APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. **14**, 853–856 (2000)

NOTE

Interaction between CO_2 and propylene over $Rh–Co/Al_2O_3$ catalysts†

L. B. Shapovalova,* G. D. Zakumbaeva, A. V. Gabdrakipov, I. A. Shlygina and A. A. Zhurtbaeva
The Institute of Organic Catalysis & Electrochemistry of the Ministry of Education and Science of the Republic of Kazakstan, 142, Kunaev str., Almaty, 480100, Kazakstan

The adsorption and interaction of carbon dioxide and propylene on $Rh–Co/Al_2O_3$ catalysts have been investigated by using experimental and quantum chemical methods. It was established that in the region of 0.1–1.8 MPa and 523–673 K a complex of oxygenates and hydrocarbons is formed. It has been shown that the CO_2 molecule adsorbs associatively as well as dissociatively with formation of CO_{ads} and O_{ads}. Propylene adsorbs in the same manner. The adsorption mechanism is determined by the structure and composition of surface active centers of the $Rh–Co/Al_2O_3$ catalyst. The results of the experimental study of chemisorption of both CO_2 and propylene are correlated with quantum chemical calculations.

Keywords: carbon dioxide; propylene; catalyst; adsorption; oxygenates; quantum chemical calculations

INTRODUCTION

The studies of catalytic activation of CO_2 and its interaction with hydrocarbons are intensively increasing at the present time because of the need to decrease carbon dioxide in the atmosphere. Utilization of carbon dioxide can solve the problem of the greenhouse effect by involving the carbon in the production of artificial oil, different organic compounds and synthesis gas ($CO+H_2$).

Recently the results of a study of the interaction between hexene-1 (propylene) and carbon dioxide on $Ru–Co/Al_2O_3$ have been published.[1,2] In this paper the process of interaction between CO_2 and propylene over $Rh–Co/Al_2O_3$ cluster-type catalysts has been studied.

EXPERIMENTAL

The process was carried out in a flow-type reactor at various temperatures from 523 to 673 K and pressures from 0.1 to 1.8 MPa. The space velocity was 100–120 h^{-1}. The mixture $C_3H_6/CO_2 = 1/4$ was used. Catalysts were prepared by impregnation of Al_2O_3 support with a mixture of $RhCl_3$ and $Co(NO_3)_2 \cdot 6H_2O$ solutions. Then they were reduced by hydrogen at 773 K for 3 h, washed to remove Cl^- and NO_3^- ions and dried in air at 303–323 K. Catalyst was additionally reduced directly in the reactor at various temperatures from 523 to 673 K for 1 h before the reaction between CO_2 and propylene. The reaction rate was determined through propylene decrease by use of chromatographic analysis.

The IR spectra of reactants adsorbed on the catalyst surface were registered by UR-75 spectrometer in the 1200–3500 cm^{-1} range.

Quantum chemical calculations have been made on the basis of the extended Hückel method complemented with Anderson core–core repulsion as an item of total electron energy. Cluster approximation was used for calculations. A Minimal quantity of metal atoms (2–7–13) was taken into account. This approach seems reasonable,

* Correspondence to: L. B. Shapovalova, The Institute of Organic Catalysis & Electrochemistry of the Ministry of Education and Science of the Republic of Kazakstan, 142 Kunaev str., Almaty 480100, Kazakstan.
E-mail: adm@orgcat.academ.alma-ata.su
† This note is based on work presented at the Fifth International Conference on Carbon Dioxide Utilization (ICCDU V), held on 5–10 September 1999 at Karlsruhe, Germany.

Table 1 Interaction between CO_2 and propylene over $Rh–Co/Al_2O_3$

Product	Amount (mol%)			
	T_{exp} = 523 K T_{red} = 523 K P = 1.5 MPa	T_{exp} = 673 K T_{red} = 673 K P = 1.5 MPa	T_{exp} = 523 K T_{red} = 523 K P = 1.8 MPa	T_{exp} = 573 K T_{red} = 573 K P = 1.5 MPa
Methanol	22.7	18.4	8.4	16.8
Formaldehyde	3.4	1.7	0.8	4.2
Acetone	5.4	17.5	10.3	5.5
Ethanol	7.9	0.7	8.7	4.2
i-Propanol	31.0	38.3	13.9	33.6
n-Propanol	1.5	3.0	1.3	2.6
n-Butanol	1.4	1.2	1.7	—
Butyraldehyde	Trace	2.0	Trace	—
Butyric acid	20.3	7.3	37.3	33.0
Propioaldehyde	—	2.8	—	—
Other products	6.4	7.1	17.6	0.1
Conversion of C_3H_6 (%)	8.3	9.3	25.0	7.9

because, as is known, chemisorption is a highly localized phenomenon.[3]

RESULTS AND DISCUSSION

It has been established that the conversion of propylene and carbon dioxide depends on the catalyst composition and the partial pressures of the CO_2 + propylene mixture. Conversion of propylene on $Rh–Co(1:1)/Al_2O_3$ at T_{exp} = 523 K and P = 1.8 MPa is 25.0%. The reaction products are methanol (8.4 mol%), formaldehyde (0.8 mol%), acetone (10.3 mol%), ethanol (8.7 mol%), i-propanol (13.9 mol%), butanol (1.7 mol%), butyric acid (37.3 mol%), traces of butyraldehyde and other compounds. On decreasing the pressure to 1.5 MPa (T_{exp} = 523 K) the propylene conversion decreases to 8.3%. Also, the product composition changes. The yield of methanol, formaldehyde and i-propanol increases up to 22.7 mol%, 3.4 mol% and 31.0 mol% respectively. The yield of acetone and butyric acid decreases to 5.4 mol% and 20.3 mol% respectively (Table 1).

It was shown that the degree of propylene conversion is 7.9–9.3% on increasing T_{exp} from 523 to 673 K (P = 1.5 MPa). But with the temperature increase the ratio of products formed changes significantly. It is observed that there is a tendency to decrease the yields of methanol from 22.7 to 18.4 mol% formaldehyde from 3.4 to 1.7 mol% and ethanol from 7.9 to 0.7 mol%. The yield of butyric acid changes extremely. The maximal yield reaches 33.0 mol% at T_{exp} = 573 K. Then the yield of butyric acid decreases sharply to 7.3 mol% at T_{exp} = 673 K. In these conditions the yields of acetone and i-propanol increase from 5.4 mol% and 31.0 mol% respectively (T_{exp} = 523 K) to 17.5 mol% and 38.3 mol% (T_{exp} = 673 K) respectively. Propioaldehyde are formed at 673 K (2.8 mol.%) (Table 1).

In IR spectra the absorption bands at 3500, 3300 (OH groups), 3060, 3000 (=CH_2 groups), 2980, 2920, 2850 (—CH, —CH_2, —CH_3 groups), 2380, 2350 (CO^{gas}_{2ads}),2030 and 1900 cm^{-1} corresponding to linear and bridge forms of CO_{ads} on Rh^{n+} and Rh^0 are presented at chemisorption of the $CO_2 + C_3H_6$ mixture (T = 473 K) on $Rh–Co(9:1)/Al_2O_3$ catalyst. In addition, intensive absorption bands were observed in the range 1700–1300, and at 1580 and 1440 cm^{-1}. The absorption bands at 1580 and 1440 cm^{-1} correspond to the chemisorbed CO_2 molecule. With increasing cobalt concentration in the catalyst composition to 30–50 mass% the intensity of the absorption bands in the range 2400–2000 cm^{-1} increases.

The positions of the absorption bands vary a little with temperature increase from 473 to 573 K. However, the intensities of the absorption bands at 1950 and 2380–2350 cm^{-1}, and especially at 1550 and 1430 cm^{-1}, significantly increase on adsorption of the mixture on the $Rh–Co(1:1)/Al_2O_3$ catalyst. These structures are sufficiently strongly bonded with the catalyst surface and do not disappear at vacuumization.

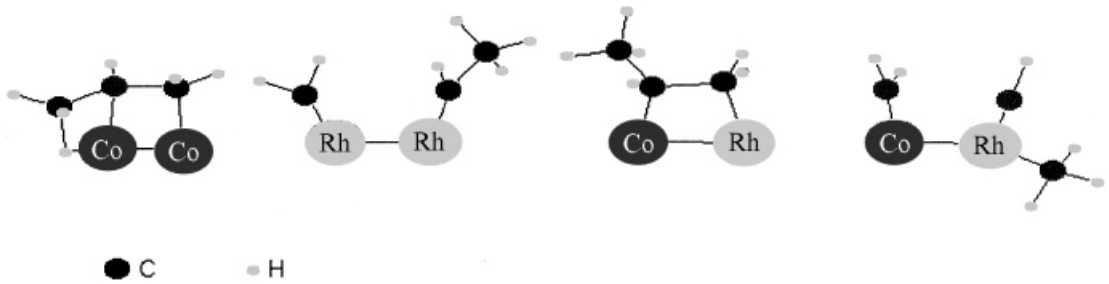

Figure 1 The structures obtained at total optimization of propylene molecule geometry.

The structure and state of the surface of the Rh–Co/Al_2O_3 catalyst were studied by physico-chemical methods of analysis. The size of the metal particles in the Rh–$Co(9:1)/Al_2O_3$ catalyst is 9–10 nm. With increase of cobalt concentration in the catalyst composition the particle size decreases. The particle size of Rh–$Co(1:9)/Al_2O_3$ catalyst is 1.5–2.0 nm. It has been established that rhodium and cobalt form the cluster structure. Their state and stability are determined by the Rh:Co ratio.

Using quantum chemical methods it has been shown that replacement of rhodium on cobalt in 13-atom clusters results in an increase of cluster stability. It grows with the increasing quantity of cobalt atoms. The formation of bimetallic structures in the catalyst is more energetically favourable than monometallic ones. The stability of the 13-atom Rh–Co clusters decreases in the series:

$$12Co\text{-}Rh_{(7)} < 12Co\text{-}Rh_{(1)} < 3Co_{(1,7,8)}\text{-}10Rh < 3Co_{(1,5,4)}\text{-}10Rh < 3Co_{(1,4,7)}\text{-}10Rh < 2Co_{(1,7)}\text{-}11Rh < 1Co_{(1)}\text{-}12Rh < 1Co_{(5)}\text{-}12Rh < 13Rh$$

The hexagonal cluster of cobalt is rather stable. On replacement of cobalt by rhodium atoms the cluster stability is sharply increased. The results of calculations show that the possibility of formation of bimetallic clusters is higher than of the monometallic ones. It is especially characteristic for catalysts with high cobalt content. It should be noted that at the location of the Rh atom in the centre of the 13-atoms cobalt cluster the maximal stabilization of the cluster occurs.

By using quantum chemical methods the adsorption of carbon dioxide and propylene on two and seven-atom mono- and bi-metallic rhodium, cobalt, and Rh–Co clusters has been investigated. It has been shown that destruction of the C=C bond occurs and CH_2 and CH_3—CH fragments are formed at propylene adsorption on the monometallic rhodium centers. The type of adsorption on bimetallic Rh–Co clusters is determined by the orientation of the C_3H_6 molecule. There are two types: the first type of orientation is where the CH_2 group of the C_3H_6 molecule is adsorbed on the rhodium atom; the second type is where the CH_2 group is adsorbed on the cobalt atom. In the first case associative adsorption of the propylene molecule takes place. In the second case the destruction of the propylene molecule with formation of CH_3, CH_2 and CH fragments occurs. At propylene adsorption on monometallic cobalt clusters the

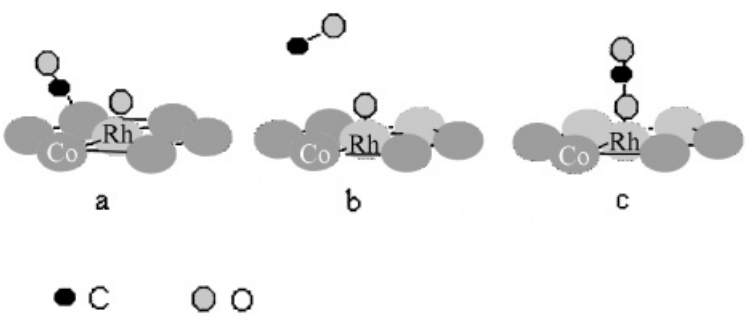

Figure 2 Total optimization of CO_2 molecule geometry on Rh–CO clusters.

formation of weak covalent bonds of Co—C_3H_6 occurs. The C=C bond weakens without further destruction (Fig. 1).

It has been observed that there is a complicated dependence of the CO_2 molecule adsorption on the Rh–Co atomic ratio in surface active centers (Fig. 2). Vertical chemisorption of the CO_2 molecule on the central rhodium atom in seven-atom Rh–Co clusters results in an associatively adsorbed CO_2 molecule. Chemisorption on one of the external rhodium atoms in such a cluster results in the dissociation of CO_2 with CO_{ads} and O_{ads} formation. Basically, carbon dioxide adsorbs associatively on monometallic rhodium and cobalt clusters.

Carbon dioxide can adsorb on the surface of Rh–Co/Al_2O_3 associatively as well as dissociatively. Interaction of associatively adsorbed carbon dioxide with propylene and products of its decomposition results in acid formation.

On some centers of bimetallic catalyst propylene is exposed to destruction with formation of C_1- and C_2-containing radicals. Their interaction with $CO_{2\ ads}$, CO_{ads}, O_{ads} results to C_1–C_3 oxygenates formation.

The results of the IR study of chemisorption of CO_2 and propylene are correlated with the quantum chemical calculations.

REFERENCES

1. Zakumbaeva GD, Shapovalova LB. Interaction of CO_2 with propylene. In *Proc. Japan–FSU Catalysis Seminar: Catalytic Science and Technology for 21 Century Life*, 1994; 28.
2. Zakumbaeva GD, Shapovalova LB, Shlygina IA. Interaction between CO_2 and propylene on Ru–Co/Al_2O_3 catalysts of cluster type. In *Advances in Chemical Conversions for Mitigating Carbon Dioxide*, Inui T, Anpo M, Izui K, Yanagida S, Yamaguchi T (eds.), *Studies in Surface Science and Catalysis*, vol. 114 Elsevier Science B.V. 1998; 171–175.
3. Hoffman R. *J. Chem. Phys.* 1963; (6), 1397.

