Physical Chemistry

Role of Co-catalyst components in carbon monoxide-assisted acetylene hydropolymerization

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The carbon monoxide-assisted interaction of acetylene with hydrogen over cobalt catalysts was studied. The role of particular components of the catalyst was revealed. The influence of the compositions of both the initial gas and the catalytic system on the yield and composition of liquid hydrocarbons was studied. The mechanism of the process was investigated by IR-spectroscopy, pulse chromatography, and the radiochemical method. It was proposed that acetylene adsorbed on the support is polymerized with the participation of hydrogen, whereas acetylene adsorbed on the metal takes part in hydrogenation and hydrocracking processes. Carbon monoxide creates additional active sites for the growth of hydrocarbon chains.

Key words: acetylene; hydropolymerization; liquid hydrocarbons; Co-catalysts.

It is known[1,2] that the following processes can occur upon the interaction of C_2H_2 with H_2 in the presence of various catalysts: acetylene polymerization and cyclization to form aromatic and unsaturated aliphatic compounds; hydropolymerization to yield paraffins; hydrogenation; hydrocracking; cracking resulting in coke formation on the surface, *etc.* The type of conversion of acetylene—hydrogen mixtures and the yields and compositions of the products formed are governed by the type of catalyst and the reaction conditions.

Previously[3–5] it has been found that in the presence of Co-systems (*e.g.*, 10 % Co/Al_2O_3), acetylene—hydrogen mixtures are converted mainly to liquid alkanes, whose yields increase with the introduction of small amounts of CO in the reaction zone. The catalysts used in this process are complex systems involving metallic and oxidized cobalt, a support, and in some cases (for example, when supporting Co on Al_2O_3), the products of the interaction of cobalt with the support, formed during high-temperature catalyst treatment (precalcination and/or prereduction).

The aim of this work is to elucidate the roles of the different components in the 10 % Co/Al_2O_3 catalyst in the interaction between hydrogen, acetylene, and carbon monoxide.

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Experimental

The catalyst was prepared by impregnating A-64 γ-Al_2O_3 with an aqueous solution of cobalt nitrate (10 wt % Co). The alumina was precalcined in an air flow at 450 °C for 2 h. Following impregnation, the catalyst was dried on a water bath and then calcined in an air flow at 450 °C for 5 h. Prior to carrying out the syntheses, the samples were reduced with hydrogen ($W = 100\ h^{-1}$) at 450 °C for 5 h.

The syntheses were performed in a flow catalytic system ($V_{Cat} = 30\ cm^3$, $p = 0.1$ MPa, $T = 210$ °C, $W = 100\ h^{-1}$, run time 2 h). After the synthesis was completed, the heavy products adsorbed on the catalyst were removed and collected while the catalyst was treated in a hydrogen flow ($W = 100\ h^{-1}$) at 450 °C for 0.5 h.

Initial gaseous mixtures and gaseous reaction products were analyzed by GC (detector — catharometer, carrier gas — helium (30 mL min^{-1}), columns: Chromosorb-102 (2 m × 3 mm) and AR-3 activated carbon (1.5 m × 3 mm)). The temperature-programmed regime was as follows: 80—150 °C, 8 deg min^{-1} for the first column, 150—200 °C, 16 deg min^{-1} for the second one.

The overall content of olefins and aromatic hydrocarbons in the liquid products was determined by measuring the change in the sample volume upon treatment with sulfuric acid. Compositions of C_{5+} paraffins were found by GLC (detector — catharometer, carrier gas — helium (25 mL min^{-1}), column — 5 % SE-30 on Chromaton N-AW-HMDS (3 m × 3 mm)). The temperature-programmed regime was 30—260 °C, 6 deg min^{-1}.

Labelled ^{14}CO was used for a radiochemical analysis. Liquid reaction products were analyzed in a setup supplied with a flow proportional radioactivity counter. After separation on a chromatographic column, hydrocarbons were burned at 650 °C in a steel U-shaped reactor filled with copper(II) oxide. The water formed was frozen out in a trap (−78 °C), and the CO_2 was diluted with methane (a quenching additive) and directed to the radioactivity counter. Two chromatograms were obtained from each analysis of the reaction products: the first chromatogram was used for determining the composition of hydrocarbons, and the second one gave information on the distribution of the radioactive tracer in hydrocarbons.

Chemisorption of gases on the surface of the cobalt catalysts was examined by the pulse gas-chromatographic method.[6,7]

In addition, acetylene and pyridine adsorption on the catalysts and supports was studied by IR spectroscopy in a vacuum system employing an UR-20 instrument. Sample acidities were estimated from pyridine adsorption. Acetylene adsorption was carried out at a pressure of 7 Torr and 60 °C.

Results and Discussion

Table 1 summarizes data on the effect of the composition of the catalyst and of the initial gaseous mixture on the yields and distribution of the products of reductive acetylene polymerization. Over Al_2O_3, C_2H_2 conversion is 45 % under the accepted reaction conditions. In this case, only liquid hydrocarbons with a high content of unsaturated compounds (~50 %) consisting of aromatic and unsaturated hydrocarbons are formed. Hydrogen produced during chemisorption of acetylene on the Al_2O_3 surface (see Ref. 2) probably involve in the formation of aliphatic C_{5+} hydrocarbons by hydropolymerization, since the replacement of argon with hydrogen has virtually no effect on the process characteristics: acetylene conversions, yields of liquid products, and their compositions are almost the same as the corresponding characteristics in experiments with argon-diluted acetylene. Hence, molecular hydrogen does not participate in the conversions of acetylene on the Al_2O_3 surface and plays the role of an inert diluent.

On the unreduced CoO/Al_2O_3 catalyst, acetylene yields liquid products which contain more unsaturated compounds than those formed by the synthesis in the presence of Al_2O_3 (see Table 1). Thus, the introduction of a transition-metal oxide into the catalyst promotes polymerization and inhibits hydrogenation. This appears to be associated with the different types of C_2H_2 adsorption on the Al_2O_3 and CoO/Al_2O_3 surfaces. On the unreduced catalyst, acetylene conversions in the acety-

Table 1. Effect of the composition of the initial reaction mixtures and catalysts on the yields and compositions of the reaction products

Initial reaction mixture	Catalyst	$C_{C_2H_2}$ (%)	$Y_{C_1-C_4}$/g m^{-3}	$Y_{C_{5+}}$/g m^{-3}	Composition of C_{5+} (%)	
					Unsaturated	Saturated
$Ar + C_2H_2$	Al_2O_3	45.3	0	23.1	48.9	51.1
	CoO/Al_2O_3*	55.6	0	23.6	90.0	10.0
	Co/Al_2O_3**	50.2	2.1	35.1	95.6	4.4
$H_2 + C_2H_2$	Al_2O_3	54.6	0	21.4	48.0	52.0
	CoO/Al_2O_3*	93.0	30.2	42.1	95.0	5.0
	Co/Al_2O_3**	98.3	157.6	87.1	24.5	75.5
$H_2 + C_2H_2 + CO$	Al_2O_3	56.2	0	30.2	57.5	42.5
	CoO/Al_2O_3*	91.8	27.0	43.1	95.0	5.0
	Co/Al_2O_3**	99.0	108.4	154.8	19.0	81.0
$Ar + C_2H_2 + CO$	Co/Al_2O_3**	64.3	0	43.2	95.0	5.0

Notes. Reaction conditions: $p = 0.1$ MPa, $T = 210$ °C, $H_2(Ar)/C_2H_2 = 1.7$, $[CO] = 7\div8$ % v/v, $W = 100\ h^{-1}$, $t = 2$ h. C — acetylene conversions, Y — yields of reaction products.

* Unreduced 10 % Co/Al_2O_3 catalyst (calcined for 5 h at 450 °C in an air flow).

** Reduced 10 % Co/Al_2O_3 catalyst (reduced for 5 h at 450 °C in a hydrogen flow after calcination).

lene—hydrogen mixtures are considerably higher (93 %) than those in the C_2H_2 + Ar mixtures. In the former case, the yield of liquid products, which consist almost completely of unsaturated hydrocarbons, is doubled. Some gaseous hydrocarbons (methane, ethylene, ethane, and C_3—C_4 hydrocarbons) are also formed.

Hence, one may suggest that acetylene polymerization proceeds on the coordinatively unsaturated sites of the catalytic system (Lewis acid sites of alumina and $CoO \cdot Al_2O_3$ mixed oxides). Some data confirming the involvement of Al_2O_3 acid sites in acetylene polymerization were reported earlier in Refs. 8, 9.

The considerable increase in acetylene conversion found for the CoO/Al_2O_3 catalyst when using acetylene—hydrogen mixtures instead of C_2H_2 + Ar can be accounted for by H_2 adsorption on the transition-metal oxide.[10] As a result, the hydrogen required for hydrocarbon formation comes from both the acetylene molecules and the gaseous mixture. Since the liquid products basically consist of unsaturated compounds, one may conclude that hydropolymerization on the CoO/Al_2O_3 catalyst practically does not take place. Because ethane and ethylene are among the gaseous products, hydrogen adsorbed on the surface appears to be involved in acetylene hydrogenation.

The conversion of the acetylene—argon mixture on the reduced Co/Al_2O_3 catalyst differs little from this processs on the unreduced sample. However, in the former case, methane and hydrogen are found among the gaseous products. This may indicate acetylene hydrocracking on metal sites of the catalyst.

The products yielded from the acetylene—hydrogen mixtures in the presence of Co/Al_2O_3 differ from the hydrocarbons that were synthesized on alumina and on the unreduced catalysts. In the former case, at almost complete acetylene conversion (98 %), 245 g m^{-3} of hydrocarbons are produced, among which 64.4 % are gaseous hydrocarbons and only 35.6 % are liquid hydrocarbons basically consisting of alkanes.

It was found[11—14] that acetylene is adsorbed on supported Ni, Rh, Pd, and Ir catalysts at 180—200 °C in two forms: dissociatively on the metals and nondissociatively over the first form. Only the first form participates in polymerization. CH_4 and C_2H_6 are readily formed during the first few minutes of the reaction mainly due to acetylene self-hydrogenation and decomposition. In this process new carbon-containing surface areas are created which can participate in polymerization or catalyze this reaction.[15]

This is consistent with the data of Table 1: on the reduced Co/Al_2O_3 catalyst, the yield of liquid hydrocarbons from the H_2 + C_2H_2 mixture is more than twice as high as that on the unreduced sample.

Hence, the presence of surface acid sites and reduced metal species is necessary for productive acetylene hydropolymerization. The latter species favor hydrogen adsorption and coke deposition which promote acetylene polymerization.[13,14]

IR and adsorption studies of the catalysts provide support for the above suggestions.

In the IR spectra of acetylene adsorbed on Al_2O_3, CoO/Al_2O_3, and Co/Al_2O_3, absorption bands at 2800—3000 cm^{-1} typical of CH_2 and CH_3 surface groups arising from acetylene hydrocracking and polymerization are detected (Fig. 1) for all three samples. Analogous data were obtained for polycrystalline cobalt.[16]

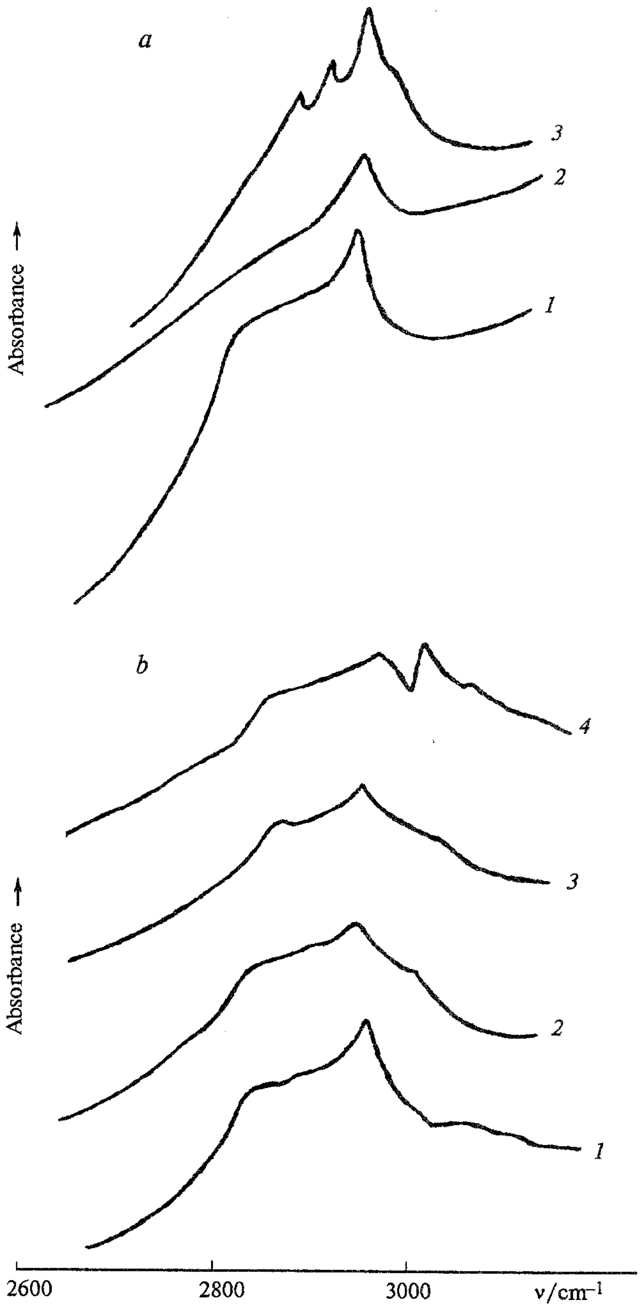

Fig. 1. IR spectra of acetylene adsorbed on the surface of Al_2O_3 (*a*) and Co/Al_2O_3 (*b*): acetylene admission at 40 °C (*1*); evacuation (*2*); addition of H_2 (*3*); heating in H_2 at 350 °C (*4*).

When H_2 is present, methane is formed on all three catalysts at $T > 350$ °C as a result of hydrocarbon hydrocracking; this process occurs to a greater extent on the metal-containing catalyst.

It is known[8,9] that acetylene can be readily polymerized on surface acid sites to form unsaturated compounds. The presence of strong Lewis acid sites on the surface of 10 % Co/Al_2O_3 is confirmed by the pyridine IR-absorption band at 1450 cm^{-1} which does not disappear upon pyridine desorption up to 700 °C.

When 7—8 % v/v CO is added to the acetylene—hydrogen mixture, the characteristics of the process for Al_2O_3 and for the unreduced catalyst remain unchanged (see Table 1). On the other hand, on the reduced catalyst, the yield of liquid products for the $C_2H_2 + H_2 + CO$ mixture increases to ~155 g m^{-3}, whereas the content of unsaturated compounds in the products of catalysis is reduced to 19 %.

No considerable change in the polymerization is found to occur on the addition of CO to the Ar + C_2H_2 mixture (see Table 1).

The results of this study can be explained by applying the model of active sites of the synthesis of liquid hydrocarbons from CO and H_2. According to this model, adsorption of the initial reagents (CO and H_2) occurs on the metal sites, whereas the formation of primary intermediates and their polymerization proceeds on the support.[17] Hence, it is likely that the role of CO in reductive acetylene polymerization consists of the creation of additional active sites for the growth of hydrocarbon chains at ~200 °C, *i.e.*, the temperature of Fischer—Tropsch synthesis on Co-catalysts. In this case, some of the CO molecules are incorporated into the growing hydrocarbon chains. This is proved by the experiments with labelled ^{14}CO (Fig. 2). It was found that CO does not participate in the formation of gaseous products of the synthesis at 210 °C. As the number of carbon atoms in the hydrocarbon chains grows, the relative molar radioactivity, expressed as the ratio between the molar radioactivity of the hydrocarbons formed and that of the original ^{14}CO, and, hence, the probability of carbon monoxide involvement in the formation of this hydrocarbon, increases.

The amounts of adsorbed carbon monoxide and acetylene are found to be 0.0, 0.003, and 0.017 mmol (g Cat)$^{-1}$ (CO) and 0.062, 0.053, and 0.089 mmol (g Cat)$^{-1}$ (C_2H_2) on Al_2O_3, CoO/Al_2O_3, and Co/Al_2O_3, respectively. The unreduced CoO/Al_2O_3 sample adsorbs less acetylene than the pure Al_2O_3 because of the change in the acidity of the latter during calcination with cobalt. The reduced Co/Al_2O_3 catalyst adsorbs a 1.4 times greater volume of acetylene than do CoO/Al_2O_3 and Al_2O_3 due to acetylene adsorption both on the acid sites of the support and the metal sites of the catalyst.[14]

In conclusion, some suggestions on the mechanism of acetylene hydropolymerization in the presence of cobalt catalysts can be made. Acetylene adsorbed on the support is polymerized to oligomers with the participation of the hydrogen atoms formed by dissociative acetylene adsorption. Acetylene adsorbed on the metal sites is involved in hydrogenation and hydrocracking. It yields intermediates, which, in the presence of the hydrogen adsorbed on the metal sites, produce saturated hydrocarbons with even and uneven numbers of carbon atoms. Carbon monoxide that is likewise adsorbed on the metal sites blocks centers for acetylene hydrogenation and creates additional sites for the growing hydrocarbon chains.

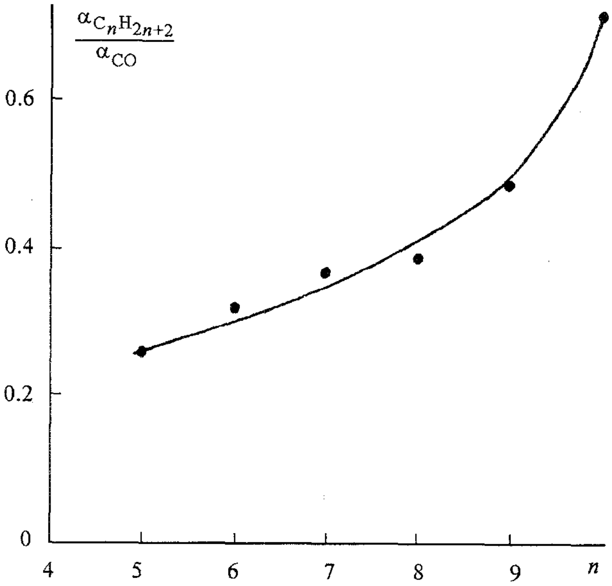

Fig. 2. Molar radioactivity of the hydrocarbons formed as a function of the number of carbon atoms in the chains (10 % Co/Al_2O_3 at p = 0.1 MPa, T = 210 °C, $H_2 : C_2H_2$ = 1.7 : 1, [CO] = 7÷8 % v/v, W = 100 h^{-1}, and t = 2 h).

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