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CO_2 REFORMING OF METHANE ON RU- CO /AL_2O_3- CATALYST

The interaction between CO_2 and CH_4 on Ru-Co/Al_2O_3 catalysts of clusters type has be-en studied with the application of the experimental and quantum-chemical methods. The basic products of CO_2+ CH_4 interaction are C_1-C_4-alcohols and C_1-C_4-acids on Ru-Co/Al_2O_3 Quantum-chemical calculation has been shown that CO_2 and CH_4 molecule can introduce into the mono- and bimetallic Co-, Ru- and Co-Ru -clusters. Quantum-chemical accounts show that C-H bonds lengthening for "CH_4 + CO_2 + M-clusters" systems are less then ones for "CH_4+ M-clusters". However, binding energy is stronger in "M-clusters+CO_2+CH_4"-systems than ones in "M-clusters+CO_2" or "M-clusters+CH_4"

INTRODUCTION

The interaction between CO_2 and CH_4 has been proposed as one of the most promising technologies for utilization of these two gases. The molecules of the greenhouse gases CO_2 and CH_4 have very strong energies of C-O and C-H-bonds. Most of reactions involving CO_2 activation contain metal atoms as the active center. The application of multicomponent metallic supported catalytic systems supply the wide opportunities for activation of molecules and the chemical syntheses on the CO_2 and CH_4 base

Recently the results of study of interaction between hexene-1 or propylene and CO_2 on Ru-Co/Al_2O_3 and Rh-Co/Al_2O_3 have been published [1-3]. In this paper the process of interaction between CO_2 and CH_4 over Ru-Co/Al_2O_3 and Ru-Co/Al_2O_3 +ZSM cluster type catalysts has been studied.

EXPERIMENTAL

The interaction between CO_2 and CH_4 on Ru-Co/Al_2O_3 and Ru-Co/Al_2O_3 modified by ZSM-zeolite catalysts of clusters type has been studied with the application of the experimental and quantum-chemical methods. Quantum-chemical calculation have been made on the basis of ZINDO-1 (quantum-chemical programs Hyperchem-6). [4-7].

The CO_2+CH_4 reaction was carried out in flow type reactor in the range of 473-723 K and pressure variation from 0.1 to 1.0 MPa. Catalysts were prepared by impregnation of support with mixture of $RuCl_3$ and $Co(NO_3)_2 \cdot 6H_2O$ solution. Then they were reduced by hydrogen at 773K during 3 hours, washed from Cl^- and NO_3^- ions and dried up in the air at 303-323K. Catalyst was additionally reduced directly in the reactor at temperatures from 473 to 673K during 1 hour before the reaction between CO_2 and CH_4.The reactant gas mixture consists in CO_2 + CH_4 diluted with Ar. The ratio of CO_2 : CH_4 : Ar is 1: 0.5 : 6.

The reaction rate was controlled on CH_4 decrease by using a chromatographic analysis. IR-spectra of reactants adsorbed on catalyst surface were recorded in a Specord IR-75 spectrometer in the 1200-3500 cm^{-1} range.

RESULTS AND DISCUSSION

The basic products of CO_2+ CH_4 interaction are C_1-C_4-alcohols and C_1-C_4-acids and aldehydes on Ru-Co/Al_2O_3 at the range of 473-723K and 0.1-1.0 MPa (Table 1). For example, the CH_4 conversion is 25.9% at T=573K and P=0.35MPa. The reaction products are methanol (3.8%), formaldehyde (1.4%), ethyl alcohol (2.7%), ethyl (1,4%) and propionic (8,6%) aldehydes, propionic (35,5%), butyric (19.5%), formic(10.8%) and acetic (20.2%) acids. At 0.6 MPa and T=573K the CH_4 conversion is 46.8%. The propionic (20.1%) and acetic (31.5%) acids, propionic aldehyde (17.8%), butanol-2 (3.8%), methanol (7.6%) and formaldehyde (1.9%) are mainly products under these conditions. Besides that there are traces of CO, O_2, H_2 and C_2-C_4-hydrocarbons.

It was calculated the adsorption models of 3 types: "M-cluster + CO_2-", "M-cluster + CH_4" and "M- cluster + CH_4 + CO_2" by quantum-chemical ZINDO methods (Table 2). There was used ZINDO method giving more high value of binding energy of molecules in comparison with real ones. But this method allows to estimate the changes in binding energy in complex : "M-cluster + molecule" depending on the cluster nature. The accounts were made in comparable conditions. It has been shown that CO_2 molecule can introduce into the mono- and bimetallic Co-,Ru- and Co-Ru -clusters. The ? E_{bind} change shows that binding energy between the atoms of the CO_2 molecule and the metal atoms of Ru-

Table 1. **The interaction of carbon dioxide and methane on 5% Ru-Co/Al_2O_3 -catalyst**

Products, %	0,35 MPa				0,6MPa			
	473K	573K	673K	723K	473K	573K	723K	673K
?C_1-hidrocarbons	-	0,4	-	2,0	0,3	0,7	0,7	1,0
Formaldehyde	5,9	1,4	3,7	3,8	1,0	1,9	4,8	1,6
Methanol	36,4	3,9	21,1	25,6	7,6	7,6	10,5	8,3
Ethyl alcohol	18,6	2,7	11,7	4,5	1,2	-	10,8	3,2
Propanol	-	-	-	-	15,7	-	6,3	1,1
Butanol-2	-	-	12,7	-	2,1	3,8	-	11,0
n-Butanol	-	-	-	-	7,8	-	16,9	10,0
Butyraldehyde	9,7	10,8	6,7	-	5,9	-	19,1	6,1
Unidentifical prodacts	-	1,4		-	-	-	-	-
Ethyl acid	29,4	20,2	23,2	-	21,5	31,5	-	0,7
Propiohaldehyde	-	8,4	-	-	-	17,8	25,4	25,4
Propionic acid	-	35,5	20,9	64,1	26,1	28,1	5,6	12,7
Butyric acid	-	15,5	-	-	10,8	8,6	-	18,8
C_{5+}oxigenetes	-	-	-	-	-	-	-	-
Conversion of CH_4, %	21,0	25,0	10,3	10,1	10,6	12,6	9,9	12,0

Table 2. **The quantum-chemical accounts of CO_2, CH_4 and CO_2 + CH_4 over Ru-, Co- and Ru-Co-clusters**

Complexes	E_{bind}	$\Delta_1 E_{bind}$	$\Delta_2 E_{bind}$	Bond lengths, Å		
	kcal/mol			C-O	C-H	M1-M1
Co4	126,70					2.82-3.84
Co4	63.29					2.84-4.11
Co10	305.42					2.82-4.35
Co2Ru2	66,51					2.67-4.86
Co2 Ru2	70,23					2.54-3.20
Ru4	38.18					2.66-3.24
Ru10	-115.57					2.66-3.12
Co4 CO_2	-1022.34	-434.60		1.38-1.39		3.39-3.91
Co10 CO_2	-991.67	-583.35		1.35-1.38		2.82-3.90
*Co2 Ru2 CO_2-1	-1165.83	-518.59		1.39-1.40		2.90-3.80
*Co2 Ru2 CO_2-2	-1188.57	-541.34		1.38-1.39		3.10-3.82
*Co2 Ru2 CO_2-3	1177.58	-530.35		1.37-1.38		3.10-3.53
*Co2 Ru2 CO_2-4	1185.79	538.56		1.37-1.39		3.09-3.84
Co2 Ru2 CO_2	-1174.28	530.77		1.41-1.42		2.97-3.80
Ru4 CO_2	-1274.88	-599.32		1.42		2.71-3.70
Ru10 CO_2	-1595.21	-765.90		1.46		2.80-3.60
Co4 CH_4	-1122.50		-184.03		1.14-1.15	2.81-3.58
Co2 Ru2 CH_4	1265.32		-330.07		1.18-1.22	3.28-3.72
Ru4 CH_4	-1382.46		-418.88		1.23-1.28	3.29-3.64
Co4 CO_2 CH_4	-2097.40		-445.19	1.37-1.38	1.10-1.12	3.28-3.66
Co2Ru CO_2 CH_4	-2371.67		722.68	1.35-1.36	1.10-1.16	2.93-4.70
Ru4 CO_2 CH_4	-2484.45		-807.13	1.43	1.10-1.15	2.70-3.67

$\Delta_1 E_{bind}$ = E_{bind} (ML_nCO_2) - E_{bind}(ML_n) - E_{bind}(CO_2 **); ΔE_{bind}** = E_{bind} (ML_nCH_4) - E_{bind}(ML_n) - E_{bind} (CH_4); **ΔE_{bind}** = E_{bind} ($ML_nCO_2CH_4$) - E_{bind} (ML_n) - E_{bind} (CO_2) - E_{bind} (CH_4) ***

****E_{bind} (ML_nCO_2)** - binding energy of "M-cluster + CO_2-", **E_{bind} (ML_n)** - binding energy of M-cluster, **E_{bind} ($ML_nCO_2CH_4$)** - binding energy of "M- cluster + CH_4 + CO_2" **E_{bind} (CO_2)** - binding energy of the CO_2 molecule, **E_{bind} (CH_4)** - binding energy of CH_4-molecules ,**E_{bind} (ML_nCH_4)** - binding energy of "M-cluster + CH_4"

, Co- and Ru-Co-clusters increases when the quantity of Ru rises. The insertion of the CO_2 molecule into the Co-, Ru- and Co-Ru-clusters changes their configurations and M-M-lengths.

Analogical phenomena are observed when the interaction between CH_4-molecules and Co-, Ru or Ru-Co-clusters takes place (Table 2). In case CH_4-adsorbtion on 4Ru-clusters the M-M-lengths are increased from 2.66-3.24 A to 3.29-3.64 A. For 2Co-2Ru- clusters the M-M-lengths are 2.67-4.86 A (without CH_4) and 3.26-3.72 A (with CH_4). 4Co- clusters are exposed to the radical changes by reason of the CH_4 adsorption: it was became plane. There are the loosing and cleavage of C-H-bonds of CH_4 molecules adsorbed on Co-, Ru- and Co-Ru-clusters. The binding energy of CH_4 molecules with mono- and bimetallic clusters are –418.88 kcal/mol (4Ru); -330.1 kcal/mol (2Co-2Ru) and –184.03 kcal/mol (4Co). The strongest bond is observed for system "CH_4+4Ru".

The figure 1 shows the optimized structures of joint adsorption of CH_4 + CO_2 on mono- and bimetallic Co-, Ru- and Co-Ru-clusters. Quantum-chemical accounts show that the C-H bonds lengthening for "CH_4 + CO_2 + M- clusters" systems are less then ones for "CH_4+ M-clusters". However, binding energy is stronger in "M-clusters+CO_2+CH_4"-systems than ones in "M-clusters+CO_2" or "M-clusters+CH_4".

IR-data of CO_2 adsorption on Co-Ru-catalysts are conformed with quantum- chemical calculations. Adsorption bands of CO_2^{gas} (2350 cm^{-1}), CO_{2ads} (1580 and 1440 cm^{-1}). CO_{ads} (1950 cm^{-1}, 2020 cm^{-1}) are presented in IR-spectra of adsorbed CO_2.

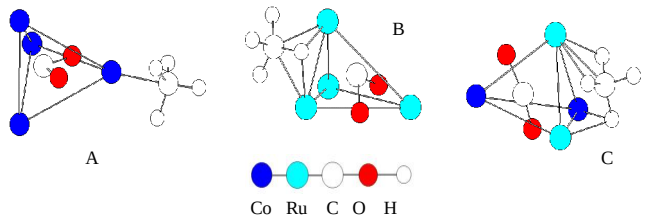

Figure 1. The optimized structures of adsorbed CO_2 and CH_4 on Co4 (A), Ru4 (B) and Co2Ru2 (C) clusters

The experimental and quantum-chemical accounts show that the mechanism of the interaction between CO_2 and CH_4 on Ru-Co/Al_2O_3 is very complicated. Probably the first stage of the CO_2 + CH_4 interaction is the cleavage of molecules bonds:

$$CH_4 > CH_{3ads} + H_{ads} \qquad CO_2 > CO_{ads} + O_{ads} > CO\wedge + O_{ads}$$
$$CH_{3ads} > CH_{2ads} + H_{ads} \qquad CO_{ads} > C_{ads} + O_{ads}$$
$$CH_{2ads} > CH_{ads} + H_{ads} > C_{ads} + H_{ads}$$

Syntheses-gas ($CO + H_2$) may be the one of the possible product This suggestion is confirmed with the results of the CO_2 + methane interaction on Ru-Co/Al_2O_3+ ZSM-zeolite catalyst. IR- Spectroscopy data of NH_3 adsorption show that the ZSM-zeolite incorporation into Ru-Co/Al_2O_3 is accompanied by the increase Lewis acidic centers (adsorption bands at 3550, 3400, 1600 cm^{-1}) and catalyst's de-structive ability. The CO and hydrogen are main products formed over Ru-Co/Al_2O_3+ ZSM-zeolite catalyst.

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Резюме

Экспериментальды және квантты-химиялық әдістерді қолдана отырып Ru-Co катализаторларында CO_2 мен CH_4 әрекеттесуі және адсорбциясы зерттелді.

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