# SPECIFIC ACTIVITY OF $\gamma$-Al$_2$O$_3$ SUPPORTED RHENIUM FOR HYDROGENA - TION AND HYDROGENOLYSIS OF BENZENE IN RELATION TO METAL CONCENTRATION AND DISPERSITY

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A negative influence of low concentration and of high dispersity of $\gamma$-Al$_2$O$_3$ supported rhenium (1.04 wt.% and 10.4 wt.% l=1.5-7.1 nm) on its specific activity for hydrogenation and hydrogenolysis of benzene at 365-573 K is described.

Описывают отрицательное влияние низкой концентрации и высокой дисперсности рения, нанесенного на $\gamma$-Al$_2$O$_3$ (1,04 вес.% и 10,4 вес.%, $\ell$ =1,5-7,1 нм), на его специфическую активность в гидрогенизации и гидрогенолизе бензола при 363-573 К.

## INTRODUCTION

The data on the hydrogenation of benzene on rhenium catalysts are rather scarce and only few works refer to the activity of rhenium for this reaction in comparison with that of platinum metals [1,2] or in relation to the physicochemical characteristics of the catalysts [3,4]. Previous investigations showed that the reaction of benzene with hydrogen on rhenium just as on ruthenium consists in hydrogenation to cyclohexane and at sufficiently high temperatures also in hydrogenolysis to normal alkanes [1]. In a further study on a number of Ru/$\gamma$-alumina catalysts, a decrease of the specific activity

of ruthenium with the decrease of average metal particle size
was established, the effect having been more pronounced for
hydrogenolysis [5]. This paper presents the results of similar
investigations on Re/γ-alumina catalysts of the metal dispersity
determined by hydrogen chemisorption.

EXPERIMENTAL

The catalysts were obtained by impregnation of a high·
purity γ-alumina ($a_s$=230 m$^2$/g) with aqueous solutions of am-
monium perrhenate (Biddle Sawyer and Co.) [6]. The investiga-
tions were carried out by a microreactor chromatographic pulse
method described previously [1,5] using a benzene dose of
7.42x10$^{17}$ molecules and 1.5-30.0 mg catalyst samples of the
grain size $\phi \leqslant 0.12$ mm for which the absence of inner diffusion
limitations had been established in preliminary tests. The ac-
tivity determined for fresh catalysts reduced by a stream of
hydrogen at 823 K during 10 h, as well as for the catalysts
redispersed by suitable preheating in oxygen gave two series of
results denoted as series 1 and 2, respectively. Thermal pre-
treatment of the catalysts of both series 1 and 2 was identical
to that applied before adsorption measurements. It consisted in
repeated heating at 823 K in the adsorption apparatus in hydro-
gen at 300 Torr (1 Torr=133.3 N/m$^2$) for 2 h and then in vacuum
for another 2 h. After transferring into the microreactor the
catalyst was heated at 753 K in a hydrogen stream over 10 h
and additionally for 2 h after each pause in measurements. Re
powder (Johnson and Matthey) preheated in hydrogen and in vacu-
um at 673 k of the 1.72 m$^2$/g surface area derived from argon
physisorption [7] was also used in this study.

RESULTS AND DISCUSSION

In Table 1 the dispersity data for the catalysts employed
in this work are given.

Figures 1 and 2 present temperature dependence of benzene
conversion on supported catalysts. On each catalyst the yield

Table 1

Dispersity data [6,7]

| Re content | Series | D (H/Re total) | $A_s$ ($cm^2$/g Re) | $\ell$ (nm) | m (mg) | $a_s$ ($cm^2$) |
|---|---|---|---|---|---|---|
|  | 1 | 0.34 | $70 \times 10^4$ | 4.0 | 30.0 | 220 |
| 1.04 wt.% | 2 | 0.90 | $190 \times 10^4$ | 1.5 | 30.0 | 600 |
|  | 2 | 0.90 | $190 \times 10^4$ | 1.5 | 10.0 | 200 |
|  | 2 | 0.90 | $190 \times 10^4$ | 1.5 | 5.0 | 100 |
| 10.4 wt.% | 1 | 0.19 | $40 \times 10^4$ | 7.1 | 2.5 | 100 |
|  | 2 | 0.26 | $55 \times 10^4$ | 5.2 | 1.5 | 90 |
| 100 wt.% | 1,2 | 0.008 | $1.72 \times 10^4$ | 166 | 5.0 | 90 |

D, $A_s$ and $\ell$ - rhenium dispersity, specific surface area and average particle size, respectively, m - mass of the catalyst sample used for activity measurement and $a_s$ - rhenium surface area in the sample.
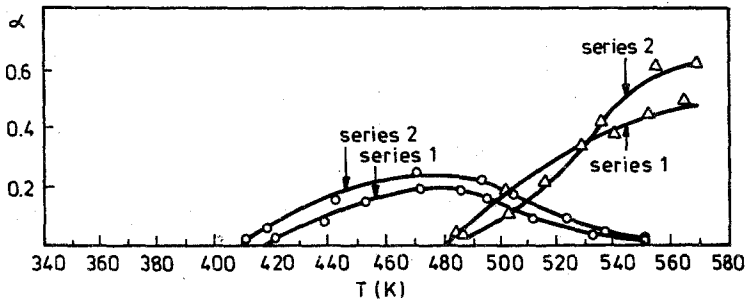


Fig. 1. Temperature dependence of benzene conversion to cyclohexane (o) and to alkanes (Δ) on the 1.04 wt.% Re/γ-Al$_2$O$_3$ catalyst (m=30.0 mg)

of cyclohexane shows a maximum at 440-480 K. Above 480 K alkanes
are      also formed with yields increasing with increasing tem-
perature. Above 530 K they are practically the only reaction
products. A similar temperature dependence of benzene conver-
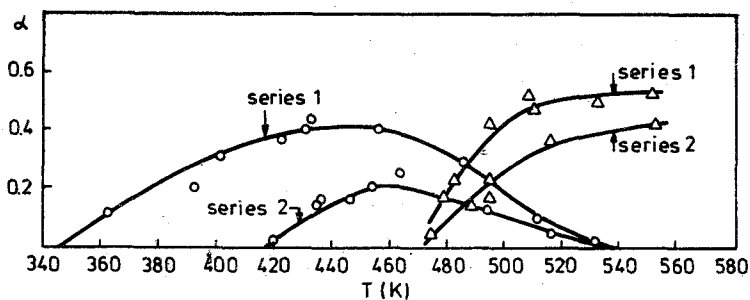sion was obtained on Re powder.



Fig. 2. Temperature dependence of benzene conversion
         to cyclohexane (o) and to alkanes (Δ) on the
         ΐ0.·4 wt.% Re/γ-Al$_2$O$_3$ catalyst (m=2.5 mg or
         1.5 mg)

The data of Figs  1 and 2 and of Table 1 indicate that
benzene conversion on various catalysts is not simply related
to the metal surface area. On the 1.04 wt.% Re/γ-Al$_2$O$_3$ catalyst
the values of α of series 2 are only slightly higher than those
of series 1 in spite of the large enhancement of the metal sur-
face area in the catalyst after the treatment with oxygen. The
values of α of series 1 on the 10.4 wt.% Re/γ-Al$_2$O$_3$ catalyst
are much higher than those obtained at 1.04 wt .% rhenium in
the catalyst although the metal surface area in the latter is
higher.
     The specific activities of the catalysts for hydrogenation
and hydrogenolysis of benzene are expressed as the mean rates
of benzene conversion to cyclohexane and to alkanes, respectively,
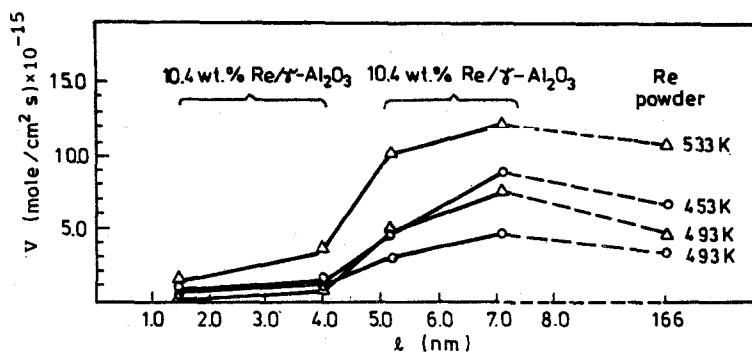per unit surface area of rhenium and calculated in a manner simi-

Fig. 3. Specific activity of rhenium for benzene
hydrogenation (o) and hydrogenolysis (Δ)
in dependence on its concentration and
average particle size.

lar to that applied for ruthenium [5]. In Fig. 3 representative
data obtained at 453 K, 493 K and 533 K are shown in dependence
on the concentration and average particle size of rhenium.

It is evident that low concentration and high dispersity
of rhenium are unfavorable for its specific activity in both
reactions and especially in hydrogenolysis. The results obtai-
ned on the 10.4 wt.% Re/γ-Al$_2$O$_3$ catalyst with $\ell$ equal to 7.1 nm
and 5.2 nm do not differ essentially from those found on Re
powder. The differences in V if any do not exceed a few tens of
pecents and seem to be insignificant. However, the decrease of
rhenium concentration in the catalyst to 1.04 wt.% and simulta-
neously of its average particle size below 5.2 nm is accompa-
nied by a sharp decrease of the specific activities to the
values which at 493 K and $\ell$=1.5 nm are lower than those on Re
powder 5 times for hydrogenation and 40 times for hydrogenoly-
sis. The apparent activation energies amount to 35-45 kJ/mol
and 45-80 kJ/mol, respectively, and does not show any distinct
dependence on the concentration and average particle size of
rhenium.

The data given for the 1.04 wt.% Re/γ-Al$_2$O$_3$ catalyst of
series 2 with $\ell$ = 1.5 nm in Figs 1 and 3 refer to the catalyst

sample with the metal surface area $a_s = 600$ $cm^2$ which was much higher that than in other catalysts. However, the low specific activity of this catalyst as compared with that found at 10.4 wt.% of rhenium seems to be real since the measurements performed at some temperatures on smaller catalyst samples of $a_s$ equal 200 $cm^2$ and 100 $cm^2$ show a linear relation between the conversion $\alpha$ and the amount of catalyst resulting in the values of V identical to those given in Fig. 3.

The negative influence of low average particle size of rhenium on its activity for the reaction of benzene with hydrogen has a parallel in that found earlier for ruthenium [5]. In both cases the results may be indicative of low activity of very small metal particles. The present results are also in agreement with those of Minachev et al. who found decreased activity of $\gamma$-$Al_2O_3$ supported rhenium for benzene hydrogenation at low concentration and high dispersity of the metal [4]. The effect seems to be connected mainly with the interaction of rhenium with $\gamma$-alumina. In this system a rather strong metal-support interaction is possible, resulting in the bonding of predominating part of the metal at low concentration to the support in the form of oxide complexes which are hardly reduced to the zerovalent state [8,9]. There are data indicating that such a reduction of supported rhenium catalysts is necessary for their activity in benzene hydrogenation [3]. The state of rhenium in the catalysts used in this study is to be dealt with in further work.

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