HYDROGENATION OF BENZENE ON TECHNETIUM CATALYSTS

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The problem of performing the hydrogenation of benzene to give cyclohexane in the production of caprolactam has led to the search for new efficient catalysts for this reaction. Kubicka [1] has shown that $Tc/\gamma\text{-}Al_2O_3$ displays activity in the hydrogenation of benzene. We have studied the activity of technetium on various supports since a significant effect of the nature of the support on the activity of technetium has been reported [2, 3].

EXPERIMENTAL

The catalysts were prepared by impregnation of various supports by an aqueous solution of ammonium pertechnetate of a given concentration in a rotary evaporator. The dried catalyst samples were roasted for 12 h at 700°C in a hydrogen stream. The Tc content in the prepared catalysts was determined radiometrically. Industrial samples of $\gamma\text{-}Al_2O_3$, MgO, Y_2O_3, ZrO_2 and KSK-2 SiO_2 were used as the supports. The catalyst activity was studied in a microcatalytic pulse system at 1 atm. The reaction products were analyzed by gas—liquid chromatography on an LKhM-8MD chromatograph using a 3 m column packed with 20% tricresyl phosphate on Celite. Electrolytically pure H_2 was introduced at 100 cm^3/min which for 1 cm^3 catalyst is $v_{vol} = 6000\ h^{-1}$. Benzene was introduced into the reactor in small pulses ($11.27 \cdot 10^{-6}$ mole benzene or multiple) using a microsyringe. The total specific surface of the catalyst was determined by the BET method relative to the low-temperature adsorption of krypton. A relative method was used for the chemisorption method for the determination of the specific surface of Tc [4, 5]. Preliminary experiments showed that the chemisorption method may be used to find the specific surface of Tc if its content in the catalyst is ≦1%. For low Tc contents, the measurements led to overestimated chemisorption capacity of the support due to the effect of the metal [6, 7].

RESULTS AND DISCUSSION

All the catalysts prepared display more or less catalytic activity in the hydrogenation of benzene except for 5% Tc/SiO_2 (0.1% conversion). Only cyclohexane is formed at 148-190°C. The rate of the reverse reaction increases with increasing temperature and lower hydrocarbons appear (Fig. 1). The benzene conversion depends on the nature of the support (Fig. 2). For approximately the same technetium content, the catalysts prepared with $\gamma\text{-}Al_2O_3$ are most active.

In order to compare the catalytic activity of Tc with its chemical analogs, we studied 2% $Re/\gamma\text{-}Al_2O_3$ under conditions identical to those described above. Figure 2 (curve 2) shows that the rhenium catalyst is less active at low temperatures and its activity drops sharply above 180°C, in contrast to the technetium catalyst of the same concentration.

The apparent activation energy calculated for the first-order reaction constants obtained using the equation of Penchev et al. [8] was close to that obtained by Kubicka [1] (33.0-35.0 kJ/mole)

$$k=\frac{F}{W}\ln\frac{1}{1-X}$$

where F is the rate of the hydrogen flow, ml/min, W is the catalyst mass, g, and X is the conversion.

Using the values obtained for the specific surface of Tc, we were able to evaluate the specific activities of the catalysts studied (Table 1).

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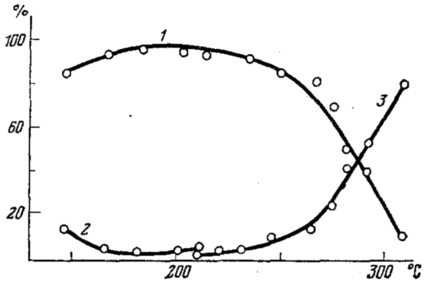

Fig. 1

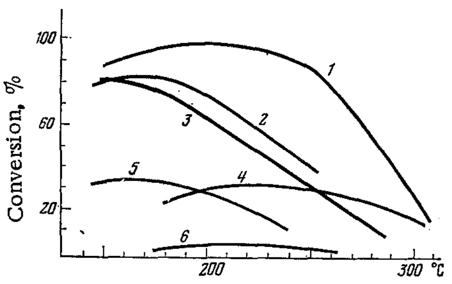

Fig. 2

Fig. 1. Change in the composition of the reaction products (%) relative to temperature on the catalyst 1.9% Tc/γ-Al_2O_3: 1) benzene, 2) cyclohexane, 3) C_2-C_6 hydrocarbons.

Fig. 2. Temperature dependence of conversion on catalysts: 1) 1.9% Tc/Al_2O_3, 2) 2.0% Re/Al_2O_3, 3) 1.1% Tc/Y_2O_3, 4) 1.8% Tc/MgO, 5) 1.0% Tc/SiO_2, 6) 5.9% Tc/SiO_2.

TABLE 1. Catalyst Characteristics

To catalyst, %/support	S_{tot} (BET)	S_{Tc} (H_2 chemisorption)	S_{Tc}, m^2 (in sample	A_{sp}, $\frac{\text{mole } C_6H_{12}}{M^2\ Tc}$
	m^2/g			
2,0Tc/Al_2O_3	86,2	30	0,3918	18,4
2,0Tc/Al_2O_3 *	86,2	30	0,3067	19,8
1,9Tc/Al_2O_3	123,5	20	0,3095	21,1
0,6Tc/Al_2O_3	139,5	35	0,1980	13,7
1,8Tc/MgO	66,5	20	0,2961	14,8
1,0Tc/ZrO_2	8,2	12	0,1666	23,3
1,1Tc/Y_2O_3	11,8	25	0,3433	27,2
5,0Tc/SiO_2	86,2	8	0,0135	16,6

*Tests repeated after six months.

Table 1 shows that A_{sp} is virtually the same for all the catalysts with the exception of 1.1% Tc/Y_2O_3, probably due to the participation of yttrium oxide in the catalysis of the hydrogenation reaction.

Thus, the effect of the nature of the support on the activity of technetium in hydrogenation is less pronounced than in the case of previously reported processes involving the dehydrogenation of alcohols and naphthenes [2, 3].

CONCLUSIONS

1. The specific activity of technetium on various supports in the hydrogenation of benzene is only slightly dependent on the nature of the support.
2. Catalysts containing technetium are more active than those containing rhenium.

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