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 \( \text{H}_2\text{PtCl}_4 \) 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 \( \text{Pt}^{n+} \), 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: \( \text{Pt}(0 < n < 2) > \text{Pt}(0) > \text{Pt}(n > 2) \).

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.

LITERATURE CITED


OLIGOMERIZATION OF ISOBUTYLENE ON OXIDES.

2. THERMAL DESORPTION OF C₂-C₄ OLEFINS FOR ALUMINUM-TUNGSTEN AND ALUMINUM-MOLYBDENUM OXIDE CATALYSTS


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 C₂-C₄ olefins for ATC, AMC, aluminum oxide, and tungsten oxide.

EXPERIMENTAL

Catalysts containing 12 wt.% WO₃ and 15 wt.% MoO₃ on γ-Al₂O₃, and WO₃, were prepared according to our previous method [1]. Prior to the measurements, the samples were heated to 600°C at 10⁻⁵ torr and then treated with air for 1 h at 0.1 MPa.


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Fig. 1. Spectra of the desorption products for the aluminum-
    tungsten oxide catalyst in the case of prior adsorption of C2-
    CO olefins: 1) (CO + CO2); 2) C3H6; 3) CH4; 4) C2H4;
    9) C4H8; 10) C2H4.

Fig. 2. Spectra of the desorption products for the aluminum-
molybdenum oxide catalyst in the case of prior adsorption of C2-
C4 olefins: 1) (CO + CO2); 2) CH4; 3) C3H6; 4) C2H4; 5)
    CO2); 10) C2H4.

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 C2H4 and C3H6 are adsorbed on Al2O3 and WO3 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 CO2 which are apparently formed due to the partial reduction
of the catalyst. In the case of C2H4 adsorbed on 12% WO3/Al2O3, C4H8 and C3H6 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-Al2O3. In the experiments with isobutylene, the conversion was 1%. In going
to WO3, the yield of conversion products under the same conditions was 1.5%. The des-
orption of hydrocarbons terminated at 400 and 300°C for Al2O3 and WO3, respectively. Pro-
ducts of the oxidation of CO and CO2 were not found in these experiments. In going to ATC and
AMC, the thermal desorption spectra showed hydrocarbons and also CO and CO2, which is par-
tially related to stronger olefin adsorption. Thus, in the case of WO3, the desorption of
isobutylene is terminated at 300°C, while for 12% WO3/Al2O3 and 15% MoO3/Al2O3, the desorption
of isobutylene is terminated at 400 and 550°C, respectively. CO and CO2 appear at these tem-
peratures, probably as a result of reaction with the catalyst lattice oxygen leading to their