

## Interaction Between Propylene and H<sub>2</sub>O over Ru-Co/SiO<sub>2</sub>-Catalysts of Clusters Type. Communication 2.

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### Abstract

The interaction between propylene and H<sub>2</sub>O on Ru-Co/SiO<sub>2</sub>-catalyst was studied. It was determined that the process of the water addition to olefin molecule is carried out with n-propanol, i-propanol and acetone formation. For clarification of the adsorption mechanism of propylene on Ru-Co-clusters the quantum-chemical calculation of interaction between it and Ru-Co, Ru-Ru, Co-Co clusters were carried out.

### Introduction

Ruthenium is the catalysts for many chemist reactions. It activates double C=C-bond and forms fine conditions for the process of hydrogen addition and the other reactions. We studied the Ru-containing catalysts in Fisher-Tropsch synthesis [1,2].

In this work the interaction between H<sub>2</sub>O and C<sub>3</sub>H<sub>6</sub> on Ru-Co/SiO<sub>2</sub>-catalyst was studied. The adsorption model of the propylene on Ru, Co and Ru-Co-clusters has been studied by use quantum-chemical methods.

### Experimental

The catalysts Ru-Co(1:1)/SiO<sub>2</sub> was prepared by support impregnation with mixture of RuOHCl<sub>3</sub> and Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O water solution. After impregnation the catalysts were reduced in hydrogen flow during 3 hours: at 773 K. Before the reaction C<sub>3</sub>H<sub>6</sub> + H<sub>2</sub>O the catalyst was reduced additionally in the reactor during 1 hour at atmospheric pressure and experiment temperature.

As the supports was used SiO<sub>2</sub>: S<sub>sp</sub> = 630-680 m<sup>2</sup>/g, V = 0,3-0,6 cm<sup>3</sup>/g, d<sub>p</sub> = 20-25 Å.

The mixture of propylene and argon in a 1:1 ratio was used as a reagent. The space velocity of reagents was varied within the 100-120 h<sup>-1</sup>.

The analysis of reaction products was carried out on chromatograph Zwet-100, (column 3,5-0,005 m,

filled with 10% SP-1200/1% H<sub>3</sub>PO<sub>4</sub> on 80/10 Chromosorb-R by Supelco firm) and on chromatograph LHM-8MD (column 3,5· 0,005 m, filled with Al<sub>2</sub>O<sub>3</sub> by Supelco firm).

The structure and state of Ru-Co/SiO<sub>2</sub> - catalyst were studied by electron microscopy [3,4].

The quantum-chemical calculations have been made according EH method modified by the atom-atom repulsion in Anderson's ASED MO approximation taking into account [3-8]. This method allows to find a bond length in accordance with standard parametrization [7]:

Atom	Orbital	H <sub>ii</sub> , eV	ζ	C
Ru	5s	10.40	2.080	
	5p	6.87	2.040	
	4d	14.90	5.380	0.5340
			2.300	0.6365
Co	5s	9.21	2.000	
	5p	5.29	2.000	
	4d	13.80	5.500	0.5680
			2.100	0.6060
C	2s	21.40	1.625	
	2p	11.40	1.625	
O	2s	32.30	2.275	
	2p	14.80	2.275	
H	1s	13.60	1.3	

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Calculations have been made according to cluster approximation. Minimum quantity of metal atoms have been examined, because of chemisorption is high-localized phenomenon. The M-M bond length was considered as fixed and identical to covalent radiuses sum [8].

For estimation of the EMX/PA method possibilities in the description of Co-Ru catalysts properties the comparison between dissociation energies

of M-O bond obtained in the calculation and taken from reference literature was made [9]. The results are represented in Table 1. As follows from Table the EMX/PA methods sets the dissociation energies of M-O bond ~ 2 times higher, but transmits the qualitative tendency (in this case) at change of the atom nature and numbers of oxygen atoms per metal atom. The quantum - chemical calculation are doing with Shlygina I.A.

**Table 1**

The dissociation energies of oxygen containing compounds of Co and Ru

Resulting compound	Starting compound	EMX/PA (a), kcal/mol	[9] (b), kcal/mol	(a-b)/a 100%
Ru + O	RuO	222,64	117	80
Ru + O	Ru <sub>2</sub> O	219,72	117	88
RuO <sub>2</sub> + O	Ru <sub>3</sub> O	197,38	119	66
Ru <sub>3</sub> + O	Ru <sub>4</sub> O	162,33	104,92,85	76
Co + O	CoO	155,65	88	77
H+Co(CO) <sub>4</sub>	HCo(CO) <sub>4</sub>	66,17	25	62

## Results and Discussion

The interaction between propylene and water on Ru-Co/SiO<sub>2</sub> catalyst takes place at relavety high pressure (0,9 MPa) and temperature (>573K). The conversion degree of propylene accounts for 28,7 % (Table 2). In the reaction products acetone (46,9 %), isopropyl (14,0 %) and propyl (39,1 %) alcohols are present. In the gas phase non-reacted propylene and small amounts of methane, ethane, ethylene, propane and CO<sub>2</sub> are found. The composition of forming alcohols indicates that OH'-group addition to propylene molecule realizes mainly against the Markovnikov's rule by scheme: CH<sub>3</sub>-CH=CH<sub>2</sub> + HOH → CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>OH. Simultaneous the addition of H<sub>2</sub>O to C<sub>3</sub>H<sub>6</sub> molecule realizes by the Markovnikov rule. The acetone and i-propanol were formed.

However the catalyst properties were changed after 10 h of its work. Only the acetone and i-propanol were formed. In these condition the conversion degree of propylene are 26,6-28,6%. Where the temperature are rised to 673 K the conversion of propylene increases: it are 42,2%.

The reason of this occurrence has been clarified. The investigations have shown, that at enough hard conditions of holding the reaction C<sub>3</sub>H<sub>6</sub> + H<sub>2</sub>O the

state of Ru-Co/SiO<sub>2</sub> were changing significantly: the insignificant part of ruthenium oxidized with formation of flying oxides (RuO<sub>4</sub>), ruthenium precipitated on reactor walls in the form of ruthenium mirror. With the aid of X-ray analysis and electron microscopy it has been established that before the reaction C<sub>3</sub>H<sub>6</sub> + H<sub>2</sub>O particle size on Ru-Co/SiO<sub>2</sub> - catalyst surface accounted predominantly for 10-25 Å, the aggregates to 200 Å and X-ray amorphous structures identified as Ru-Co clusters [1]. After holding the reaction the accounts of ruthenium particles on the surface diminished, their dimension increased (>>10 Å) and α-cobalt appeared. The ruthenium oxidation with flying oxides formation can run both with participation of water vapors and with participation of oxygen forming on catalyst surface during water molecules dissociation.

Thus the investigations have shown that on the surface of Ru-Co/SiO<sub>2</sub> catalyst simultaneously exist two type of active centers (clusters) able to activate propylene molecule in a different way. The centers responsible for holding the reaction C<sub>3</sub>H<sub>6</sub> + H<sub>2</sub>O against the Markovnikov's rule are the Ru-Co clusters enriched with the ruthenium.

For clarification of the adsorption mechanism of propylene adsorption on Ru-Co clusters the quantum-chemical calculations of interaction between it and

**Table 2**  
The products of reaction  $\text{H}_2\text{O} + \text{C}_3\text{H}_6$  on  $\text{Ru-Co}/\text{Al}_2\text{O}_3$

Reaction conditions		Degree of conversion of $\text{C}_3\text{H}_6$	The products, mass. %			
P, MPa	T, K		acetone	propio-haldehyde	iso-propyl alcohol	Propyl alcohol
0,9	573	26,6	46,9	trace	14,0	39,1
0,9*	573	19,7	28,7	trace	71,3	trace
0,9**	573	28,6	21,0	-	79,0	-
0,9***	673	42,2	25,8	-	74,2	-

\* - The results after the catalyst work during 10 h.

\*\* - The results after the catalyst work during 15 h.

\*\*\* - The results after the catalyst work during 10 h and then it was reduced at 673 K,  $T_{\text{react}} = 673$  K.

$\text{Ru-Co}$  ( $m=2$ ),  $\text{Ru-Ru}$  ( $m=1$ ) and  $\text{Co-Co}$  ( $m=1$ ) clusters were carried out. During the calculations it was assumed that carbon atoms of  $\text{C-C}$ -bond are situated parallel to  $\text{M-M}$ -bond (Fig. 1). The distance at which the cluster and adsorbable molecule begin to interact is determined by the nature of active center (Fig.2). The adsorption complex of propylene on monometallic ruthenium cluster more strongly connected than on cobalt one ( $\Delta E=10-15$  kcal/mol).

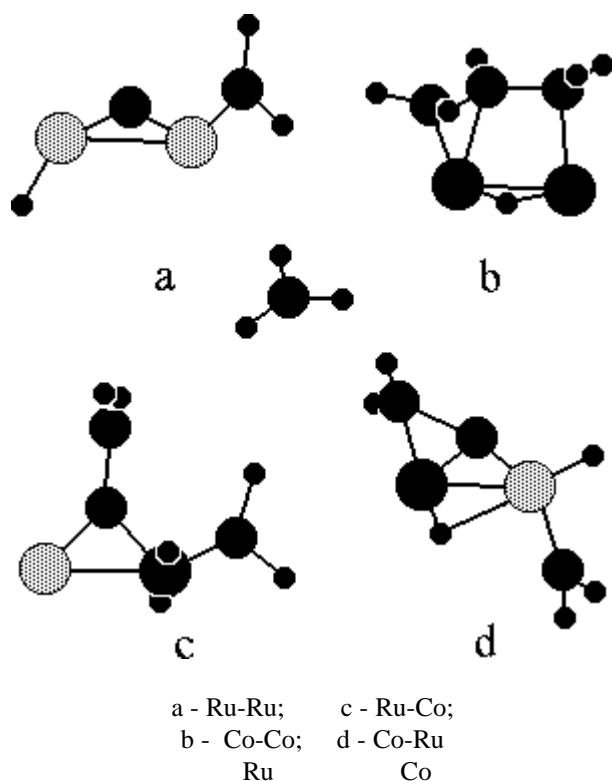


Fig 1. The result of propylene molecule geometry optimization over biatomic active centers

The bond energy of propylene with bimetallic  $\text{Ru-Co}$  centers is near to values characteristic for  $\text{Co-Co}$  centers.

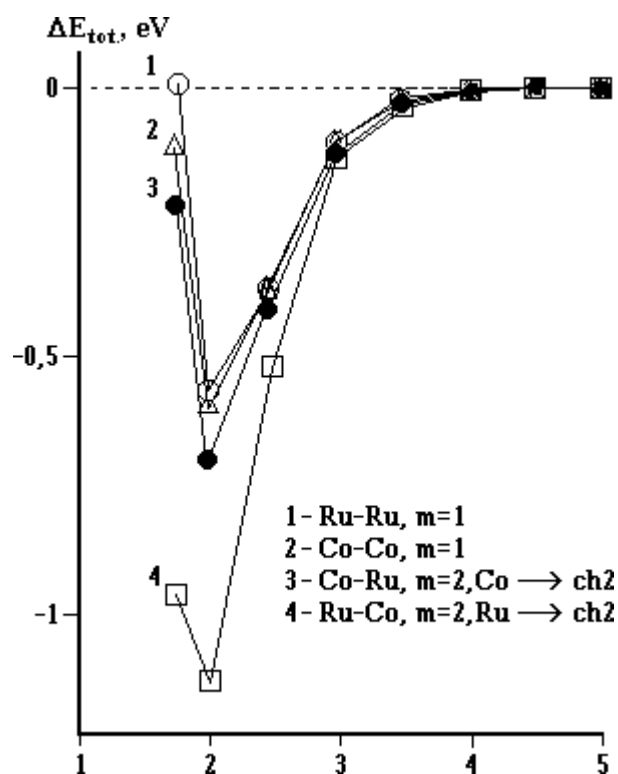
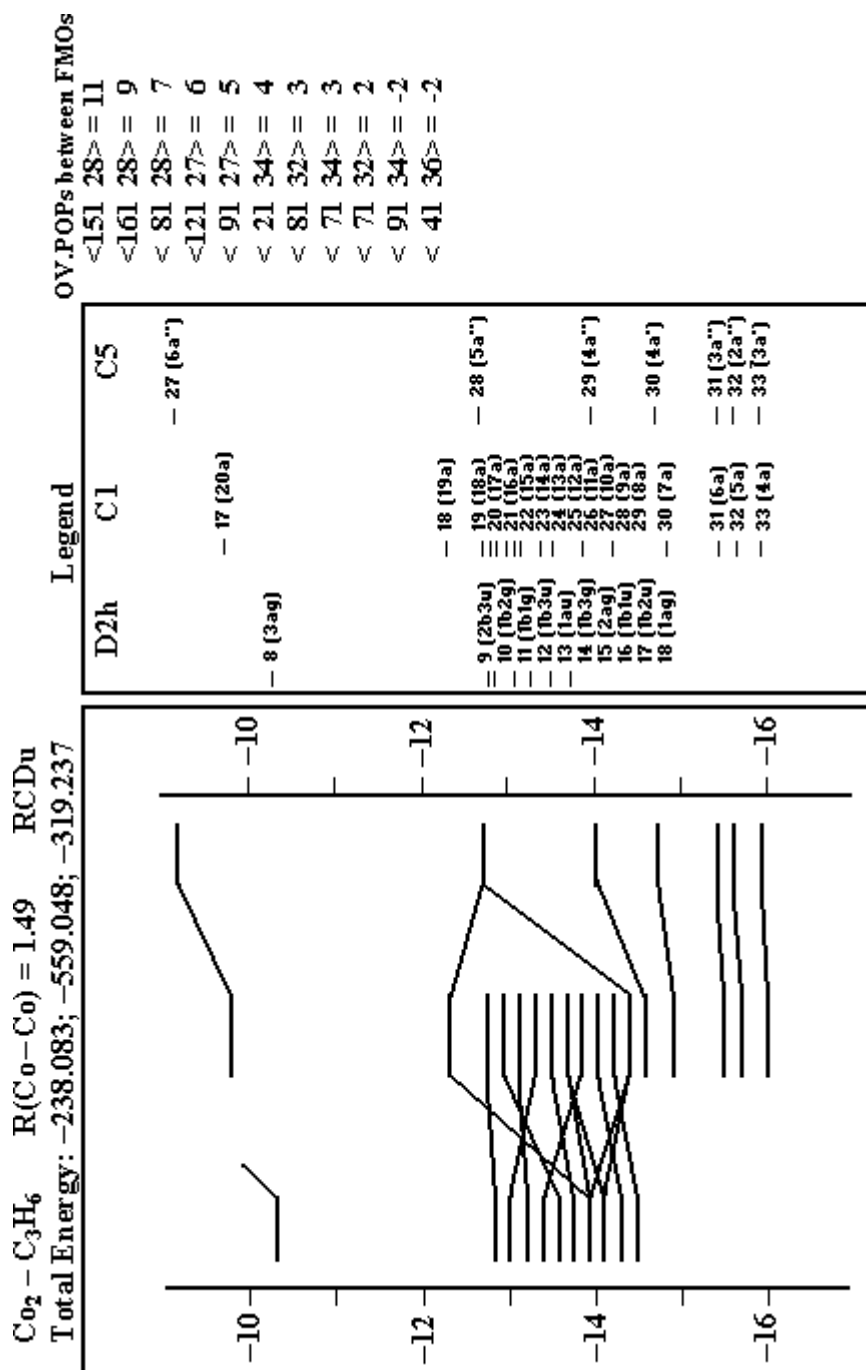


Fig. 2. The potential curve of propylene molecule approach to biatomic active center

On the Fig. 3 the diagram of interaction between fragment (1) of  $\text{Co-Co}$ -center orbitales and fragment of propylene molecule (2) with fixed structure geometry is represented. From the diagram it is follows that HOMO (high occupied molecular orbital) of propylene interacts with one of occupied cobalt orbitals forming occupied and free molecular orbitals of ad-

Fig. 3. The interaction between complex Co-Co... C<sub>3</sub>H<sub>6</sub> orbitals fragments

sorption structure Co–Co–C<sub>3</sub>H<sub>6</sub>. The deposit of HOMO of fragment (2) into occupied orbital of adsorption structure accounts for 40,0 % from two electrons and from LFMO (low free molecular orbital) - 36,0 %.

HOMO of C=C double bond has  $\pi$ -binding

character. During the interaction with Co–Co-cluster the settlement of  $\pi$ -component of propylene C=C-bond decreases. At the same time the partial electron density transfer from propylene to cobalt takes place. The weak bonds formation between C=C-bond atoms and Co–Co-cluster atoms is observed (Table 3).

**Table 3**

The overlap settlement and atomic charges in M<sub>2</sub>–C<sub>3</sub>H<sub>6</sub>

cluster	dE <sub>tot</sub> , kcal/mol	M <sub>1</sub> -C <sub>1</sub> (N)*	M <sub>1</sub> -C <sub>2</sub> (N)	q(M <sub>1</sub> ) e	M <sub>2</sub> -C <sub>1</sub> (N)	M <sub>2</sub> -C <sub>2</sub> (N)	M <sub>2</sub> -C <sub>3</sub> (N)	q(M <sub>2</sub> ) e
Co <sub>1</sub> -Co <sub>2</sub>	81,2	0,29	0,01	-0,72	0,01	0,19	0,24	-0,49
Co <sub>1</sub> -Ru <sub>2</sub>	160,8	0,32	0,23	0,08	-0,03	1,13	0,99	-1,88
Ru <sub>1</sub> -Co <sub>2</sub>	136,2	-0,02	0,77	-2,03	-0,02	0,56	0,73	0,07
Ru <sub>1</sub> -Ru <sub>2</sub>	226,3	0,76	0,87	-1,01	0,00	0,94	0,00	-1,96

\* N - Bond population

So during the interaction between propylene molecule and monometallic Co–Co-cluster the formation of weak covalent bonds between them takes place.

At the propylene adsorption on monometallic Ru–Ru-cluster the electron density transfer from HOMO and HOMO-1 of propylene to d-orbitals of ruthenium takes place (Fig. 4). The composition of two high occupied orbitals of C<sub>3</sub>H<sub>6</sub> (Fig. 4) indicates that at electrons removal from them the probability of C=C, and C–C and C–H bonds break increases. It is confirmed by the results of full optimization of propylene geometry at its adsorption on monometallic Ru–Ru-clusters: C–C-bonds break takes place.

It must be noted that in the case of interaction between propylene and bimetallic Ru–Co clusters the very complicated picture is observed: the significant electron density transfer from olefin molecule orbitals to d-orbitals of ruthenium in bimetallic Ru–Co cluster takes place (independently of that it the tertiary carbon atom adsorbs on ruthenium or cobalt atom). At the same time the olefin C–C bonds loosens substantially down to their break (Fig. 1).

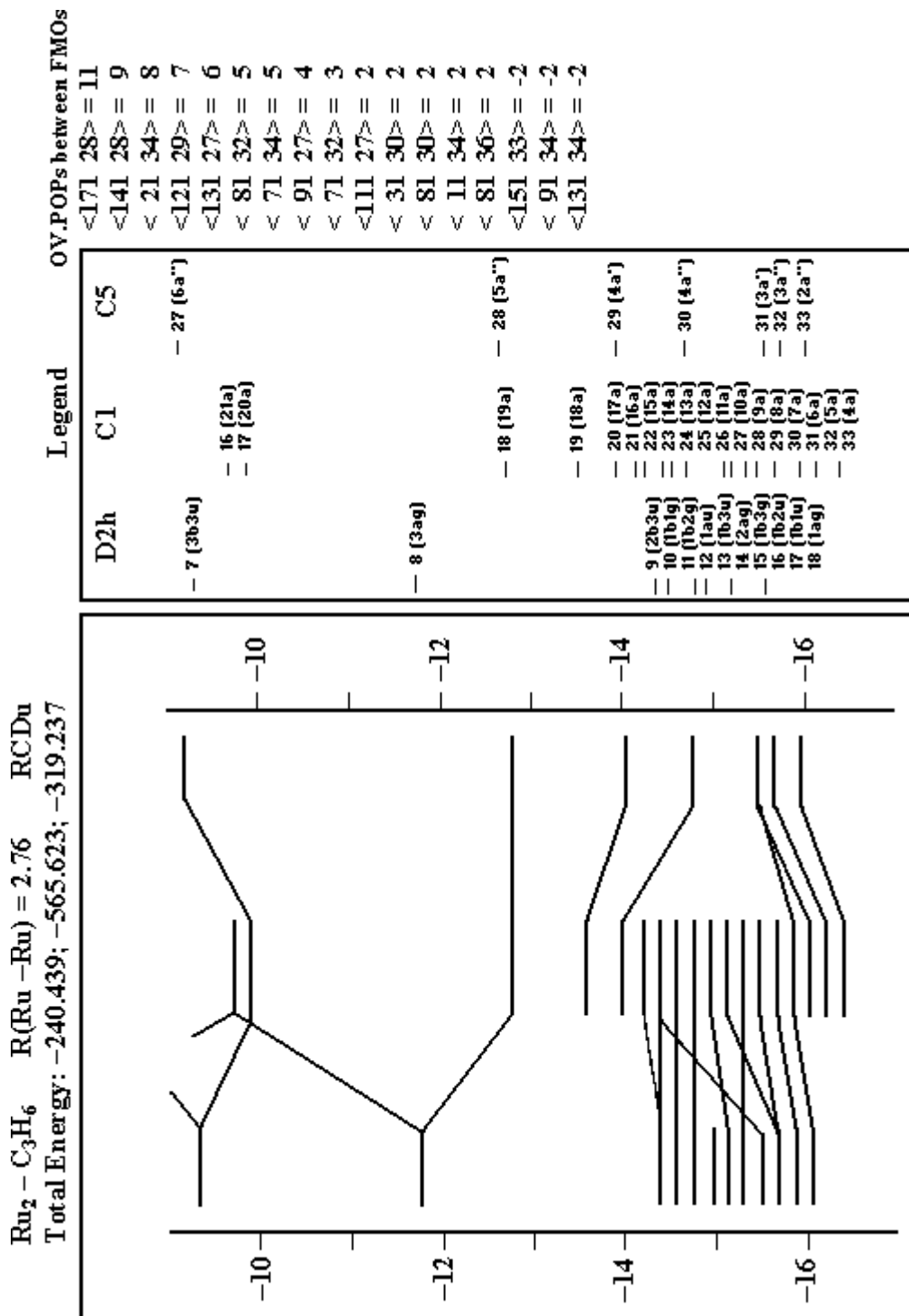
It was calculated the propylene adsorption on 4 atomic mono - and bimetallic ruthenium and cobalt clusters by quantum-chemical method. Since the formation of atomic oxygen at water hemisorption was proposed the calculations were made with

“preliminary adsorbed” oxygen taking into account. During C<sub>3</sub>H<sub>6</sub> molecule adsorption on monometallic 4Co–O cluster the weakening of C=C-bond takes place but the molecule doesn’t decay (Fig. 5). At interaction between C<sub>3</sub>H<sub>6</sub> molecule with monometallic 4Ru–O-cluster the loosening of C=C and C–C-bonds is so much that it leads to their break with C<sub>1</sub> and C<sub>2</sub>-containing structures formation.

It must be noted the at such an optimization the interaction between C<sub>3</sub>H<sub>6</sub> molecule and “preliminary adsorbed” oxygen isn’t observed, though during the calculations the oxygen atom position was optimized together with propylene geometry. As follows from the data on Fig. 6 in the structure with optimized geometry oxygen leaves deep into 4 atomic cluster.

The investigations have shown that in the presence of one ruthenium atom in bimetallic 4 atomic Ru–3Co-cluster the significant loosening (down to the break) of all the carbon-carbon bonds of olefin molecule takes place, it is illustrated by partial optimization of CH<sub>3</sub>–CH–3CoRu complex, where CH<sub>3</sub>CH-structure is situated at one of cobalt atoms (Fig. 6).

The results of quantum-chemical calculations show that the decay of the propylene molecules are possible on the Ru-containing clusters. This fact is coviaborated by the experiments. The CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> molecules are formed. On the other hand simultaneously the reactions of the direct interaction be-

Fig. 4. The interaction between complex Ru-Ru... C<sub>3</sub>H<sub>6</sub> orbitals fragment

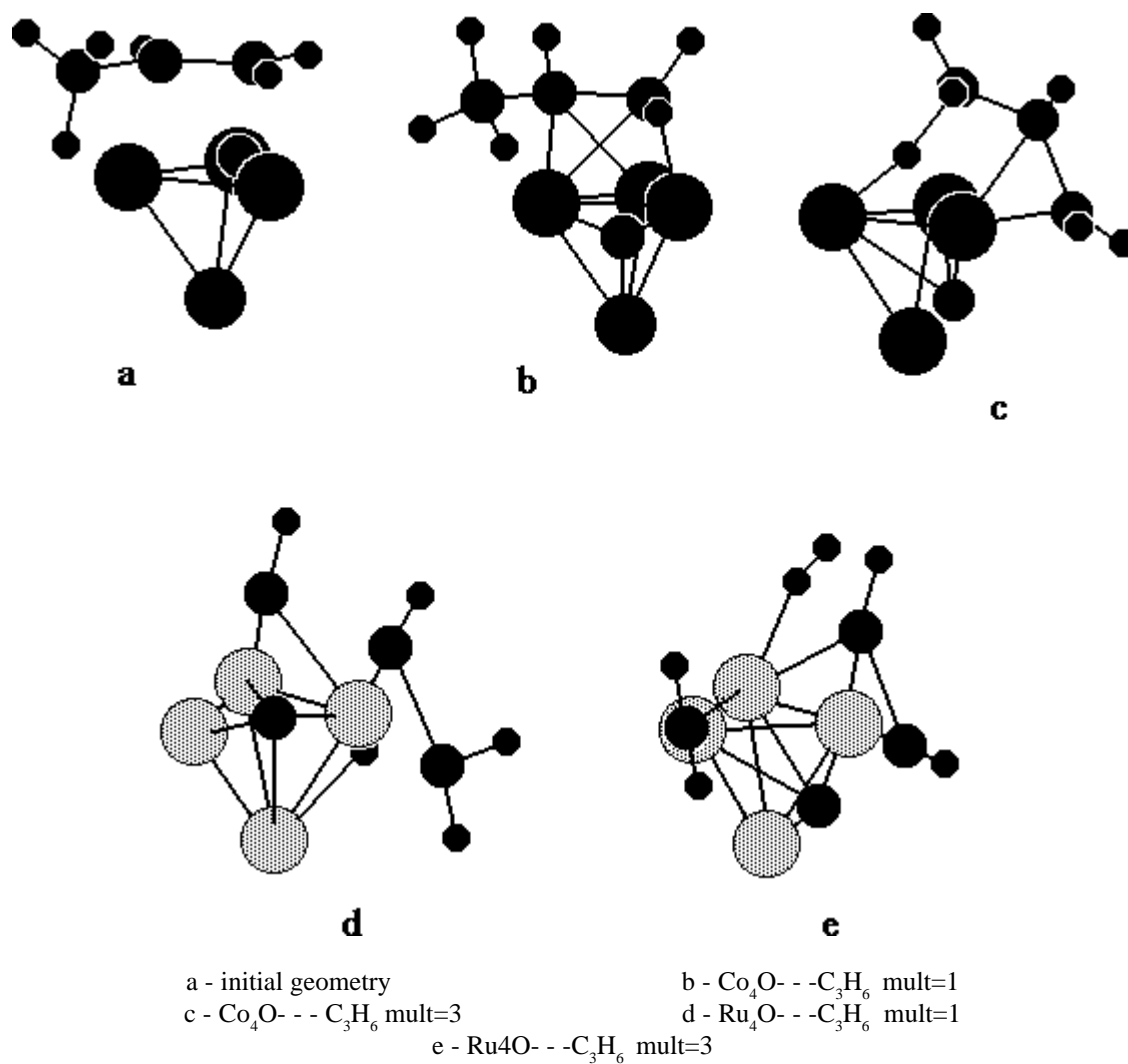


Fig. 5. The result of propylene molecule geometry optimization over tetra-atomic clusters with “adsorbed” oxygen atom

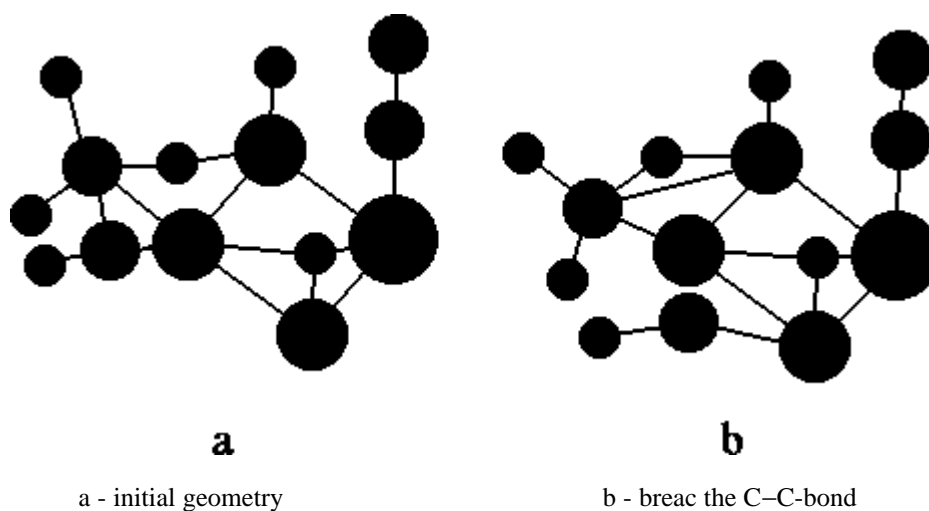


Fig. 6. The first stage of hydrocarbon “residuals”  $\text{CHCH}_3$  geometry optimization on tetra-atomic cluster  $\text{Co}_3\text{Ru}$

tween the propylene and the H<sub>2</sub>O proceeded and the n-propanol and iso-propanol are formed.

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