FORMATION OF PROPYLENE IN THE REACTION OF METHANE with acetylene on a ${\tt NiO}_{\rm x}/{\tt BN}$ heterogeneous catalyst

Ε.	F. Kvashina, N. V. Chapysheva,	UDC 541.128.13:547.313.3:
Ε.	Yu. Gan'kina, V. N. Chukalin,	542.91:547.211:547.
I.	N. Ivleva, and Yu. G. Borod'ko	314.2

Reaction of methane with acetylene in the presence of a heterogeneous NiO_X/BN catalyst in the temperature range 300-450°C results in the formation of propylene (1% yield). Using ¹³CH₄ it was found that propylene arises both as a product of acetylene conversion and as a hydromethylation product of C₂H₂ with methane. The ratio of heavy and light C₃H₆ in the product mixture was 1:4.

The liquid-phase hydromethylation reaction of acetylene with methane has been shown [1, 2] to occur in the presence of organometallic nickel compounds.

$$CII_{4} + IIC = CII \rightarrow CII_{3} - CII = CH_{2}$$
(1)

The characteristics of this reaction (1) on heterogeneous catalysts containing nickel on various oxide supports $(SiO_2, Al_2O_3, MgO, etc.)$ have also been studied previously [3]. It was found that the methane carbon atom was not incorporated in the propylene product composition, i.e., the latter arose as a product of acetylene conversion only.

Since oxygen-containing support materials induce quite active acetylene decomposition in the temperature range 100-500°C, this makes it difficult either to interpret the catalytic properties of nickel or to decide the question of whether propylene arises solely as the result of acetylene conversion, or if propylene is formed at least in part as a result of C_2H_2 hydromethylation by methane.

This question can be addressed by selecting the experimental conditions such that the yield of C_3H_6 from methane-acetylene is significantly higher than from acetylene alone, and by using labeled ¹³CH₄ in the experiment.

EXPERIMENTAL

Nickel oxide was of a chemically pure grade; $^{13}CH_4$ was 85% enriched, and ultradisperse boron nitride was prepared by a plasma chemical method [4]. Gas mixtures were analyzed chromatographically using an LKhM-8MD chromatograph, and mass-spectrometrically using a MI-1201 instrument.

The catalyst was prepared in the following way. Nickel oxide and boron nitride were mixed beforehand in a 1:7 ratio. The mixture was then annealed in a H₂ atmosphere for 1 h at 500°C; the catalyst was then pumped under vacuum at the same temperature for an extended period of time. The reactions were carried out in a (continuous) flow reactor. The initial pressure of the gaseous reactant mixture was 600 mm Hg, and the gas flow rate was 1 min⁻¹. The initial composition of the reactant mixture was, in mm Hg: C_2H_2 :He = 70:530 (mixture 1); $CH_4:C_2H_2:He = 70:70:460$ (mixture 2). Magnetic susceptibility measurements were made using the Faraday method in the temperature range 80-293 K with a field intensity of 1-10 kOe [5]. Sample preparation and all measurements were carried out in an inert atmosphere. The concentration of ferromagnetic nickel (m_f) was determined from the ratio $n_f = \mu_f/\sigma$, where σ is the specific or limiting saturation magnetization for Ni, equal to 55.5 G·cm³/g; μ_f is the magnetic moment for the ferromagnetic component in the sample, determined from the slope of the curve $\chi = f(1/H)$; and H is the magnetic field strength.

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TABLE 1. C_1-C_4 Product Distribution for Conversion of Product Mixtures on NiO_x/BN Catalyst at 573 K after 10 min

				Reaction products								
Initial mixture p, mm Hg				C·10°, mole/liter								
	CH₄	C_2H_2	He	СН4	C ₂ H ₆	C₂H4	C3H8	C ₃ H ₆	C_4H_{10}	C4H8	C_2H_2	
•	70 	70 70	460 530	66,00 0,88	0,02 0,02	7.50 4.30	-	1,12 0,90	0,02 0,03	0,06 0,05	0,21 0,11	



Fig. 1. Propylene concentration in the sample as a function of time for mixtures 1 (1) and 2 (2). Initial mixture, mm Hg: 1) C_2H_2 :He = 50:550, 2) CH_4 : C_2H_2 : He = 50:50:500. NiO_x/BN catalyst, 573 K.

RESULTS AND DISCUSSION

The catalyst used in the present study was NiO_x/BN . Hexagonal boron nitride proved to be relatively inert with respect to acetylene: BN does not catalyze acetylene conversion, or reaction of the methane-acetylene mixture, in the temperature range 300-500°C.

Nickel oxide in the starting material sample NiO/BN is diamagnetic (the small degree of ferromagnetism (2-3%) is due to the presence of metallic nickel impurity [6]). After annealing under H_2 at 500°C the concentration of ferromagnetic nickel in the NiO/BN catalyst was as high as 75-90%.

Catalytic transformation of either C_2H_2 itself, or a $CH_4-C_2H_2$ mixture, on this catalyst leads to the formation of the same products: ethane, ethylene, propane, propylene, methane, and C_4 -hydrocarbons. However, the quantitative composition of the hydrocarbon product mixture differs in each case in the initial product samples (Table 1). The yields of propylene from acetylene and a methane-acetylene mixture as a function of time are illustrated in Fig. 1. We can see from this data that in the case of the reaction of pure acetylene on freshly prepared catalyst, propylene is formed in significant amounts in the conversion products after 10 min (curve 1), while in the case of reaction of a methane-acetylene mixture C_3H_6 appears in the product mixture in the same proportions after only 2 min (curve 2). The presence of an "induction" period in curve 1 can probably be explained on the assumption that propylene formation requires the time necessary for methane generation from acetylene, and that the former is needed for C_3H_6 formation.

It should be noted that under the process conditions "active carbon" is formed on the catalyst surface, which results in identical, rapid decomposition of both acetylene and a methane-acetylene mixture. This apparently explains the observation that after a fixed period of time the catalytic characteristics of different nickel-containing catalysts become identical, independent of the type of support used.

The yield of propylene from a $CH_4/C_2H_2 = 1$ mixture in the temperature range 300-450°C is always greater than the yield from acetylene alone (Table 2). As the temperature is increased from 300 to 450°C the absolute concentration of propylene in the reaction products decreases. However, the yield from acetylene itself at elevated temperatures decreases more steeply than

TABLE 2. Yield of $[C_3H_6]$ as a Function of Temperature and the Composition of the Initial Reactant Mixture

	[C3II6] · 10	IC.H.I.		
T , K	mixture 1*	mixture 2*	$\frac{\left[C_{3}H_{6}\right]_{1}}{\left[C_{3}H_{6}\right]_{1}}$	
573 653 723	$ \begin{array}{c c} 9.0 \\ 5.1 \\ 1.7 \end{array} $	11.2 7.2 2,6	1,24 1,41 1,53	

*Initial composition, mm Hg: C_2H_2 :He = 70:530 (1); $CH_4:C_2H_2$:He = 70:70:460 (2).

the yield obtained by catalytic conversion of a methane-acetylene mixture. This suggests that in the case of reaction of a methane-acetylene mixture the yield of propylene formed via hydromethylation of acetylene increases with increasing temperature.

These results allowed us to select the reaction conditions for an experiment with $^{13}CH_4$: process temperature 450°C, v = 1min⁻¹; reaction mixture 2.

The reaction products for these two mixtures $CH_4/C_2H_2 = 1$, and ${}^{13}CH_4:C_2H_2 = 1$, were analyzed chromatographically and by mass spectroscopy. From the data in Table 1 we note the propane and C₄-products are formed in trace amounts. Therefore, we can conlude, within experimental error, that the intensity of the ion peak at m/e 42 in the mass spectra of the reaction mixtures is due to the concentration of propylene, and that the intensity of the m/e 43 peak is due to the concentration of propylene enriched with the ¹³C isotope. For propylene itself the intensity ratio (α) for the m/e 43 ion peak (the natural isotopic abundance of ¹³C in propylene) to the m/e peak is 3.5%. In the mass spectra of the product mixtures formed from CH_{μ} + $C_{2}H_{2}$ under the selected experimental conditions the value of α = $6 \pm 1\%$. The discrepancy between these values of α can be attributed to the contributions of propane and butane, which are formed in small amounts. Upon substitution of CH_4 by $^{13}CH_4$ the value of α increased to 33 ± 10%. This fact provides direct evidence for the participation of methane in propylene formation. Based on analysis of the mass spectra of the products obtained upon catalytic conversion of a ${}^{13}CH_4/C_2H_2 = 1$ mixture we can estimate the ratio of the "heavy" propylene ${}^{13}C_{3}H_{6}$ to "light" $C_{3}H_{6}$. This analysis revealed that at 450°C the ratio of labeled propylene (m/e 43), formed via hydromethylation of acetylene by methane, to propylene $C_{3}H_{6}$ (m/e 42) obtained via catalytic transformation of pure acetylene was 1:4.

The results of this study have thus demonstrated that for freshly prepared NiO_X/BN catalyst the yield of propylene from a methane-acetylene mixture is higher than the yield for the reaction of pure acetylene. Experiments with ¹³CH₄ further established unequivocally that the carbon atom in methane is incorporated with the composition of the propylene product.

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