Table 2). The difference in the behavior of the mono- and polydispersed catalysts is apparently related to the nature of the active sites and the complex nature of the effect of temperature on their composition, extent of reduction of the metal, and particle size. The catalysts obtained by impregnation of the support with a solution of H_2PtCl_6 contain chlorine ions which inhibit the hydrogenation of DMEC. The chlorine ions are eliminated upon thermal treatment in a hydrogen stream in addition to the reduction of platinum and the catalyst activity increases. Platinum in the monodispersed catalysts is surrounded by organic ligands and is found as Pt^{n+}, where $0 < n < 2$. The ratio of the zero-valent platinum species to the charged platinum forms is altered and the elimination of the organic residues accompanied by carbonization of the surface and partial caking of the platinum occurs with increasing reduction temperature. These factors lead to a decrease in catalytic activity in the hydrogenation of DMEC with increasing treatment temperature of the monodispersed samples.

CONCLUSIONS

1. The surface composition, electronic state, and catalytic activity were studied for monodispersed (33 Å) and polydispersed platinum catalysts on various supports. Platinum in the starting monodispersed catalysts is in an oxidation state from zero to +2. The specific activity of platinum in the hydrogenation of dimethylethynylcarbinol decreases in the series: $Pt(0 < n < 2) > Pt(0) > Pt(n \geqslant 2)$.

2. Ions in the polydispersed catalysts and carbon-containing fragments in the monodispersed catalysts reduce the catalytic activity of platinum in the hydrogenation of dimethylethynylcarbinol.

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OLIGOMERIZATION OF ISOBUTYLENE ON OXIDES.

2. THERMAL DESORPTION OF C_2-C_4 OLEFINS FOR ALUMINUM-TUNGSTEN AND ALUMINUM-MOLYBDENUM OXIDE CATALYSTS

Yu. S. Khodakov, K. Anders, P. A. Makarov,
R. Feldhaus, Z. Novak, and Kh. M. Minachev

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In our previous work [1], we showed that the oligomerization of isobutylene proceeds rapidly on aluminum-tungsten (ATC) and aluminum-molybdenum (AMC) oxide catalysts [2]. Under these conditions (120-180°C; 600-2400 h^{-1} space velocity), ethylene and propylene do not react [1]. These differences in olefin reactivity may be explained only on the basis of a study of the oligomerization mechanism. This study was carried out in the present work by the thermal desorption method for C_2-C_4 olefins for ATC, AMC, aluminum oxide, and tungsten oxide.

EXPERIMENTAL

Catalysts containing 12 wt.% WO_3 and 15 wt.% MoO_3 on γ-Al_2O_3 and WO_3 were prepared according to our previous method [1]. Prior to the measurements, the samples were heated to 600°C at 10^{-4} torr and then treated with air for 1 h at 0.1 MPa.

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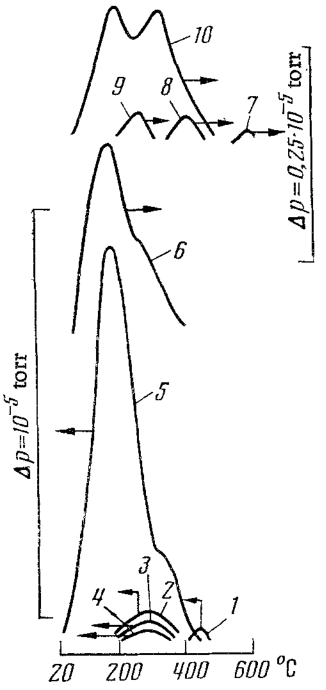

Fig. 1

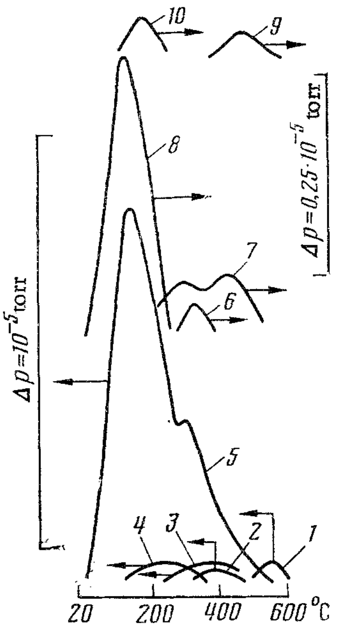

Fig. 2

Fig. 1. Spectra of the desorption products for the aluminum-tungsten oxide catalyst in the case of prior adsorption of C_2-CO olefins. i-C_4H_8: 1) ($CO + CO_2$); 2) C_3H_6; 3) CH_4; 4) C_2H_4; 5) C_4H_8. C_3H_8: 6) C_3H_6. C_2H_4: 7) ($CO + CO_2$); 8) CH_4; 9) C_4H_8; 10) C_2H_4.

Fig. 2. Spectra of the desorption products for the aluminum-molybdenum oxide catalyst in the case of prior adsorption of C_2-C_4 olefins: i-C_4H_8: 1) ($CO + CO_2$); 2) CH_4; 3) C_3H_6; 4) C_2H_4; 5) i-C_4H_8. C_3H_6: 6) CH_4; 7) ($CO + CO_2$); 8) C_3H_6. C_2H_4: 9) ($CO + CO_2$); 10) C_2H_4.

The ampul for the desorption studies was connected to a vacuum system, gas inlet system, and an MKh-7301 monopolar mass spectrometer. The olefin adsorption was carried out for 30 min at 20°C and 250 torr. The products which desorb at 600°C were analyzed in the range from m/z 1 to 100. The system for linear heating of the ampul holding the sample, the measurement procedure, and the purification of the compounds used were described in our previous work [3].

RESULTS AND DISCUSSION

Figures 1-4 show that C_2H_4 and C_3H_6 are adsorbed on Al_2O_3 and WO_3 reversibly. In the other cases, the olefin adsorption is partially irreversible. This leads to a series of products of thermal desorption including hydrocarbons with lower molecular weight than for the starting compound and also CO and CO_2 which are apparently formed due to the partial reduction of the catalyst. In the case of C_2H_4 adsorbed on 12% WO_3/Al_2O_3, C_4H_8 and C_3H_6 are also observed among the desorption products which are apparently formed in an oligomerization reaction and, possibly, by metathesis. The conversion of the adsorbate upon desorption may be estimated from the ratio of the areas for the desorption curve of a given product to the sum of the areas of all the desorption peaks [3].

The data given in Figs. 1-4 indicate that the decomposition of the olefins is least in the case of γ-Al_2O_3. In the experiments with isobutylene, the conversion was 1%. In going to WO_3, the yield of conversion products under the same conditions was 1.5%. The desorption of hydrocarbons terminated at 400 and 300°C for Al_2O_3 and WO_3, respectively. Products of the oxidation of CO and CO_2 were not found in these experiments. In going to ATC and AMC, the thermal desorption spectra showed hydrocarbons and also CO and CO_2, which is partially related to stronger olefin adsorption. Thus, in the case of WO_3, the desorption of isobutylene is terminated at 300°C, while for 12% WO_3/Al_2O_3 and 15% MoO_3/Al_2O_3, the desorption of isobutylene is terminated at 400 and 550°C, respectively. CO and CO_2 appear at these temperatures, probably as a result of reaction with the catalyst lattice oxygen leading to their

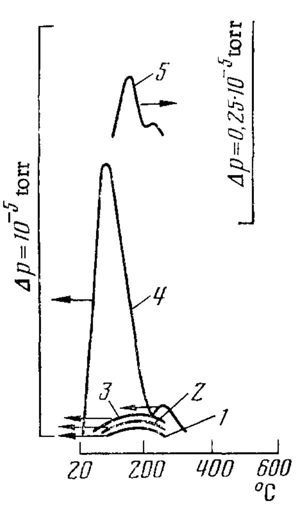

Fig. 3

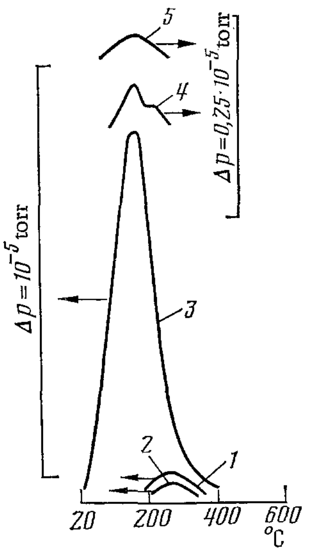

Fig. 4

Fig. 3. Spectra of the products of desorption for WO_3 in the case of prior adsorption of i-C_4H_8 and C_3H_6. i-C_4H_8: 1) C_3H_6; 2) C_2H_4; 3) CH_4; 4) i-C_4H_8. C_3H_6: 5) C_3H_6.

Fig. 4. Spectra of the products of desorption for Al_2O_3 in the case of prior adsorption of C_2-C_4 olefins: i-C_4H_8: 1) C_3H_6; 2) C_2H_4; 3) i-C_4H_8. C_3H_6: 4) C_3H_6. C_2H_4: 5) C_2H_4.

partial reduction. It is interesting to note that in the case of C_2H_4, the regions for the release of hydrocarbons and of CO and CO_2 are distinct. This finding indicates that CO and CO_2 may be formed due to reaction of high-molecular-weight oligomerization products with the catalyst.

The yields of the products (10^{-8} mole/m^2) formed in the thermal desorption of isobutylene are as follows:

Product	Al_2O_3	WO_3	12% WO_3/Al_2O_3	15% MoO_3/Al_2O_3
CH_4	0.05	0.1	5	0.5
C_2H_4	0.2	0.4	8	0.8
C_3H_6	0.1	0.4	4	0.3
C_4H_8	22	36	46	68
CO	–	–	0.11	0.12
CO_2	–	–	0.12	–

The greatest decomposition is found for the 12% WO_3/Al_2O_3 catalyst. The C_1-C_4 hydrocarbons are likely formed in cracking reactions, which may be represented according to Magaril [4] as follows:

$$(CH_3)_3CH \xrightarrow{-CH_4} CH_2{=}CHCH_3 + H_2 \xrightarrow{-CH_4} CH_2{=}CH_2$$

In accord with this scheme, ethylene is formed by the loss of CH_4 from propylene. However, C_2H_4 is not obtained from propylene under these conditions (see Fig. 2). These findings indicate that the C_1-C_3 hydrocarbons are formed concurrently in the decomposition of the same activated complex. A second hypothesis is possible, namely, that irreversibly adsorbed isobutylene is isomerized to n-butylene and the cracking of n-butylene gives the observed product composition.

On the whole, our results indicate that ethylene and propylene are adsorbed in approximately equal amounts but in much smaller amounts than isobutylene. Data are given below for the reverisble adsorption of olefins on the catalysts studied (the adsorption of ethylene on Al_2O_3 was taken as unity) relative to 1 m^2 surface.

Olefin	Al_2O_3	WO_3	12% WO_3/Al_2O_3	15% MoO_3/Al_2O_3
C_2H_4	1.0	–	16	2
C_3H_6	7	8	21	4.4
i-C_4H_8	220	36	460	680

These data permit us to explain the lack of activity for the 12% WO_3/Al_2O_3 catalyst in the oligomerization of ethylene and propylene by their low adsorption. In the experiments with isobutylene, dimers and trimers were not found upon desorption which might have been formed if the oligomerization proceeded by reaction of only adsorbed molecules. In this case, we may assume that the dimerization occurs through a collisional mechanism between an isobutylene molecule from the gas phase and an adsorbed isobutylene molecule. The first-order kinetics for the dimerization [1] indicates in this case that the surface of the aluminum-tungsten oxide catalyst under the reaction conditions is virtually completely occupied by isobutylene.

CONCLUSIONS

1. The products of the thermal desorption of ethylene, propylene, and isobutylene previously adsorbed at 20°C on an aluminum-tungsten oxide catalyst, aluminum-molybdenum oxide catalyst, aluminum oxide, and tungsten oxide were studied in the range from 20 to 600°C. The desorption products contain hydrocarbons with lower molecular weight than the compounds adsorbed as well as CO and CO_2.

2. Ethylene and propylene are adsorbed in approximately equal amounts which are significantly less than the amount of isobutylene adsorbed. Products of the isomerization of isobutylene were not found.

3. The lack of activity of the catalysts in the oligomerization of ethylene and propylene is presumably the result of the low adsorption of these olefins. The oligomerization of isobutylene proceeds by a collisional mechanism with the surface occupied by isobutylene.

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HYDROGENATION OF CARBON MONOXIDE ON NICKEL-CONTAINING CATALYSTS

V. V. Lunin, O. V. Kryukov,
M. M. Savel'ev, and A. L. Lapidus

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Catalytic systems containing intermetallides and their hydrides are active in the transformation of hydrocarbons and nitrogen-containing organic compounds, the synthesis of ammonia, and the methanation of carbon oxides [1-5]. The method for the preparation of intermetallide catalysts involves prior oxidation–reduction treatment at 200-350°C [6] which is accompanied by partial [7] or complete [4] decomposition of these compounds. The catalyst surface is enriched in the active component (Ni, Co, and Fe), and the hydride-forming element (Zr, Hf, rare-earth elements) are selectively oxidized. The formation of a surface ferromagnetic layer of nickel in the ZrNi intermetallide proceeds under more vigorous conditions and at a lower rate than in the case of the hydride $ZrNiH_{2.8}$ [8, 9]. Hence, it was of interest to compare the action of catalysts with the same atomic ratio of metals but differing in method of preparation. In the present work, we studied catalysts containing the ZrNi intermetallide, hydride $ZrNiH_{2.8}$, and 32% Ni/ZrO_2 obtained by combined deposition in the hydrogenation of carbon monoxide under comparable conditions. In all the samples, the Ni:Zr ratio was 1. For this ratio, the ZrNi intermetallide adsorbs the greatest amount of H_2 with the formation of the hydride $ZrNiH_{2.8-3.0}$ [6, 10].

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