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The influence of thermal pretreatment of Re/γ-alumina catalysts in hydrogen on their activity for hydrogenation and hydrogenolysis of benzene

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The specific activity of Re/γ-alumina catalysts (10.4 and 1.04 wt% Re) preheated in hydrogen at 550–800°C for benzene hydrogenation and hydrogenolysis at 80–300°C has been found to not change or to increase with increasing pretreatment temperature, respectively. The results are discussed in relation to the metal dispersion.

Keywords: Re/γ-alumina; H_2 pretreatment; benzene hydrogenation and hydrogenolysis

1. Introduction

The data on the reaction of benzene with hydrogen on rhenium catalysts are rather scarce and only few works refer to the activity of rhenium for this reaction in comparison to that of platinum metals [1,2] or in relation to some physicochemical characteristics of the catalysts [3–5]. Previous investigations showed that the reaction of benzene with hydrogen on rhenium just as on ruthenium resulted in hydrogenation to cyclohexane and at sufficiently high temperatures also in hydrogenolysis to normal alkanes [1]. The study on γ-alumina supported rhenium catalysts (10.4 and 1.04 wt%) revealed some differences in the activity of rhenium for both reactions in relation to its concentration and dispersion [5]. In the present work hydrogenation and hydrogenolysis of benzene at 80–300°C has been investigated on the same catalysts preheated in hydrogen at 550–800°C of the surface area and dispersion of rhenium characterized in ref. [6]. The investigations provided the first data on the dependence of the specific activity of rhenium for hydrogenation and hydrogenolysis of benzene on the temperature of the catalyst pretreatment in hydrogen. New data on the differences in the sensitivity of both reactions to the dispersion of rhenium are also presented.

2. Experimental

The experiments were performed on the catalysts obtained by impregnation of a high-purity γ-alumina ($a_s = 230\ m^2/g$) with aqueous solutions of ammonium perrhenate (Biddle Sawyer Co.), subjected to the standard pretreatment in hydrogen and in vacuo at 550°C and on the same catalysts heated additionally in hydrogen at 300 Torr pressure (1 Torr = 133.3 N/m^2) at 600, 700 or 800°C for 5 h and 15 h followed by degassing at the same temperature for 2 h [6].

The surface area and dispersion of rhenium were determined from hydrogen chemisorption at 300°C using a pulse chromatographic method [6]. Additionally, for some samples of the 10.4 wt% Re/γ-alumina catalyst, estimation of the mean crystallite or particle size of rhenium has been done by X-ray diffraction and transmission electron microscopy (Philips CM 20). Unfortunately, we did not succeed in obtaining such estimations for the 1.04 wt% Re/γ-alumina catalyst.

The reactions of benzene with hydrogen were studied with a microreactor pulse method in a chromatographic system described previously [1,5], using catalyst samples weighting 2.5 or 30 mg and a benzene dose of 7.42×10^{17} molecules. After transferring into the microreactor the catalyst was heated in a stream of hydrogen at 500°C for 20 h and after each pause in the experiments additionally for 2 h. The pulses of benzene vapour diluted by hydrogen to 0.25 cm^3 volume were introduced on the catalyst every 20 min, necessary for changing the catalyst temperature and sweeping out the residue of hydrocarbons from the previous experiment. Electrolytical grade hydrogen purified by passing over a Deoxo catalyst (Engelhard) at 20°C and a 5A molecular sieve at −195°C was used as a reactant and carrier gas.

3. Results and discussion

The characteristics of the catalysts used in the study are given in table 1. The chemisorption data show that the tenfold decrease in the concentration of rhenium in the catalyst subjected to the standard pretreatment at 550°C is accompanied by the twofold increase in its surface area and dispersion. The increase of the pretreatment temperature of the catalysts from 550 to 800°C results in a gradual decrease of the metal surface area and dispersion. The change is not very significant and does not exceed 30 or 40%. A rather small change of the dispersion of rhenium in the high percentage catalyst upon the applied thermal pretreatment emerges also from the values of the mean crystallite size determined by the X-ray method l(X-ray), as well as of its mean particle size determined by electron microscopy l(TEM), given also in table 1. Both X-ray and electron diffractograms obtained for this catalyst contained only the lines of γ-alumina and of the metallic phase of rhenium. This indicates that at the applied temperatures of hydrogen pretreatment of the catalyst the prevailing part of rhenium compound supported on γ-alumina was reduced to the zero-valence rhenium.

Table 1
Characteristics of the catalysts[a]

H_2 pre-treatment	A_s (10^4 cm^2/g Re)	D (H/Re)	l(chem) (nm)	l(TEM) (nm)	l(X-ray) (nm)	m (mg)	a_s (cm^2)
10.4 wt% Re/γ-Al_2O_3 catalyst							
550/20[b]	81	0.39	3.4	3.6 (3.6)[d]	5.4	2.5	210
550/20, 600/5[c]	78	0.37	3.5	3.9		2.5	200
550/20, 600/15[c]	70	0.33	4.0		5.5	2.5	180
550/20, 700/5	69	0.32	4.0	3.6		2.5	180
550/20, 700/15	65	0.31	4.2			2.5	170
550/20, 800/5	65	0.31	4.2	4.9		2.5	170
550/20, 800/15	63	0.30	4.4		6.0	2.5	160
1.04 wt% Re/γ-Al_2O_3 catalyst							
550/40[b]	164	0.77	1.7			30	510
550/40, 600/5[c]	155	0.74	1.8			30	480
550/40, 600/15[c]	190	0.90	1.5			30	590
550/40, 700/5	128	0.61	2.2			30	400
550/40, 700/15	138	0.66	2.0			30	430
550/40, 800/5	131	0.62	2.1			30	410
550/40, 800/15	106	0.51	2.6			30	330

[a] A_s, D and l(chem) denote rhenium specific surface area, dispersion and average particle size, calculated from chemisorption data [6], m is the mass of the catalyst sample used for activity measurement, a_s the rhenium surface area in the sample.

[b] 550°C 20 h (or 40 h).

[c] 550°C 20 h (or 40 h) and 600°C 5 h (or 15 h).

[d] Average particle size of rhenium after activity measurements.

The temperature dependence of benzene conversion on all catalysts was similar to that described previously [5]. In each case the yield of cyclohexane showed a maximum at a temperature within the range of 160–200°C. Above 180–210°C alkanes were also formed with yield increasing with temperature. They consisted mainly of methane which above 260°C was practically the only reaction product. Fig. 1 presents typical results obtained on the catalysts given the standard pretreatment at 550°C and on those preheated additionally at 800°C for 5 h.

In general, the conversion of benzene to cyclohexane, as well as to alkanes decreased with increasing pretreatment temperature. The data of fig. 1 show that the maximal decrease of the conversion to cyclohexane amounts to several tens percent and could be related to decreasing surface area of rhenium. Only the conversion to alkanes on the high-percentage catalyst is enhanced by about 20% at increase of the pretreatment temperature from 550 to 800°C.

It is to be added that the fraction of benzene converted to cyclohexane or to aliphatic hydrocarbons was well reproducible (within 10%) and no change of the sample activity was observed during several weeks. This indicates that the catalysts and their active surface did not undergo any significant change during the reaction

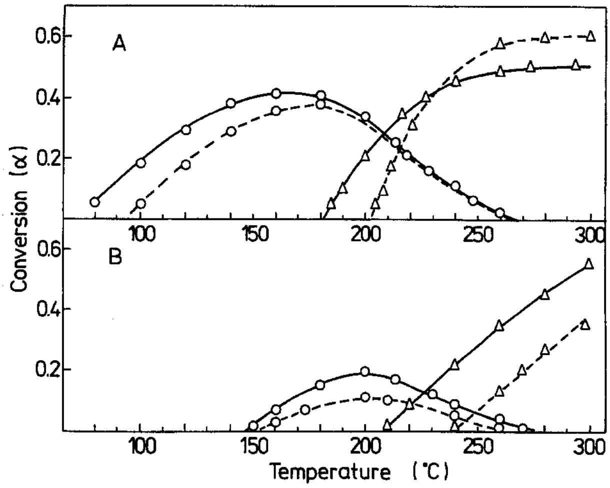

Fig. 1. Temperature dependence of benzene conversion to cyclohexane (○) and to alkanes (△) on the catalysts preheated in hydrogen at 550°C (——) and at 800°C (- - -); (A) 10.4 wt% Re/γ-alumina catalyst, (b) 1.04 wt% Re/γ-alumina catalyst.

and multiple activity measurements. The stability of the high-percentage catalyst was also confirmed by the values of *l*(TEM) and by the electron diffractograms which were identical before and after the activity measurements (cf. table 1). The chemisorption and X-ray investigations were not performed after the reaction as they required much larger samples than those used in the activity measurements.

Using plots like these in fig. 1 and the chemisorption data of table 1 the specific activity of the catalysts for hydrogenation and hydrogenolysis of benzene at various temperatures was determined. It was expressed as the mean rate V of benzene conversion to cyclohexane or to alkanes, respectively, per unit surface area of rhenium and calculated in a manner analogical to that applied previously [5]. In fig. 2 representative data obtained at 180 and 280°C are shown in dependence on the temperature of the catalyst pretreatment in hydrogen.

It is evident that the influence of the applied thermal pretreatment of the catalysts in hydrogen on their specific activity depends on the reaction and is different for the 10.4 wt% Re/γ-alumina and for the 1.04 wt% Re/γ-alumina catalyst. No effect is observed for hydrogenation of benzene on both catalysts and for benzene hydrogenolysis on the low-percentage catalyst. However, the specific activity of the high-percentage catalyst for benzene hydrogenolysis increases with the pretreatment temperature reaching the maximum gain of about 60% for the catalyst preheated at 800°C. The apparent activation energies for hydrogenation and hydrogenolysis amounted to 38–46 kJ/mol and 71–82 kJ/mol, respectively, and did not change significantly with the catalyst pretreatment.

Following previous data [5] it seems of interest to consider the present results in relation to rhenium concentration and dispersion. In fig. 3 the specific activity of

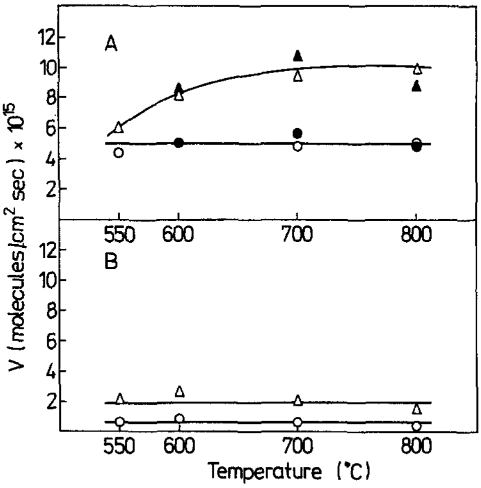

Fig. 2. Specific activity of the catalysts for benzene hydrogenation at 180°C (○, ●) and hydrogenolysis at 280°C (△, ▲) in dependence on the temperature of their hydrogen pretreatment for 5 h (○, △) or 15 h (●, ▲); (A) 10.4 wt% Re/γ-alumina catalyst, (B) 1.04 wt% Re/γ-alumina catalyst.

the catalysts for benzene hydrogenation at 180°C and hydrogenolysis at 280°C is plotted in dependence on the content and average particle size of rhenium l(chem) including the results obtained previously for rhenium powder [5].

In agreement with previous results [5] the data of fig. 3 show that low concentration and high dispersion of rhenium are disadvantageous for its activity in both reactions, the effect being more pronounced for hydrogenolysis. The specific activity of the low-percentage catalyst with the average particle size of rhenium $l = 1.7$–2.6 nm is for both reactions several times lower than that of the high percentage catalyst with $l = 3.4$–4.4 nm and of rhenium powder with $l = 166$ nm. The specific activity of the high-percentage catalyst for hydrogenation is close to that of

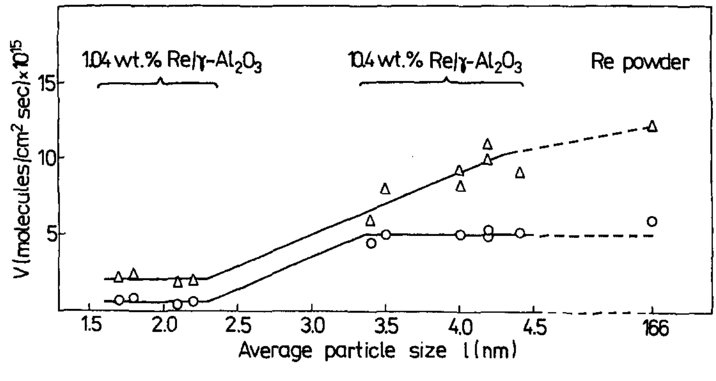

Fig. 3. Specific activity of the catalysts for benzene hydrogenation at 180°C (○) and hydrogenolysis at 280°C (△) in dependence on rhenium concentration and average particle size.

rhenium powder and does not change at increase of rhenium average particle size from 3.4 to 4.4 nm following the applied increase of the catalyst pretreatment temperature. However, the above increase of l is accompanied by an almost twofold enhancement of the specific activity of the catalyst for hydrogenolysis. The results may be indicative of low activity of very small metal particles for both reactions and of particularly high specificity of active sites in hydrogenolysis. The negative influence of decreasing particle size of rhenium on its activity for hydrogenation of benzene has a parallel in the effects reported for other metals like palladium [7], ruthenium [8], rhodium [9] and nickel [10,11]. A high suppression of hydrocarbon hydrogenolysis by increased dispersion of metals is known as well [12].

The data presented allow us to conclude that the influence of the increasing temperature of hydrogen pretreatment of Re/γ-alumina catalysts from 550 to 800°C on their activity for benzene hydrogenation consists mainly in decrease of the metal surface area. Hence the activity referred to the unit surface area of rhenium is independent of the catalyst pretreatment. However, simultaneous increase of the average particle size of rhenium is advantageous for benzene hydrogenolysis and results in a significant enhancement of the catalyst activity for that reaction. More detailed description and interpretation of the effect requires further work. It seems especially appropriate to extend the range of rhenium loadings and of the catalyst pretreatment.

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