The properties of supported rhenium catalysts in the dehydrogenation of cyclohexane

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The 2 % Re/sibunite catalyst is more active than 2 % Re/γ-Al_2O_3 and 2 % Re/θ-Al_2O_3 catalysts in the dehydrogenation of cyclohexane into benzene (T = 350 °C, w = 0.5 h^{-1}). The substitution of NH_4ReO_4 by $HReO_4$ in the preparation of the catalyst enhances its activity by a factor of 1.3. Treatment with HNO_3 or oxalic acid increases the selectivity by a factor of 1.2 and 1.35, respectively, the overall conversion of cyclohexane being 32—40 %.

Key words: supported Re-catalysts, cyclohexane, dehydrogenation.

Previously[1] with supported Pd-catalysts as examples, we demonstrated the influence of the support on their activity and selectivity in the dehydrogenation of cyclohexane, depending on the character of the interaction of the support with an active phase.

In this work, we studied the influence of some factors on the dehydrogenating activity and selectivity of the supported Re-catalysts. They include: the amount of the supported phase of the starting Re^{VII} compounds, preliminary oxiditive treatment (nitric and oxalic acids), and support (sibunite, γ- and θ-Al_2O_3).

Experimental

The reaction was studied in a flow-type quartz reactor containing 2.7 g of a catalyst. Cyclohexane was added through a dosing apparatus at a mass rate w of 0.5 h^{-1} in a flow of hydrogen (υ = 9.4 L h^{-1}). The reaction products were analyzed by GLC using a 3 m×3 mm column filled with polyethyleneglycol adipate (15 %) on Chromosorb P and by refractometry.

Sibunite is granulated pyrocarbon (batch 1001-II), filled mass was 0.6 g cm^{-3}, specific surface $S_{sp}(N_2)$ was 680 m^2 g^{-1}, S_{sp}(phenol) was 230 m^2 g^{-1}, and granule dimensions were 2—3 mm.

γ-Al_2O_3, granulated, S_{sp} was 235 m^2 g^{-1}, filled mass was 0.63 g cm^{-3}, total pore volume V_Σ was 0.65 cm^3 g^{-1}, pore radius r_1 was 220 Å, r_2 < 40 Å, volume V_{r_1} was 0.2 cm^3 g^{-1}, V_{r_2} was 0.45 cm^3 g^{-1}, resistance to abrasion (X_{30}) was 4.1 %, and granule dimensions were 0.8—1.2 mm.

θ-Al_2O_3, granulated, S_{sp} was 60 m^2 g^{-1}, filled mass was 0.6 g cm^{-3}, V was 0.7 cm^3 g^{-1}, r was 200 Å, X_{30} was 5.5 %, granule dimensions were 0.4—0.8 mm, contains 5 % of γ-Al_2O_3.

Catalysts were prepared by the impregnation method. NH_4ReO_4 or $HReO_4$ were used as the initial compounds. Pretreatment of the support was carried out with 13 % nitric or oxalic acid (of a ratio ReO_4^- : $C_2O_4^{2-}$ = 1 : 5). The catalyst samples dried at 120 °C were reduced with hydrogen at 500 °C before the experiment.

Results and Discussion

The results of the study of the interrelation between the state of rhenium on the support surface, the nature of the support, and the activity of catalysts in different reactions were described previously.[2—6] A high degree of dispersion of rhenium on the γ-Al_2O_3 surface is, most likely, due to the strong interaction of the metal with acceptor sites of the oxide support.[3,6] In contrast to the oxide supports, in the case of carbon supports, the starting Re^{VII} compounds are reduced to the metal state more easily, and the strong interaction between the metal and the support is not observed.

With a Re/sibunite catalyst, its dehydrogenating properties were studied depending on metal concentrations, which were equal to 1 and 2 %. It follows from the data presented in Table 1 that benzene and cyclohexene are the reaction products on the 1 % Re/sibunite catalyst at 350 °C and w = 0.5 h^{-1}. The increase in the reaction temperature from 350 to 400 °C results in an increase in the total degree of conversion and in the selectivity of benzene formation; the degree of conversion of cyclohexane into cyclohexene also increases. At high percentage of Re (2 %), an increase in overall conversion and selectivity with respect to benzene is observed without any change in cyclohexene yield.

Catalysts containing 2 % rhenium were used in subsequent experiments. As can be seen from the Table 1, the overall conversion of cyclohexane at 350 °C and w = 0.5 h^{-1} is 32.4 wt. % (sibunite), 15.2 wt. % (γ-Al_2O_3), and 9.7 wt. % (θ-Al_2O_3). The selectivity with

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Table 1. The properties of supported rhenium-containing catalysts in dehydrogenation of cyclohexane

Catalyst*	T/°C	Degree of conversion into			Total degree of conversion	Selectivity of transformation into		
		benzene	cyclohexene	toluene		benzene	cyclohexene	toluene
1	350	3.6	0.3	—	14.1	25.5	2.1	—
	405	4.8	1.0	—	15.1	31.8	6.6	
	455	8.6	1.7	—	23.5	36.6	7.2	
	350	2.0	—	—	2.0	100.0	—	
	400	8.7	1.9	—	24.9	35.2	8.0	
	400	5.9	—	—	10.2	58.1	0.1	
2	350	11.7	0.2	0.2	32.4	36.1	0.7	0.7
	400	16.1	0.2	0.2	38.0	42.4	0.4	traces
	450	18.1	1.3	0.2	49.3	38.1	2.6	0.4
	450	21.3	2.1	0.3	39.6	53.8	5.3	0.8
	350	5.5	0.3	—	15.8	34.8	1.6	—
3	400	14.6	1.0	0.2	26.0	56.2	3.8	0.8
	400	11.5	0.3	traces	22.1	52.0	1.4	traces
4	350	12.4	traces	traces	27.8	44.6	traces	0.1
	400	20.0	0.9	0.3	32.4	61.7	2.8	0.9
	400	13.3	0.9	0.2	37.2	35.8	2.4	0.5
5	350	13.1	0.3	0.2	30.6	42.8	1.0	0.7
	400	15.6	0.9	0.3	44.3	35.2	2.0	0.7
	400	14.0	1.0	0.2	29.8	47.0	0.4	0.7
6	400	23.0	0.6	0.3	40.3	57.1	1.5	0.7
	400	14.1	0.6	0.2	37.5	37.6	1.6	0.5
7	350	3.6	0.1	—	15.2	23.7	0.3	—
	400	3.9	0.9	—	23.2	16.8	3.9	
	450	1.4	0.4	—	10.3	13.6	3.8	—**
8	350	4.9	0.3	—	9.7	50.5	3.1	—
	400	6.0	1.2	—	15.8	37.9	7.6	—
	450	3.7	1.8	—	14.7	25.2	12.2	—
	350	2.1	0.2	—	9.2	22.8	2.8	—
9	400	11.0	1.2	—	18.0	61.2	6.6	—
	400	9.3	1.3	—	16.1	57.8	8.1	—
	450	4.2	1.9	—	18.3	23.0	10.4	—**

* Catalysts: 1 % Re/sibunite obtained from NH_4ReO_4 (**1**), 2 % Re/sibunite obtained from NH_4ReO_4 (**2**), 2 % Re/sibunite obtained from $HReO_4$ (**3**), 2 % Re/sibunite treated with 13 % HNO_3 for 0.5 h (**4**), 2 % Re/sibunite treated with 13 % HNO_3 for 1 h (**5**), 2 % Re/sibunite treated with oxalic acid (**6**), 2 % Re/γ-Al_2O_3 (**7**), 2 % Re/θ-Al_2O_3 (**8**), 2 % Re/θ-Al_2O_3 treated with oxalic acid (**9**).

** Methylcyclopentane and methylcyclopentene are detected in catalyzates.

respect to benzene decreases on going from Re/θ-Al_2O_3 to Re/sibunite and Re/γ-Al_2O_3. When temperature is increased from 350 to 400 °C, the selectivity with respect to benzene varies as follows: 42.4 % (sibunite), 37.9 % (θ-Al_2O_3), and 16.8 % (γ-Al_2O_3) (see Table 1). Thus, the Re/sibunite catalyst is more sensitive to the increase in temperature than Re/oxide catalysts.

It was demonstrated[7] that in the case of low-percentage Re-catalysts supported on γ-Al_2O_3 a higher metal concentration was necessary to attain the same degree of coating as for α-Al_2O_3. Supported Re-catalysts demonstrated similar dehydrogenation activity: 0.2 % on C (beech carbon), 0.5 % on α-Al_2O_3, and 1.5 % on γ-Al_2O_3. Besides, the reaction temperature for the Re/C-catalyst must be 60 °C higher than for Re/oxide samples.[7]

The activity of the 2 % Re-catalysts studied, which was estimated according to the overall conversion of cyclohexane, can be ranged as follows: Re/sibunite > Re/γ-Al_2O_3 > Re/θ-Al_2O_3, which correlates with the values of the specific surfaces of the supports (680, 235, and 60 $m^2 g^{-1}$) as well as with the data of the preceding study.[7] Thus, the active state of rhenium particles is attained more easily on 2 % Re/θ-Al_2O_3, which has lesser specific surface of the support, than on 2 % Re/γ-Al_2O_3. It is likely that the presence of a biporous structure with pore radii r_1 220 Å and r_2 < 40 Å in γ-Al_2O_3 exerts a negative effect on the formation of active metal particles on the surface, as distinct from θ-Al_2O_3, for which r is equal to 200 Å. It is possible that the lesser activity of the samples on γ-Al_2O_3 is also due to stronger interaction of the metal with the surface than in the case of θ-Al_2O_3. It is known[2] that strong interaction of γ-Al_2O_3 with a metal results in formation of highly dispersed rhenium particles on the surface, which hinders their reduction.

It was established with the 2 % Re/sibunite catalyst that the selectivity of the dehydrogenation of cyclohexane into benzene on a catalyst prepared from $HReO_4$ is 1.3 times higher than the corresponding value obtained in the case of NH_4ReO_4. It seems to be related to a greater ease of reduction of Re^{VII} on the surface of a sample formed from perrhenic acid. A similar effect of the nature of the starting rhenium compounds was shown with Re/oxide catalysts in hydrogenation of benzene. In contrast to Re/sibunite catalysts, strong interaction of the metal with the support occurs on them.[3]

The study of the influence of the pretreatment of supported Re-catalysts with dilute 13 % nitric and oxalic acids demonstrates that the increase in the duration of the support treatment from 0.5 to 1.0 h at 350 °C and w = 0.5 h^{-1} almost does not affect the overall activity and stability of the 2 % Re/sibunite catalyst. An increase in temperature to 400 °C leads to an increase in the selectivity of a catalyst treated with nitric acid for 0.5 h to 61.7 % compared to 35.2 % for the catalyst treated with the acid for 1 h. It is possible that the decrease in the dimensions of the particles of reduced rhenium takes place, and its degree of dispersion increases on the treatment of sibunite with nitric acid. Similar effects have been observed[8] for a Pd/C catalyst upon its treatment with HNO_3.

The influence of the pretreatment with oxalic acid on the change in dehydrogenating activity was followed with the most active rhenium catalysts on sibunite and θ-Al_2O_3 supports. The treatment with oxalic acid manifests itself to a greater degree, when sibunite is used as a support rather than θ-Al_2O_3. Thus, the selectivity of conversion into benzene increases on the 2 % Re/sibunite catalyst by a factor of 1.35 (from 42.2 to 57.1 %) (T = 400 °C, w = 0.5 h^{-1}), whereas on the 2 % Re/θ-Al_2O_3 catalyst this increases by a factor of 1.2 (from 50.5 to 61.2 %) (the overall conversion of cyclohexane in both cases is ~40 %). It is conceivable that the introduction of oxalic acid into supported rhenium catalysts contributes to more uniform distribution of the metal on the support, which leads to enhancement of its dehydrogenating properties. This can be evidenced by the results of an investigation,[9] which demonstrate that oxalic acid strongly competes with H_2PtCl_6 when the latter is supported on Al_2O_3. In the absence of additives, Pt is distributed nonuniformly, and the metal mainly localizes on the Al_2O_3 surface. The introduction of oxalic acid contributes to a more uniform distribution of platinum and its penetration into pores, especially into narrow ones, which improves the characteristics of reforming catalysts.

It follows from the data presented in Table 1 that toluene is formed on the Re/sibunite catalysts, probably through alkylation of benzene with gaseous reaction products. Methylcyclopentane and methylcyclopentene were detected as reaction products along with cyclohexene on the Re/oxide catalysts **7** and **9**. Dehydrogenation of cyclohexane on these catalysts seems to proceed through an intermediate formation of five- and six-membered rings, which is consistent with the published data.[2]

References

1. M. A. Ryashentseva, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 422 [*Russ. Chem. Bull.*, 1993, **42**, 387 (Engl. Transl.)].
2. M. A. Ryashentseva and Kh. M. Minachev, *Renii i ego soedineniya v geterogennom katalize* [*Rhenium and Its Compounds in Heterogeneous Catalysis*], Nauka, Moscow, 1983, 210 pp. (in Russian).
3. Kh. M. Minachev, V. I. Avaev, E. S. Shpiro, M. A. Ryashentseva, and G. V. Antoshin, in *Nanesennye metallicheskie katalizatory prevrashcheniya uglevodorodov. Tez. vsesoyuz. soveshch.* [*Supported Metal Catalysts of Hydrocarbon Transformations. Abstracts of Papers of All-Union Conf.*], Nauka, Novosibirsk, 1978, 131 (in Russian).
4. M. F. J. Johnson and V. M. LeRoy, *J. Catal.*, 1974, 434.
5. A. Webb, *J. Catal.*, 1975, 485.
6. R. V. Dmitriev, V. I. Avaev, M. A. Ryashentseva, and Kh. M. Minachev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1977, 2448 [*Bull. Akad. Sci. USSR, Div. Chem. Sci.*, 1977, **26** (Engl. Transl.)].
7. G. Rienäker, *Zeitschr. Chem.*, 1964, 180.
8. G. R. Heal and L. L. Mkayula, *Carbon*, 1988, 815.
9. M. D. Smolikov, A. S. Belyt, I. E. Smirnova, F. M. Zatolokina, and V. K. Duplyakin, *Heterogeneous Catal., Proc. 7th Int. Symp. Bourgas*, Vratza, 1991, Part 1, 395.

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