SYNTHESIS OF ALIPHATIC HYDROCARBONS FROM CO AND H₂ ON Rh-COMPLEX CATALYSTS

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Reports [1, 2] on the activity of catalysts based on metal complexes in the synthesis of aliphatic hydrocarbons from CO and H_2 have recently appeared. Rhodium carbonyl in a mixture with Lewis acids catalyzes the formation of C_1-C_4 alkanes from CO and H_2 . The introduction of a reducing agent, particularly metallic Al, into such systems sharply increases the yields of the hydrocarbons [3].

The purpose of the present work was to investigate the catalytic properties of a transition-metal complex-Lewis acid-reducing agent system (Rh_nL_m -AlBr₃-Al).

EXPERIMENTAL

The complexes $Rh_4(CO)_{12}$, $[Rh(CO)_2Cl]_2$, $Na_2[Rh_{12}(CO)_{30}]$, and $(Ph_3P)_3RhCl$ were synthesized according to the methods described in [4-7], and pure-grade $RhCl_3 \cdot 3H_2O$ and freshly sublimed AlBr₃ were used. The experiments were carried out in a 100-ml glass ampul, into which 4-10 mg of the rhodium compound, 0.5-1.5 g of AlBr₃, and 1-100 mg of powdered Al were introduced. The ampul was evacuated, filled with a mixture of CO and H_2 with a volume ratio ranging from 3: 1 to 1: 4 (the initial pressure was 1 atm), and heated in a furnace with an electric heating element. The temperature was maintained with an accuracy of $\pm 2^\circ$. The duration of an experiment was 10 h. The C_2 - C_4 hydrocarbons and CO₂ were analyzed by GLC on an LKhM-8MD chromatograph (10 m × 3 mm column with 10% HMPA on Chromaton N-AW, 25°C). A mixture of CO, H_2 , N_2 , O_2 , and CH_4 was analyzed on the same chromatograph (1.5 m × 3 mm column with 5 Å molecular sieves, 50°C).

DISCUSSION

The components $Rh_4(CO)_{12}$, $AlBr_3$, and Al taken separately, as well as the two-component $Rh_4(CO)_{12}$ -Al system, are inactive in the synthesis of alkanes from CO and H₂. The two-component $Rh_4(CO)_{12}$ - $AlBr_3$ and $AlBr_3$ -Al systems have insignificant catalytic activity (Table 1). In the presence of the $AlBr_3$ -Al system, products with an increased relative concentration of C₄ hydrocarbons are formed without any CO₂ in them, in contrast to the mixtures formed when the $Rh_4(CO)_{12}$ - $AlBr_3$ system is used.

The $Rh_4(CO)_{12}$ -AlBr₃-Al catalytic system is more active than the two-component systems tested. Here 22 moles of CO are converted into hydrocarbons per gram-atom of Rh, and the extent of conversion of CO (K_{CO}) is 89 vol. %. Increasing the Al: AlBr₃ mole ratio in the $Rh_4(CO)_{12}$ -AlBr₃-Al system to 0.2 (Fig. 1) increases K_{CO} from 4 to 89%. A further increase in the amount of Al in the system has no influence on K_{CO} . The composition of the reaction products varies as Al: AlBr₃ is increased to 0.05 (the relative concentration of C_4H_{10} increases, and the relative concentrations of C_3H_8 and CO_2 decrease) and then remains practically unchanged. An increase in the relative concentration of Al in the AlBr₃-Al system has a similar influence on K_{CO} . However, as the Al: AlBr₃ ratio is varied in the 0.1-0.4 range, K_{CO} increases only by a factor of 2, the quantity of CH_4 in the synthesis products decreases by a factor greater than 4, and the fraction of isobutane

TABLE 1. Effect of the Composition of the Catalytic System on the Synthesis of Alkanes from CO and H_2 (150°C, 10 h, CO: $H_2=1:4$, mole ratio RH: AlBr₃: Al: CO=1:200:40:25)

		Reaction products, vol. %						
Catalytic system	^K CO, vol. %	CO2	CH₄	C_2H_6	C_3H_8	i-C₄H10	n-C4H10	
Rh4 (CO)12-AlBr3 AlBr3-Al Rh4 (CO)12-AlBr3-Al	4 5 89	12 0 0	43 22 47	5 5 8	40 11 14	0 61 30	0 1 1	

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Fig. 1. Dependence of K_{CO} and the composition of the reaction products on the A1: AlBr₃ mole ratio in the Rh₄(CO)₁₂-AlBr₃-A1 system (150°C, 10 h, CO: H₂=1:4, mole ratio Rh: AlBr₃: CO=1: 200:25): 1) K_{CO} ; 2) CO₂; 3) CH₄; 4) C₂H₆; 5) C₃H₈; 6) i-C₄H₁₀; 7) n-C₄H₁₀.

Fig. 2. Dependence of K_{CO} and the composition of the reaction products on the A1: AlBr₃ mole ratio in the AlBr₃-A1 system (150°C, 10 h, CO: H₂=1: 4, mole ratio AlBr₃: CO=200: 25). The notation is explained in Fig. 1.

increases from 38 to 72% (Fig. 2).

When the Rh: AlBr₃ ratio in the Rh₄(CO)₁₂-AlBr₃-Al system ranges from 1:60 to 1:300 and the Rh: Al: CO ratio is constant, the composition of the reaction products and the value of K_{CO} remain unchanged.

The structure of the Rh complex has a significant effect on the catalytic properties of the $Rh_nL_m^-AlBr_3$ -Al and $Rh_nL_m^-AlBr_3$ systems (where L is the ligand) (Table 2). In the case of the two-component $Rh_nL_m^-AlBr_3$ systems, the extent of conversion of CO is very low and amounts to 4-5% on the catalysts containing $Rh_4(CO)_{12}$ and $Na_2[Rh_{12}(CO)_{30}]$ and 0.1-0.2% in the presence of $[Rh(CO)_2Cl]_2$ and $RhCl_3 \cdot 3H_2O$. The introduction of metallic Al into the $Rh_nL_m^-AlBr_3$ system results, as we have already noted, in an increase in its catalytic activity. The composition of the reaction products for the rhodium complexes used is very close to. but different from the composition of the mixtures formed in the presence of $RhCl_3 \cdot 3H_2O$. The presence in the molecule of the original Rh complex of ligands (CO and Ph_3P) which stabilize the lower oxidation states of the metal results in the formation of a system with a higher catalytic activity than in the case of the RhCl_3-AlBr_3-Al system. These ligands apparently prevent the conversion of the rhodium in the original complex into metallic Rh upon interaction with the AlBr_3-Al reducing system. Thus, in the systems under study the rhodium complex is clearly mainly responsible for the synthesis of alkanes from CO and H₂, in agreement with the data in [2].

The CO: H_2 ratio in the original gaseous mixture has a strong influence on the synthesis of hydrocarbons (Table 3). The increase in the concentration of CO in the mixture lowers the extent of conversion of CO into hydrocarbons and the concentration of methane and propane in the reaction products and increases the relative concentration of the butanes.

> TABLE 2. Influence of the Nature of the Rhodium Compound on the Catalytic Activity for the Rh_nL_m -AlBr₃-Al System (150°C, 10 h, CO: H_2 =1:4, mole ratio Rh: AlBr₃: Al: CO=1:200:40:25)

Rh _n L _m		Reaction products, vol. %					
	^K CO, vol.%	CH1	C ₂ H ₅	C ₃ H ₈	i-C4H10	<i>n</i> -C ₄ H ₁₀	
Rh ₄ (CO) 12 [Rh (CO) 2Cl]2 Na2[Rh12 (CO) 30] (Ph3P) 3RhCl RhCl3 · 3H2O	89 84 87 80 15	47 47 46 50 37	8 8 9 6 13	14 14 15 13 12	30 29 29 30 35	1 2 1 1 3	

CO : H ₂	Extent of	Extent of conversion of CO			Reaction products, vol. %					
	vo1. %	mole CO/g-at Rh	CH4	C ₂ H ₆	C3H8	i-C4H10	n-C4H10			
3:1 1:1 1:3 1:4	5 17 73 89	5 10 22 23	24 36 41 47	11 7 9 8	8 12 14 14	49 40 34 30	8 5 2 1			

TABLE 3. Influence of the CO: H_2 Ratio in the Original Gaseous Mixture on K_{CO} and Composition of the Reaction Products (150°C, 10 h, mole ratio Rh: AlBr₃: Al=1:200: 40)

In the case of the $Rh_4(CO)_{12}$ -AlBr₃-Al system, the composition of the reaction products does not depend on the duration of the experiment in the 1-10-h range. The extent of conversion of CO in the presence of this system increased from 30 to 92% as the synthesis temperature was increased from 100 to 170°C. The composition of the reaction products changed only slightly.

According to the data in [8], the rhodium complexes $Rh_4(CO)_{12}$, $Rh_6(CO)_{16}$, $Rh(acac)_2(CO)_2$, $Al_2[Rh_{12}(CO)_{30}]_3$, $Na_2[Rh_{12}(CO)_{30}]$, etc. catalyze the formation of methanol, glycols, glycerol, and other oxygen-containing compounds from CO and H_2 at high pressures. Alkanes were not found in the reaction products. It has been postulated that the $[Rh_{12}(CO)_{30}]^2$ anion, which is the true catalyst of the synthesis of the oxygen-containing compounds, forms from the original complexes under the conditions of the reaction [9].

The addition of a Lewis acid to a rhodium complex directs the process in the direction of the formation of alkanes. It is known that metal carbonyls form adducts with Lewis acids [10-13], i.e.,

$$L_n M_m CO + AIX_3 \rightarrow L_n M_m COAIX_3$$

where L is a ligand; M denotes Fe, Ru, and Co; and X denotes Cl, Br, and alkyl.

The reaction of a Lewis acid with a coordinated CO molecule, on the one hand, promotes the cleavage of the C-O bond and, on the other hand, facilitates the nucleophilic attack of the hydride ion on the coordinated CO molecule (step 2 in the scheme) and thereby permits the realization of the reduction of CO to alkanes under milder conditions than those necessary for the synthesis of the oxygen-containing compounds. This is consistent with the scheme of the mechanism for the synthesis of hydrocarbons from CO and H_2 proposed in [14]:

$$M-H \xrightarrow{CO} M-CO \rightarrow M-C=O \xrightarrow{H_2} M-CH_2 \xrightarrow{H_2} M-CH_2 \xrightarrow{H_2} M-CH_3 \xrightarrow{H_3} M-OH + CH_4$$

$$M-H \xrightarrow{I} 2 \xrightarrow{H} 3 \xrightarrow{I} 0H 4 \xrightarrow{I} 0H 4 \xrightarrow{I} 0H 4 \xrightarrow{I} 0H + CH_4$$

$$M-C=O \xrightarrow{H_2} M-CH-OH \xrightarrow{H_2} M-CH_2CH_3 \xrightarrow{H_3} M-CH_2CH_3$$

$$M-C=O \xrightarrow{H_2} M-CH-OH \xrightarrow{H_2} M-CH_2CH_3 \xrightarrow{H_3} 0H + CH_2CH_3$$

When A1 is added to an AlBr₃ melt, the concentration of metallic A1 in the melt at 145°C reaches 0.017% [15]. Thus, a homogeneous aprotic system having strong reducing and acid properties is apparently formed under the conditions studied. This system binds the H₂O formed during the synthesis, preventing the decomposition of the Rh complex and resulting in an increase in K_{CO} . The removal of water from the reaction zone decreases the probability of chain termination (step 6 in the scheme) and causes an increase in the fraction of C_2-C_4 hydrocarbons in the reaction products.

CONCLUSIONS

1. The activity and selectivity of the $Rh_nL_m-AlBr_3-Al$ catalytic systems in the synthesis of the lower alkanes from CO and H₂ are greatly dependent on the nature of the rhodium complex, the component ratio, and the reaction temperature.

2. The catalytic systems containing $Rh_4(CO)_{12}$, $[Rh(CO)_2Cl]_2$, $Na_2[Rh_{12}(CO)_{30}]$, and $(Ph_3P)_3RhCl$ with the ratios A1: AlBr₃=0.2 to 0.4 and Rh: AlBr₃=1: 60 to 1: 300 are the most active. Decreasing the CO: H_2 ratio in the original gaseous mixture from 3: 1 to 1: 4 increases the extent of conversion of CO from 5 to 89%.

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DEPENDENCE OF THE DIRECTIONS OF DEHYDRATION ON Al₂O₃ OF METHYLATED 2-BUTANOLS ON THEIR STRUCTURE

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The dehydration of 2-alkanols over Al_2O_3 proceeds with the predominant formation of cis- β -olefins [1, 2]. The dehydration of these alcohols over the oxides of thorium, chromium, or rare earths produces mainly α -olefins [3-5]. The attention of investigators of the mechanism of dehydration of alcohols over Al_2O_3 has been focused on ascertaining the reasons for the predominant formation of olefins in the cis form and the establishment of the mechanism (E_1 or E_2) for the elimination of the water fragments [1, 2, 6, 7]. At the same time, the reasons for the predominant formation has apparently not been investigated.

The investigation of the influence of water on the direction of the dehydration of 2-methyl-2-butanol (2-MB) and 3-methyl-2-butanol (3-MB) over Al_2O_3 in [8] showed that the addition of water vapor to the carrier gas increases the ratio of the yield of β -olefins to the yield of α -olefins (β : α) in the case of the dehydration of 2-MB and, conversely, decreases this ratio in experiments with 3-MB. In order to ascertain the reasons for the different effects of water on the direction of the reaction, the effect of a more basic agent should be studied. For this purpose, in the present work we investigated the dehydration of 2-MB and 3-MB containing diethylamine (DEA) in various concentrations.

EXPERIMENTAL

The procedures for carrying out the experiments and the analysis of the reaction products have been described in [8]. The experiments were carried out at 160°C in a current of H_2 freed of O_2 and H_2O . The conditions of the experiments (the rate of supply of the alcohol and the amount of Al_2O_3) were selected such that the extent of conversion of the alcohol would not exceed 2%. The catalyst was treated with hydrogen freed of O_2 and H_2O at 550°C before each run.

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