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NOTES

Activity of Variously Supported Rh Catalysts for Toluene Steam Dealkylation

In a previous kinetic study (*1*) of toluene steam dealkylation on Rh/Al_2O_3, fresh catalyst samples had to be used throughout due to activity decay. Similar problems have also been reported by others (*2*, *3*). In order to extend the kinetic investigation, a search for a more stable catalyst has been undertaken. One reason for activity decline was reported to be the adsorption of polycyclic aromatic by-products on acidic sites of the carrier, which can be contained by the addition of alkali (*2*). An additional reason may be the sensitivity of the γ-Al_2O_3 structure to water vapor (*4*). A more stable support from the latter point of view, i.e., alumina stabilized by SiO_2 deposition (*5*), has therefore been employed and is compared with the previously proposed α-Cr_2O_3 (*2*). Moreover, the addition of alkali has also been tested with the aim of reducing side reactions due to surface acidity.

Catalysts were prepared either by adsorption from excess $RhCl_3$ solution or by the incipient wetness impregnation method, using 0.149–0.177 mm (80–100 mesh) particles of the following supports: (i) Kaiser SAS γ-Al_2O_3, (ii) and (iii) Snamprogetti RP- and KP-silica-stabilized alumina, (iv) α-Cr_2O_3. The latter was prepared by the Burwell method, calcining at 880°C and taking care to avoid the "glow phenomenon" (*6*). Solutions of K_2CO_3 or KNO_3, $LiNO_3$, and $CsNO_3$ were employed for alkali addition by the impregnation technique. The usual procedure (*1*) included rhodium reduction in a slow H_2 stream at 330°C during 2 hr, before the eventual addition of alkali; in the case of catalyst KRA6 the adsorption order was inverted. While deionized water was generally employed, the RA3 catalyst was prepared using a $RhCl_3$ solution in tap water.

Rh content was determined by uv-visible spectrophotometry (*7*) in the case of Al_2O_3 supports (attack with $KHSO_4$), and by atomic absorption spectroscopy when the support was Cr_2O_3 (attack with KNO_3–Na_2CO_3 mixture, followed by $KHSO_4$). Overall BET surface area, pore volume, and pore size distribution were determined (*8*) by N_2 physical adsorption at liquid N_2 temperature, after outgassing at 10^{-3} Pa and 200°C for 2 hr. Examples of pore size distribution are given in Fig. 1. The metal surface area was measured by the gc pulse method with O_2 (*9*). The exposed fraction of rhodium in each case was ≥ 0.99. Overall surface acidity was determined by titration with *n*-butylamine in anhydrous *iso*-octane or benzene (*10*) in the presence of bromothymol blue (pK_a -1.5), 4-(phenylazo)-diphenylamine (pK_a $+1.5$), and methyl red (pK_a $+4.8$). Concentration of acidic centers up to pK_a -1.5 and to pK_a $+4.8$ are given in Table 1. All alumina-supported catalysts revealed acidity of the intermediate strength, with the same trend shown in Table 1 for the total surface acidity (max 0.16 for RA11, min. 0.04 mmol/g for RKA5, KRA6, and RLA8).

Catalytic activity was tested by runs

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TABLE 1

Composition, Properties, and Initial Activity of Different Rh Catalysts.

Type	Support	BET surface area[a] (m^2/g_{cat})	Average pore radius (nm)	Rh wt%[b]	Rhodium surface area[b] (m^2/g_{cat})	Surface acidity[c] ($mmol/g_{cat}$)		N[d] (hr^{-1})
						(pK_a +4.8)	(pK_a −1.5)	
RA1[e]	KP–Al_2O_3	233	5.8	0.83	3.8	0.41	0.03	116
RA2[e]		262	5.7	0.68	3.1	0.43	0.03	117
RA3[e]		242	5.1	0.65	3.0	0.41	0.03	103
RA4[f]	RP–Al_2O_3	58	9.0	0.64	3.0	0.29	<0	26
RKA5[f]	(+K)[g]	70	11.2	0.67	3.1	0.17	<0	29
KRA6[f]	(+K)[g]	74	12.2	0.62	2.9	0.18	<0	26
RKA7[f]	KP–Al_2O_3 (+K)[g]	241	5.2	0.62	2.3	0.29	<0	140
RLA8[f]	(+Li)[g]	275	4.9	0.67	3.0	0.18	<0	114
RCA9[f]	(+Cs)[g]	264	5.8	0.63	2.9	0.33	<0	120
RA10[f]	SAS–γAl_2O_3	328	4.5	0.63	2.9	0.59	0.04	246
RA11[e]		319	4.6	0.72	3.3	0.60	0.05	401
RC1[f]	α–Cr_2O_3	10.1	55	0.19	1.3	0.04	<0	—[h]
RC2[f]		11.7	43	0.64	2.2	0.04	<0	81
RKC3[f]	(+K)[g]	9.7	66	0.65	2.0	<0	<0	171
RKC4[e]	(+K)[g]	10.1	45	0.68	2.1	<0	<0	197

[a] Usually within ±3%.

[b] Within ±5%.

[c] Methyl red (pK_a +4.8), bromothymol blue (pK_a −1.5).

[d] Turnover rate in standard runs.

[e] Prepared by adsorption from excess $RhCl_3$ solution.

[f] Prepared by incipient wetness impregnation.

[g] 0.010 g atom of added alkali per 100 g of support.

[h] Not evaluated, due to very low conversion.

in standard conditions (460 ± 1°C; atmospheric pressure; water:toluene molar ratio R_w = 10 ± 0.5; time factor τ = ca. 0.17 g cat × hr/ml liquid toluene; catalyst mass, 1.7–2.5 g). Every catalytic charge was conditioned in N_2 at 470 to 480°C overnight before the run. Samples of the effluents were taken after run times from 3 to 10 hr. The fixed bed flow reactor, general set-up, and analytical methods were as described earlier (*1*). Catalytic activity has been expressed as turnover rate N (molecules of reacted toluene/hr × surface Rh atom), calculated from the average values of conversion and time factor over the sampling time. The characteristics and standard performance of the catalysts are summarized in Table 1. Further values of the turnover rate were measured for the chromia-based catalysts at the same conditions but at higher temperature values

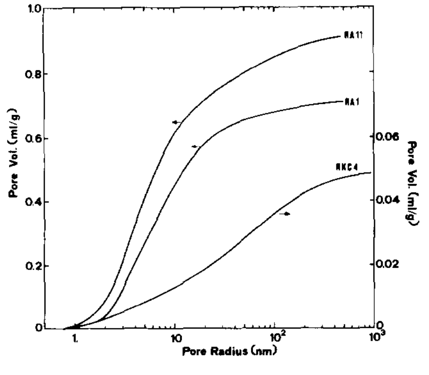

FIG. 1. Examples of pore size distribution.

TABLE 2

Behavior of Different Rh Catalysts in Extended Runs[a]

Catalyst	RA 10	RA 11	RA 1	RKC4	RKC4[b]
y_i[c]	0.278	0.526	0.172	0.152	0.463
y_f[d]	0.136	0.246	0.118	0.143	0.329
Overall surface area[e] (m^2/g cat)					
Initial	290	313	249	9.3	9.3
Final	174	179	219	9.0	8.9
Selectivity[f]	0.78	0.72	0.64	0.75	0.62
CO/CO_2 in gaseous products					
Exptl.	0.53	0.45	2.2	0.016	0.43
Equil.[g]	0.014	0.022	0.011	0.015	0.10
Reacted water/reacted toluene (mol)	3.7	3.3	4.1	3.9	5.0

[a] $R_w = 10 \pm 0.5$; $T = 461 \pm 3$°C; $\tau = 0.166 \pm 0.005$ g cat × hr/ml liquid toluene; run time = 45–50 hr.

[b] Temperature 567 ± 5°C.

[c] Average conversion from first three analyses.

[d] Average conversion from last three analyses.

[e] Approximate measurements by the "one-point" version of the BET technique.

[f] mol of benzene/mol of reacted toluene.

[g] Calculated for the water gas shift reaction in the average conditions of each run.

(close, although not identical), with the following results: RC1, 497 (at 569°C); RKC3, 745 (at 561°C); RKC4, 593 (at 559°C).

From the point of view of initial activity at 460°C (turnover rate for standard runs) four classes of catalysts can be recognized, in the following order of performance of the corresponding supports: SAS γ-Al_2O_3 > α-Cr_2O_3(+K) > KP-Al_2O_3 > RP-Al_2O_3. The activity of RA11 catalyst was found comparable to that of the analogous one made with F-110 Alcoa γ-Al_2O_3, previously measured (*1*).

Some representative catalysts of the best classes were also tested for longer times, with the results given in Table 2. The activity decline during the run time was not associated with regular changes in selectivity, CO/CO_2 ratio in the produced gas, or molar ratio of reacted water and toluene; therefore, average values of these parameters have been reported. As far as selectivity is concerned, the data of Table 2, confirmed by the selectivities of the standard runs (not reported in Table 1), indicate that at 460°C the catalysts supported on KP-Al_2O_3 behave less satisfactorily than the others.

The composition of the gaseous products (H_2, CO_2, CO, and small amounts of CH_4) for the various catalysts differs mainly in the CO/CO_2 ratio. Experimental values, compared with equilibrium ones in Table 2, prove that CO is a primary product, and that the best catalyst for its conversion to CO_2 is the chromia-based RKC4, in agreement with previous reports (*2*).

Reaction stoichiometries were calculated by taking into account experimental values of the CO/CO_2 ratio and corrected values of the selectivity to benzene (for a 100% material balance). They usually reproduced the experimental ratios of reacted H_2O: toluene very well and the ratio of total gas over benzene in the products fairly well. Corrected selectivities ranged from 80 to 84% for catalysts RA10, RA11, and RKC4 at 461°C.

Decline of the catalytic activity during extended runs was expressed as $(y_i - y_f)/(y_i \times \text{run time})$. Such an activity loss at 461°C was 1.5 (percentage per hour) in the case of both RA10 and RA11, 0.90 for RA1, and 0.15 for RKC4; at 567°C it was 0.77 for RKC4. Overall surface area, measured on the catalysts after the extended runs, showed a decrease with respect to the fresh catalysts (Table 2). The change was not large in the case of KP-Al_2O_3- or α-Cr_2O_3-supported RA1 and RKC4, but 40% or more in the case of SAS-γ-Al_2O_3-supported RA10 and RA11. Therefore the larger loss in activity of the last two catalysts may be correlated with the dramatic loss in total surface area.

After a 45-hr run time, catalyst RA1, although rather stable in its BET surface area, showed a decrease in metal surface area from 3.8 to 1.4 m^2/g. In connection with this fact, an increase of turnover rate N from 116 to 226 hr^{-1} was calculated. However, the net observed effect was a loss in activity of this catalyst, mainly attributable to sintering of the metal.

As to surface acidity, its reduction, in the range examined, affected the performance of silica-stabilized alumina-based catalysts (see N values in Table 1) only slightly, if at all. On the other hand, the potassium addition to the chromia-based catalysts clearly proved useful. One reason for such a different effect could be that the few and weak chromia acid sites have been completely neutralized, while on aluminas this was effected only for the strongest ones.

When a comparison is possible, results indicate a better behavior of the catalysts prepared by adsorption from excess solution than by incipient wetness impregnation (see RA10-RA11 and RKC3-RKC4, Table 1), probably owing to metal distribution effects (*11*).

As a conclusion, silica-stabilized alumina has proven to be of limited usefulness as the oxide component of a Rh catalyst for toluene steam dealkylation. The expected improvement of the catalyst life with respect to γ-Al_2O_3 has actually been attained; however, the results are not as good as those obtained with α-Cr_2O_3.

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REFERENCES

1. Beltrame, P., Ferino, I., Forni, L., and Torrazza, S., *Chim. Ind.* (*Milano*) **60**, 191 (1978).
2. Kochloefl, K., Proc. 6th Intern. Congr. Catalysis (London 1976), p. 1122. Chem. Soc., London, 1977.
3. Grenoble, D. C., *J. Catal.* **51**, 203, 212 (1978).
4. Dowden, D. A., *I. Chem. E. Symp. Ser.* 27, 18 (1968).
5. Buonomo, F., Fattore, V., and Notari, B. (to Snamprogetti S.p.A.), U.S. Patent 4,013,590 (March 22, 1977).
6. Baker, F. S., Carruthers, J. D., Day, R. E., Sing, K. S. W., and Stryker, L. J., *Disc. Faraday Soc.* **52**, 173 (1971).
7. Ayres, G. H., Tuffly, B. L., and Forrester, J. S., *Anal. Chem.* **27**, 1742 (1955).
8. Gregg, S. J., and Sing, K. S. W., "Adsorption, Surface Area and Porosity." Academic Press, New York, 1967.
9. Buyanova, N. E., Karnaukhov, A. P., Koroleva, N. J., Kulishkin, N. T., Rybak, V. T., and Fenelonov, V. B., *Kinet. Katal.* **16**, 741 (1975).
10. Benesi, H. A., *J. Amer. Chem. Soc.* **78**, 5490 (1956); Bertolacini, R. J., *Anal. Chem.* **35**, 599 (1963).
11. Moss, R. L., *in* "Experimental Methods in Catalytic Research" (R. B. Anderson and P. T. Dawson, Eds.), Vol. II, Chap. 2. Academic Press, New York, 1976.

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