PHYSICAL CHEMISTRY

HYDROGENATION OF CARBON MONOXIDE OVER TECHNETIUM CATALYSTS

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UDC 542.941.7:546.262.3-31: 546.718

Supported Tc catalysts are active in CO hydrogenation, their activity depending on the nature of the support. The reaction proceeds predominantly toward methane formation. All catalysts studied yielded very little C_2 and C_3 hydrocarbons. The thermal desorption data indicate that the CO strongly bound to the substrate is responsible for CH₄ formation.

Keywords: technetium, catalyst, hydrogenation, carbon monoxide.

Technetium catalysts are used in aromatization of alkanes and cyclohexanes, benzene hydrogenation, and dehydrogenation of alcohols [1, 2].

In the present work catalytic properties of technetium catalyst samples were studied in the hydrogenation of CO.

EXPERIMENTAL

The catalysts were prepared by soaking the support material in a NH₄TcO₄ aqueous solution followed by drying at 100°C for 2 h. The hydrogenation was carried out for 2 h at 270°C and 12 h at 500°C. The supporting materials were γ -Al₂O₃, SiO₂ (KSK-2), Y₂O₃, and MgO obtained by decomposition of hydroxides precipitated from the corresponding nitrate salt solutions. The size of the support granule was 1.5-2.0 mm. The Tc content of the catalyst was determined radiometrically.

The catalytic hydrogenation was performed in a KL-1 apparatus. The starting material was supplied in 0.64 ml-size pulses to the catalyst. The CO and H₂ were predried over molecular sieves at $\sim 20^{\circ}$ C. The starting gas mixture was CO:H₂ = 1:2 by volume.

The (CO + H_2) pulses were carried out in a 40 ml/min helium flow over the catalyst. The product yield increased with the number of pulses. Therefore the process was carried out until the product yield remained unchanged [3]. The number of pulses required to reach a constant yield was 30-40 pulses at low, and 10-15 at high temperature.

The gas mixtures were analyzed on a Tsvet-100 chromatograph. The starting mixture was analyzed using a 1-m 5 Å molecular sieve packed column at 25°C, and the effluent gases on a 3-m polysorb column at 70°C, with a flame-ionization detector.

The catalyst surface area was determined using the BET method with low-temperature krypton adsorption. The Tc specific surface area was determined by hydrogen chemisorption at 25°C. For calculations the comparative method was used. The average Tc particle size (D) was calculated using

$$D = \frac{6 \cdot 10^4}{S_{\rm sp} \rho}, \, {\rm A} \, [4],$$

where S_{sp} is the specific Tc coverage in m²/g Tc, and ρ the Tc metal density equals 11.5 g/cm³.

Thermal desorption was carried out in a stream of Ar by the linear programming method increasing the temperature from 20 to 1000° at 20 K/min.

RESULTS AND DISCUSSION

The basic characteristics of the catalysts are given in Table 1.

It was established that the original support materials do not exhibit any catalytic activity at all experimental conditions. In the presence of Tc all catalysts predominantly produced methane. The reaction started at ~210°C and the conversion of CO(X) into methane increased with increasing temperature. The highest conversion yields were obtained with Tc/ γ -Al₂O₃, and

Institute of Physical Chemistry, Russian Academy of Sciences, 117915 Moscow. Translated from Izvestiya Akademii Nauk, Seriya Khimicheskaya, No. 7, pp. 1507-1511, July, 1992. Original article submitted May 24, 1991.



Fig. 1. Temperature dependence of the Tc specific activity on various supports: 1) γ -Al₂O₃; 2) SiO₂; 3) Y₂O₃; 4) ZrO₂; 5) MgO.

Fig. 2. Thermal desorption spectrum from the $Tc/\gamma\text{-}Al_2O_3$ surface: 1) CO; 2) H_2.

Catalyst	$S_{gen}, (m^2/g)$	S _{sp} , (m²/g Tc)	D. Å
1.7% Tc/γ-Al ₂ O:	82.7	91.0	57
1.7% Tc/MgO	33.4	106.7	49
2.3% Tc/SiO ₂	130.5	45.5	115
1.0% Tc/Y ₂ O ₃	30.5	95.0	55
1.1% Tc/ZrO ₂	5.3	41.5	126

TABLE 1. Properties of the Catalysts

the lowest with Tc/MgO (>5% conversion at 380°C) in the temperature range studied. The catalyst activity calculated per 1 g Tc decreased in the following order (Fig. 1):

$$Tc/\gamma - Al_2O_3 > Tc/SiO_2 \sim Tc/Y_2O_3 > TcZrO_2 > Tc/MgO(200-300^\circ)$$
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Support	T. 'G	X. %	Composition (vol. %)			Ε.	
			Сн.	C₂Hε	C3H6	(kJ/mole)	
γ-Al₂O₃	240 300	28.0 74.0	81.0 96.2	17.9 3.9	1.1	127.5	
SiO_2	360 230 310	84.0 0.5 25.0 75.0	100.0 64.0 81.1	26.4 16.7	9.5 2.3	118.6	
MgO	270 300 360	0.4 2.0	95.8 72.7 76.1 79.4	4.2 20.4 20.6	6.7 3.2		
Y_2O_3	290 360	8.0 34.0	80.9 87 9	16.7	2.4	100.7	
ZrO2	240 270 310	1.0 12.0 38.5	65.8 79.9 88.5	25.1 16.9 10.9	9.1 3.2 0.6	124.4	

TABLE 2. Hydrogenation of CO with Tc-Coated Catalysts

TABLE 3. Characteristics of the Thermal Desorption Spectra

	Hydrogen			Carbon monoxide		
Catalyst	Tmax, -C	E _Á . (kJ/mole)	S, %	T _{max} , ·c	E _A . (kJ/mole)	S. %
2.3% Te SiO2 1.7°, Te 7-312O2	125 420 920 190 500	11.0 25.2 32.4 8.7 14.9	32.2 18.7 49.1 41.6 58.4	160 410 920 180 460	10.2 20.2 24.0 12.4 14.4	3.9 57.9 38.2 9.9 90.1
17°, Te/My()	160 410 820	9.0 15.5 42.0	20.1 45.5 34.4	180 400 850	7.3 26.0 36.0	14.9 49.1 36.0

At 210-280°C the reaction products contain some C_2H_6 and C_3H_8 (Table 2). The amounts of these hydrocarbons increases steeply with increasing X at T > 300°C and maximum X is reached at T > 350°C.

It was shown by gas-liquid chromatography that no olefins are being formed but a small amount of CO₂ has been found. The CO₂ content increased with increasing temperature at T > 300 °C. The CO₂ presence can be explained by the less than stoichiometric H₂:CO ratio, and by the possibility of CO reacting with H₂O formed during the hydrogenation process. The reaction 2CO \neq CO₂ + C is also not excluded.

The activation energy of the CH_4 formation reaction was calculated for low X values (Table 2). The results are in agreement with the literature [3, 5, 6].

The H₂ and CO thermal desorption spectra from Tc catalysts exhibit two distinct maxima; some samples have also a third peak (Table 3). This indicated the inhomogeneity of the Tc catalyst surfaces. The thermal desorption spectra of CO and H₂ from Tc/ γ -Al₂O₃ are given in Fig. 2. It can be concluded that CO forms stronger and weaker bonds on two different substrate sites, the portion of the stronger bond being larger.

The thermal desorption kinetics follows a second-order reaction which is indicative to the dissociative character of the gas adsorption. The thermal desorption activation energies are given in Table 3. For all catalysts the activation energies E_A of the weakly bound forms are practically the same, whereas that for the strongly bound forms differ. It appears that the strongly bound CO is effective in the hydrogenation reaction on technetium catalysts, since the CH₄ and CO₂ contents in the effluent increase with increasing temperature when, at the same time, the presence of strongly bound CO is higher. The presence of small amounts of C₂ and C₃ in the effluent can be explained by the effect of an insignificant amount of weakly bound forms of H₂ and CO. It was shown in [7] that the weakly bound forms of CO participate in the synthesis of liquid hydrocarbons.

It has been shown in [1] that complex active centers are being formed by interaction of the deposited Tc and the substrate. Such an interaction does not take place at SiO₂ and the deposited Tc is reduced to the metal. On γ -Al₂O₃, Y₂O₃, and MgO Tc is, along with the metallic form, also present in an ionized form, which had a modifying effect on the catalytic process of dehydrogenation of hydrocarbons and alcohols [1]. The CO hydrogenation process occurred on all studied catalysts. The high activity of the SiO₂-based catalyst indicates that the reaction is taking place on the metallic Tc sites.

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