	31	1.0
3	280	80	99.5	58	30	6.5	0	5.5	0

* Product numbers are given in Table 4.

the hydrocarbons alone would form, and the oxygenated compounds would be completely absent. Therefore, in order to enhance the selectivity for fused bi- and polycyclic hydrocarbons and inhibit the cyclopentanone hydrodeoxygenation reaction to cyclopentane, it was decided to use a two-layer catalyst. The first layer of the catalyst to face the cyclopentanone–hydrogen vapor–gas mixture was the RPFIC specimen treated at a high temperature, and the second layer was the catalyst that had not been subjected to the high-temperature heat treatment (Table 10, runs 7–9). Under the optimal conditions found for the reductive dimerization/polymerization of cyclopentanone, the overall selectivity for bi- and polycyclic hydrocarbons was higher than 99% (Table 10, run 7).

Reaction Routes of the Reductive Dimerization/Oligomerization of Cycloalkanones and Cycloalkanols

When considering possible routes for the reductive dimerization and oligomerization of cycloalkanones and cycloalkanols, we proceeded first of all from the composition and structure of the intermediate and final products presented in Tables 2, 4, and 6. The structures given in these tables were proved by electron-ionization mass spectrometry. However, the position of the double bond in unsaturated fused hydrocarbons IV, V, VII, XVII and XX could not be determined by this technique.

From the products of the cyclopentanone reaction with hydrogen, cyclopentylcyclopentane (III, bp 79°C/19 mmHg, d_4^{20} 0.862, n_D^{20} 1.463), dicyclopentylcyclopentane (isomer mixture) (bp 143°C/11 mmHg), and bis(cyclopentylcyclopentane) (isomer mixture) (bp 181°C/1 mmHg) were isolated using high-performance rectification [8]. The physicochemical constants of the isolated hydrocarbons were close to those reported in the literature [22, 24].

It was shown by special experiments that isolated carbonyl compounds IX and XI react with hydrogen on the RPFIC to give the same products as those formed in the reaction of cyclopentanone or cyclopentanol with hydrogen. The position of the carbonyl group relative to the cyclopentyl rings in the molecules

of IX and XI was determined using the procedure involving H/D exchange of H atoms in the α-position to the carbonyl group in a KOD-packed chromatographic column [25]. In this case, 2,5,5-trideutero-2-cyclopentylcyclopentanone (IX-D$_3$) and 2,5-dideutero-2,5-cyclopentanone (XI-D$_2$) were detected in the mass spectra. Thus, bicyclic and tricyclic ketones IX-D$_3$ and XI-D$_2$ isolated from the products contain cyclopentyl group in the α-position of the carbonyl group.

IX-D$_3$

IX-D$_2$.
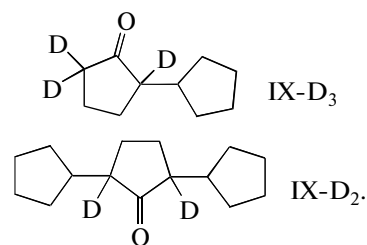
The detection of deuterium-labeled α-substituted bi- and tricyclic ketones IX-D$_3$ and XI-D$_2$ allows us to state with a high degree of confidence that in terms of the macroscopic mechanism of synthesis of fused bicyclic and polycyclic hydrocarbons on the RPFIC, the aldol condensations of the corresponding ketones is responsible for C–C bond formation in these hydrocarbons, with the condensations evidently proceeding with participation of acid–base RPFIC centers. The bicyclic and tricyclic ketones produced from cyclo-

Table 6. Products of the reactions of cyclopentanol and cyclohexanol with hydrogen on RPFIC

Product number	Product
XXVI	
XXVII	
XXVIII	

pentanone in the condensation reactions undergo further hydrodeoxygenation yielding fused bi- and polycyclic hydrocarbons. The likely routes of the formation of fused bi- and polycyclic hydrocarbons in the cyclopentanone reaction with hydrogen on the RPFIC are shown in the scheme.

The macroscopic mechanism proposed explains the formation of all fused bicyclic and polycyclic saturated hydrocarbons on RPFICs. At the same time, it should be noted that not all intermediate oxygenated compounds shown in scheme 1 could be identified among the products. Neither unsaturated ketones nor 2-(2-cyclopentyl-cyclopentylidene)-1-cyclopentanone (XXIX) from

which 1,2-dicyclopentylcyclopentane is produced were found. The fact that product XXIX was not detected suggests either a higher rate of its hydrodeoxygenation to the corresponding hydrocarbon as compared with the hydrodeoxygenation rate of tricyclic ketone XI containing the carbonyl group on the middle ring (Table 2) or that 1,2-dicyclopentylcyclopentane is produced via the mechanism other than aldol condensation. It may also be supposed that the formation of fused bi- and polycyclic hydrocarbons with six-membered rings by the cyclohexanone or cyclohexanol reaction with hydrogen follows a scheme analogous to Scheme 1.
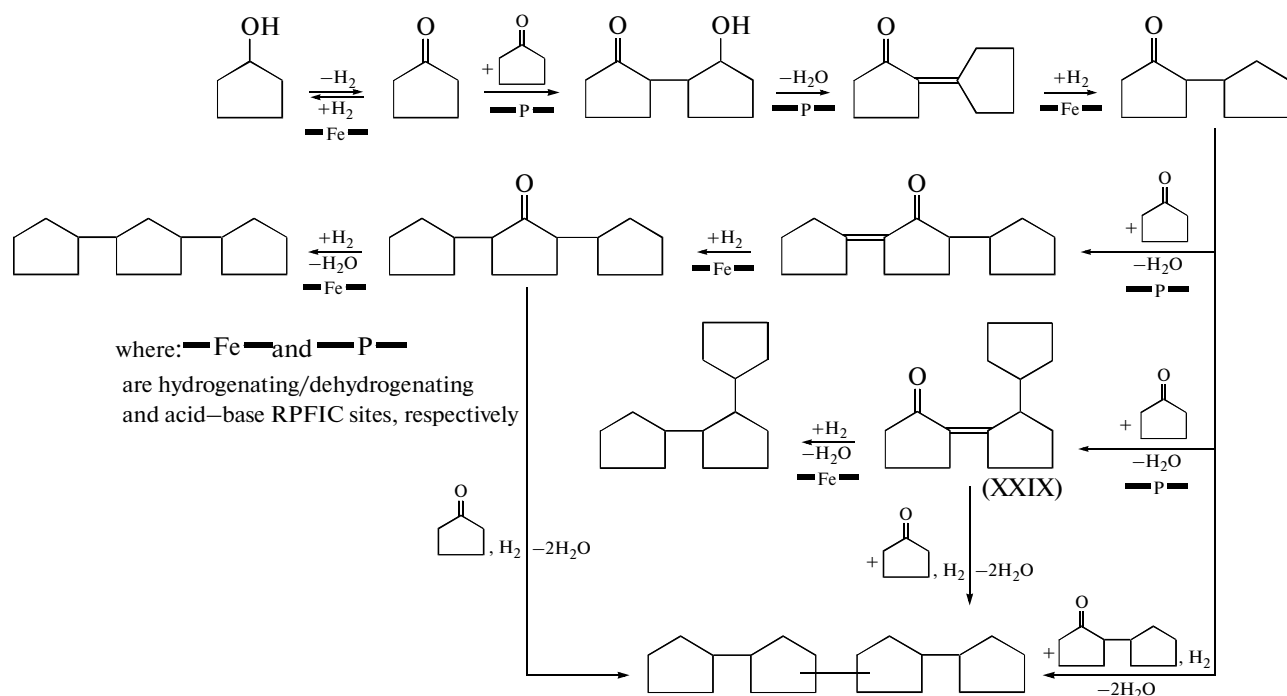
Scheme 1. Possible routes of the formation of bicyclic and polycyclic hydrocarbons in the reaction of cyclopentanone with H_2 on RPFIC.

Reductive Coupling of Benzaldehyde and Benzyl Alcohol

Unlike cyclopentanone or cyclohexanone, benzaldehyde does not contain H atoms in the α-position to the carbonyl group, and aldol condensation is not possible. At the same time, it is known that dibenzyl is produced in the reaction of benzaldehyde or benzyl alcohol with hydrogen on iron catalysts [5, 26]. On the other hand, the reductive coupling of benzaldehyde is conducted in the presence of a WCl_6-LiAlH$_4$, WCl_6 or WCl_4−BuLi metathesis reaction catalyst, resulting in *trans*- and *cis*-stilbenes, dibenzyl, and other products [27−30]. The products of the reaction of benzaldehyde with hydrogen in the presence of the RPFIC were found to include the following compounds

(Table 11) [31, 32]. Table 12 presents data on the reaction of benzaldehyde, benzyl alcohol, or related compounds with hydrogen on the RPFIC . It is seen from Table 12 that the benzaldehyde products include dibenzyl (XXXII), *trans*-stilbene (XXXIII), toluene (XXXI), benzene (XXX), 1,2,3-triphenylpropane (XXXIV), benzyl alcohol (XXXVI), and dibenzyl ether (XXXVII). From the data on the products of the benzaldehyde reaction with H_2, four possible schemes for the formation of dibenzyl (XXXII) can be proposed.

Scheme A comprises the following macrostages: benzaldehyde hydrogenation to benzyl alcohol, its dehydration to give dibenzyl ether, and hydrodeoxygenation of the ether to XXXII:

Table 7. Synthesis of fused bicyclic and tricyclic hydrocarbons from a cyclopentanol-cyclohexanol mixture and hydrogen on RPFIC ($p_{H_2} = 0.5$ MPa, hydrogen space velocity of 10^3 h^{-1}, specific feed rate of alcohol mixture is 160 g h^{-1} kg^{-1} Ct, RPFIC composition is 4.7% V_2O_5 + magnetite to 100% on unreduced sample basis)

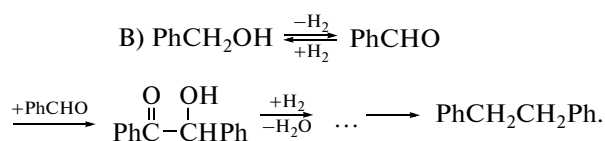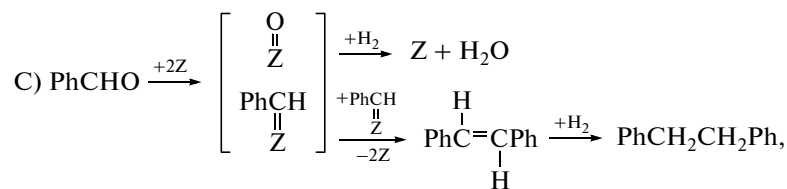| Run no.	T, °C	Cyclopentanol/cy-clohexanol ratio	Alcohol conversion, %		Selectivity for products*, %							
			cyclopen-tanol	cyclohex-anol	I	III	VI	XVI	XXVI	XXVII	XXVIII	total products with C=C bond
1	350	1 : 10	99**	99	25	20	13.5	5	15	3	0	18.5
2	300	3 : 1	99**	99	32	27	0	1	6.5	15	10	8.5

* Product numbers are as given in Tables 2, 4 and 6. ** Product composition is given on a converted-cyclopentanol basis

A) PhCHO $\xrightarrow{+H_2}$ PhCH$_2$OH

$\xrightarrow[-H_2O]{+PhCH_2OH}$ (PhCH$_2$)$_2$O $\xrightarrow[-H_2O]{+H_2}$ PhCH$_2$CH$_2$Ph.
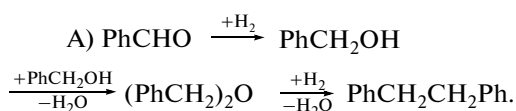
Scheme B includes the following macrostages: benzyl alcohol dehydrogenation to benzaldehyde, benzoin condensation of benzaldehyde to benzoin, and subsequent hydrodeoxygenation of benzoin to XXXII:

B) PhCH$_2$OH $\underset{+H_2}{\overset{-H_2}{\rightleftarrows}}$ PhCHO

$\xrightarrow{+PhCHO}$ PhC($\overset{O}{\|}$)–CHPh($\overset{OH}{|}$) $\xrightarrow[-H_2O]{+H_2}$ ... $\longrightarrow$ PhCH$_2$CH$_2$Ph.

Scheme C suggests the metathesis of benzaldehyde at the carbonyl group to form the surface benzylidene intermediate, its conversion to *trans*-stilbene, and hydrogenation of XXXIII to dibenzyl:

C) PhCHO $\xrightarrow{+2Z}$ $\begin{bmatrix} \overset{O}{\underset{Z}{\|}} \\ PhCH \\ \overset{\|}{Z} \end{bmatrix}$ $\xrightarrow{+H_2}$ Z + H$_2$O $\xrightarrow[-2Z]{+PhCH(\|Z)}$ PhC($\overset{H}{|}$)=CPh($\overset{}{\underset{H}{|}}$) $\xrightarrow{+H_2}$ PhCH$_2$CH$_2$Ph,

where Z is the RPFIC surface.

Scheme D includes the reaction of benzaldehyde with toluene to give XXXII:

D) PhCHO + PhCH$_3$ $\xrightarrow[-H_2O]{+H_2}$ PhCH$_2$CH$_2$Ph.
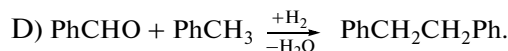
To discriminate each possible mechanism of the formation of dibenzyl, reactions with hydrogen, we studied the reduction reactions with hydrogen for dibenzyl ether, benzyl alcohol, benzaldehyde, a mixture of benzaldehyde and *p*-xylene (toluene analog in Scheme D), and *trans*-stilbene.

On the basis of the results obtained (Table 11), it can be concluded that the contribution of Scheme A to the formation of XXXII is insignificant because of a low yield of dibenzyl (less than 2%) in the reaction of dibenzyl ether with H$_2$ (Table 12, run 5).

After the reaction of the mixture of benzaldehyde and *p*-xylene, 1-phenyl-2-(4-methylphenyl)ethane could not be detected even in a trace amount, thus allowing route D to be rejected.

Benzoin in the reaction with H$_2$ (Table 12, run 6) transforms into dibenzyl in a 92% yield. However, the

products of the benzaldehyde reaction with H$_2$ were not found to contain benzoin in any of the runs. 1,2,3-Triphenylpropane (XXXIV) present in the products can be indirect evidence for the benzoin condensation reaction. Furthermore, the total rate of dibenzyl (XXXII) formation from benzaldehyde (Table 12, run 1) is approximately two times that from benzoin (run 6). All these facts suggest that not all amount of dibenzyl detected can be formed according to Scheme B.

To elucidate the feasibility of the benzaldehyde reaction with H$_2$ via Scheme C involving the intermediate formation of *trans*-stilbene, experiments were performed to detect the surface benzylidene species Z=CHPh using in situ chemical trapping during the course of the reaction. Diazomethane or D$_2$O was used as a trap. Styrene was supposed to form in the case of diazomethane:

PhCH($\overset{}{\underset{Z}{\|}}$) $\xrightarrow{+CH_2N_2}$ PhCH=CH$_2$,
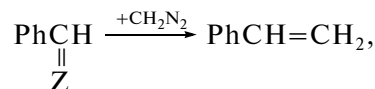
and dideuterotoluene in the case of D$_2$O

Table 8. Synthesis of fused bi-, tri-, and polycyclic hydrocarbons from cyclopentanone and hydrogen on RPFIC (hydrogen space velocity of 10^3 h^{-1})

Run no.	RPFIC promoter*	T, °C	p_{H_2}, MPa	Specific feed rate of ketone (g h^{-1} kg^{-1} Ct)	Ketone conversion, %	Selectivity for products**, %											
						I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
1	4.7% V$_2$O$_5$ + 1% CuO	250	0.8	160	99.5	7	0	35	2.5	1	50	0	4	0	0	0	0.5
2	The same	250	0.15	160	99	11	0	9	16	4	31	6	2	7	2	7.5	0.5
3	The same	300	0.15	160	99.5	18	0	9	7	6.5	20.5	3	1.5	8	0.5	21	5
4	4.7% V$_2$O$_5$ + 2.5% CuO	250	0.8	160	99.5	6	0	36.5	2.5	1.5	47.5	0	6	0	0	0	0
5	4.7% V$_2$O$_5$ + 0.5% CuO	250	0.8	160	99.5	4.5	0	42	2.5	0	46	0	5	0	0	0	0
6	4.7% V$_2$O$_5$ + 2% CuO	250	1.0	240	99.5	5.5	0	40.5	1.5	0	47	0	5.5	0	0	0	0
7	6% V$_2$O$_5$ + 2% CuO	260	0.8	205	99.5	4.5	0	41	2	0	46.5	0	6	0	0	0	1
8	4.7% V$_2$O$_5$	250	0.8	160	99.5	14	0	29	6	2	42	2	0	2	0	2	1
9	The same	280	0.3	160	99.5	6.5	0	15	5.5	6	38	3	7.5	1.5	0.5	14	2.5
10	The same	280	0.8	320	99.5	25	0	11	5	4.5	28	3	0	1	0.5	21	1
11	4.5% V$_2$O$_5$ + 3.8% BaO	250	0.8	160	99.5	19	0	30	5	0	33	0	0	0	0	9.5	3.5
12	9% Al$_2$O$_3$	250	0.8	160	99.5	35	0	35	5	3	22	0	0	0	0	0	0
13	Unpromoted	250	0.8	160	96	39	0	11.5	19.5	8	12	1	0	4	3	2	0
14	3.1% Al$_2$O$_3$ + 2.2% CaO + 0.7% K$_2$O***	250	0.8	160	93	18	0	7	6	2	6	0	5	9	5	29	13
15	1% Al$_2$O$_3$ + 1.5% BaO	250	0.8	160	93	10	0.5	14.5	9.5	1	36	7	8	1.5	1	7	4

* The RPFIC composition is given on unreduced sample basis, the rest is magnetite to 100%. ** Product numbers are as given in Table 2. *** The industrial ammonia synthesis catalyst SA-1, OST 6-03-78–80.

Table 9. Synthesis of fused bi-, tri-, and polycyclic hydrocarbons from cyclohexanone and hydrogen on RPFIC (hydrogen space velocity is 10^3 h^{-1})

| Run no. | Catalyst* | T, °C | p_{H_2}, MPa | Specific feed rate of ketone (g h^{-1} kg^{-1} Ct) | Ketone conversion, % | Selectivity for products**, % | | | | | | | | | | | |
						XIII	XIV	XV	XVI	XVII	XVIII	XIX	XX	XXI	XXIII	XXIV	XXV
1	4.7% V$_2$O$_5$	300	1.0	160	99.5	20.5	29	18	24	0	0	7	0	1.5	0	0	0
2	The same	350	1.0	160	99.5	24.5	34	9	19	5.5	3.5	4.5	0	0	0	0	0
3	4.7% V$_2$O$_5$ + 1% CuO	300	0.8	160	99.5	23	22	17	29	0	0	9	0	0	0	0	0
4	6% V$_2$O$_5$ + 1% CuO	350	1.0	200	99	21.5	22.5	18.5	28.5	0	0	9	0	0	0	0	0
5	3.1% Al$_2$O$_3$ + 2.2% CaO + 0.7% K$_2$O***	300	0.8	160	93	22	6	0.5	13.5	13.5	1	2.5	3	26	5.5	2	4.5

* The RPFIC composition is given on unreduced sample basis, the rest is magnetite to 100%. ** Product numbers are as given in Table 4. *** The industrial ammonia synthesis catalyst SA-1, OST 6-03-78-80.

Table 10. Synthesis of fused bi-, tri-, and polycyclic hydrocarbons from cyclopentanone and hydrogen on the thermally treated RPFIC (p_{H_2} = 1.0 MPa, hydrogen space velocity of $10^3\ h^{-1}$, RPFIC composition is 4.7% V_2O_5 + 0.5% CuO + magnetite to 100% on unreduced sample basis)

Run no.	Catalyst heating temperature, °C	Heating time, min	Synthesis temperature, °C	Specific feed rate of ketone (g h⁻¹ kg⁻¹ Ct)	Ketone conversion, %	Selectivity for products*, %											
						I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
1	1000	60	220	100	75	0	0	0	11	0	4	1.5	0	27.5	39	8	10
2	1000	2	220	100	80	0	0	0	7.5	0	3	1	0	17	9	54	8.5
3	700	2	220	100	98	0	0	1	11	0	33	1	0	5	0	48	1
4	650	10	300	100	99.5	1	0	3	33	0	48	6	1	1	0	1	6
5	600	10	300	100	99.5	1	0	1	41	0	49	4	2	0	0	0	2
6	600	2	300	100	99.5	6	0	4	46	0	34	5	2	0	0	0	3
7	700**	2	250	84	99.5	0	0	19	17	0	59	1	4	0	0	0	0
8	800**	4	250	108	99.5	0	0	20	16	0	61	0	3	0	0	0	0
9	1000**	8	250	170	99.5	1	0	21	21	0	52	4	2	0	0	0	0

* Product numbers are as given in Table 2. ** Subjected to high-temperature heating was the upper half of the RPFIC-bed.

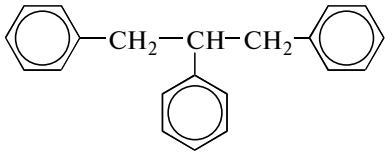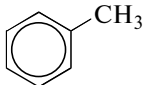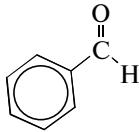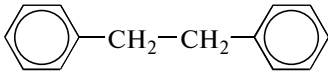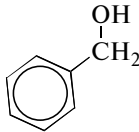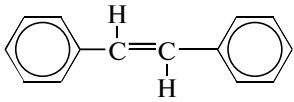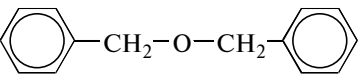$$PhCH \xrightarrow[Z]{+D_2O} PhCHD_2 + H_2O.$$
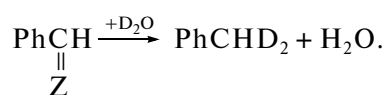
The products were analyzed using the GC–MS technique; but neither styrene nor dideuterotoluene was detected among the products of the benzaldehyde reaction with H_2.

At the same time, the admixture of D_2O lowered the benzaldehyde conversion from 72% (Table 12, run 1) to 47% (Table 12, run 3), the selectivity for dibenzyl from 32 to 4% (by a factor of 8), and the selectivity for *trans*-stilbene from 6 to 0.1% (by a factor of 60); the selectivity for toluene remained almost unchanged, being 60 to 64.8%, respectively. If dibenzyl resulted from the hydrogenation of *trans*-stilbene, the selectivity for XXXII and XXXIII in the run with $D_2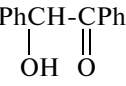O$ would decrease to equal extents, an outcome that is inconsistent with the data of Table 12. Probably, *trans*-stilbene is produced from benzaldehyde according to scheme C and dibenzyl forms according to scheme B. Note that a special experiment showed that *trans*-stilbene is quantitatively hydrogenated with hydrogen on the RPFIC. Therefore, dibenzyl in the reaction of benzaldehyde with H_2 can be partially produced as a result of *trans*-stilbene hydrogenation.

All of the above data on Reductive Dimerization and Oligomerization of cycloalkanones, cycloalkanols, benzaldehyde, and benzyl alcohol to fused hydrocarbons on the RPFICs are difficult to explain in terms of only intermediate condensation reactions (aldol and benzoin condensations). Obviously, a certain amount of hydrocarbons and oxygenated compounds in the presence of the RPFIC is produced via other mechanisms. The examined reactions of reductive dimerization and oligomerization of carbonyl

Table 11. Products of the reactions of benzaldehyde, benzyl alcohol, and related compounds with hydrogen on RPFIC

Product number	Product	Product number	Product
XXX	(benzene ring)	XXXIV	$Ph-CH_2-CH(Ph)-CH_2-Ph$
XXXI	$C_6H_5-CH_3$	XXXV	$Ph-CHO$
XXXII	$Ph-CH_2-CH_2-Ph$	XXXVI	$Ph-CH_2-OH$
XXXIII	$Ph-CH=CH-Ph$	XXXVII	$Ph-CH_2-O-CH_2-Ph$

Table 12. Products of the reactions of benzaldehyde, benzyl alcohol, and related compounds with hydrogen on RPFIC (hydrogen space velocity of 10^3 h^{-1}, RPFIC composition is 5.0% V_2O_5 + magnetite to 100% on unreduced sample basis)

Run no.	Starting substrate (SS)	T, °C	p_{H_2}	p_{SS}	Specific feed rate of SS (g h^{-1} L^{-1} Ct)	Hydrogen space velocity, h^{-1}	SS conversion, wt %	XXX	XXXI	XXXII	XXXIII	XXXIV	XXXV	XXXVI	XXXVII
1	PhCHO	220	96	4	240	1000	72	0	60	32	6	0.6	–	1	0.4
2	PhCHO	250	96	4	240	1000	97	1.5	82.7	15	0.1	0.1	–	0.1	0.5
3	PhCHO*	220	96	4	210	1000	47	0	64.8	4	0.1	0	–	31	0.1
4	PhCH$_2$OH	250	54	23	520	300	96	0.1	57	29	0.1	0.5	12	–	0.8
5	(PhCH$_2$)$_2$O	220	81	4	120	300	38	0	93.8	5	0.1	0	1	0.1	–
6	PhCH-CPh (OH, O)	220	50	0.7	90	1000	95	0	0.1	97.9	0	2	0	0	0

* Run with D$_2$O.

compounds and alcohols can be of interesting as methods for preparing fused-ring hydrocarbons in preparative and industrial petroleum chemistry.

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