

Activity and Structure of Rh/Cr₂O₃ Catalysts for Toluene Steam Dealkylation

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The catalytic activity of Rh/Cr₂O₃ in toluene steam dealkylation has been correlated with catalyst properties and structure. The maximum exploitation of the precious metal was found for a concentration of rhodium not higher than ca. 0.8 wt%. At higher Rh loading, increasing amounts of the precursor Rh³⁺ ions probably diffuse within the crystal lattice of the support, during the preparation of the catalyst, and in such a form they are not reduced to active Rh⁰. The progressive loss observed in reaction selectivity is likely to be due to the change conferred by such Rh³⁺ ions on the properties of the chromia.

INTRODUCTION

In a previous work (1) it was observed that some Rh/Cr₂O₃ catalysts, prepared in the same way, catalyzed the toluene steam dealkylation (TSD) with comparable overall reaction rate, although their rhodium content changed by more than one order of magnitude, i.e., from ca. 0.2 to over 4 wt%. It is well known that the properties of a supported metal catalyst, particularly metal dispersion, depend on many variable parameters, inherent in the method of preparation (2). Moreover, RhCl₃ seems to be superior to other precursors in producing a good metal dispersion, at least in Rh/Al₂O₃ catalysts which have not aged (3). It therefore seemed interesting to prepare a series of Rh/Cr₂O₃ catalysts using RhCl₃, in order to determine the limiting value of rhodium concentration in the catalyst which would correspond to the maximum catalytic exploitation of the precious metal and to in-

vestigate why, beyond such a limiting value, the metal is less well exploited.

EXPERIMENTAL

Catalysts. Four K-promoted Rh/Cr₂O₃ catalysts were prepared, by adsorption from excess RhCl₃ aqueous solution, as previously described in detail (4). The α -Cr₂O₃ support (0.149–0.177 mm particles, 80–100 mesh) was prepared from chromium nitrate by the Burwell method and carefully calcined at 1150 K in order to avoid the so-called glow phenomenon (5). Particular care was also taken to repeat exactly the same procedure during the preparation of the whole set of catalysts, the only parameter changing being the concentration of the RhCl₃ solution. The main physicochemical characteristics of the catalysts (Table 1) were determined as reported earlier (4). Transmission electron microscope (TEM) micrographs were taken by means of a Philips EM 300 instrument. A Cambridge Stereoscan 150-Link Systems 860 apparatus was employed for scanning electron micro-

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TABLE 1

Main Physicochemical Characteristics of the Catalysts^a and Activity in Toluene Steam Dealkylation at 733 K, Atmospheric Pressure, H₂O/Toluene = 10/1 (mol) Feed Ratio, $\tau = 0.164$ (g Cat. h/ml Liq. Toluene)

Catalyst	Rh (wt%)	S_{BET}^b (m ² /g cat.)	S_M^c (m ² /g cat.)	$\frac{\text{Rh}^{*d}}{\text{Rh}}$	y^e	S_B^f	N^g
RKC1	0.25	11	1.20	1.0	0.082(±0.008)	85(±5)	190
RKC2	0.68	10	2.11	1.0	0.156(±0.010)	75(±6)	197
RKC3	1.84	14	2.10	0.3	0.132(±0.015)	70(±5)	160
RKC4	4.39	13	2.13	0.1	0.136(±0.014)	60(±4)	170

^a All the catalysts have been K-promoted, by adding 0.01 g atoms of K per 100 g of support, by incipient wetness impregnation with aqueous K₂CO₃.

^b Total surface area by BET one-point technique (N₂ adsorption).

^c Rhodium surface area by O₂ adsorption (Ref. (8)). Confidence limits of data ±10% (triplicated measurement). Data obtained after subtracting the amount of O₂ (ca. 0.2 Nml/g cat.) adsorbed by pure chromia, as determined on the bare support.

^d (Exposed/total) Rh from O₂ selective adsorption analysis.

^e Toluene fractional conversion (mol).

^f Mol% selectivity to benzene.

^g Turnover rate (mol of reacted toluene/h g atom of exposed Rh).

scope and electron probe microanalysis (SEM-EPMA). Electron paramagnetic resonance (EPR) measurements were made using a Varian V-4502 Century Series instrument. Detail of instrumental analysis will be given later.

Activity measurements. The catalytic activity in toluene steam dealkylation (TSD) was measured by employing a continuous, stainless-steel tubular reactor. The apparatus, procedure and analysis of the entry and exit streams from the reactor were described elsewhere (6).

RESULTS AND DISCUSSION

The catalytic activity comparison tests were performed under identical conditions on 1.5 g samples of fresh catalyst at atmospheric pressure, 733 K, H₂O/toluene = 10/1 feed molar ratio and time factor $\tau = 0.164$ (g cat. h/ml liq. toluene). The results (Table 1) show that overall conversion $y =$ (reacted/fed) toluene (mol) grows with increasing rhodium concentration, reaching a plateau quite rapidly, while selectivity S_B (mol%) to the desired product (benzene) falls progressively. On the other hand, by

taking into account the turnover rate N (h⁻¹), it may be noticed that the exposed rhodium shows a comparable specific activity for the whole set of catalysts. As a consequence, a concentration of rhodium higher than ca. 0.8 wt% appears not only economically useless, but also catalytically detrimental, due to loss of selectivity.

The low exploitation of supported metals at high concentration is generally ascribed to the growth in size of the metal crystallites with increasing metal content (7). Therefore, a first investigation concerned the control of metal dispersion, to complement the data (Table 1) obtained by O₂ adsorption (8). X-Ray diffractometric analysis (Debye method) showed that in any case the size of Rh crystallites was below the sensitivity limit of such a technique. Indeed, the analysis of more than 20 TEM micrographs (see later), taken on different samples of each catalyst, showed that less than 1% of visible Rh particles exceeded 0.01 μm in apparent diameter. More than 80% of such particles were smaller than 0.004 μm , and it is well known (9) that the size of crystallites for a XRD image from

powders to become detectable ranges usually from 10^{-6} to 2×10^{-5} cm. Furthermore, an interesting result was that the diffractometric pattern of our chromia appeared virtually unaltered by the presence of rhodium, even at the highest concentration.

An analysis by SEM-EPMA was then conducted, with the purpose of determining the location of rhodium within the catalyst particles. Many samples of each catalyst were analyzed. The specimens were prepared by embedding the catalyst powder as such (80–100 mesh) in epoxy resin. After cutting and polishing as usual, a deposition *in vacuo* of a thin layer of gold followed. Typical results are shown in Fig. 1. Owing to the relatively low concentration, the rhodium signal was in any case quite weak and of comparable strength for the whole series of catalysts. In fact, for any of our specimens, when collecting from at least 6K up to over 300K counts in EPMA analysis, the signal given by rhodium at 2.69 keV (RhL α) ranged between 8.5 and 11% of that given at 5.95 keV (CrK β_1) by the chromia matrix. As to the partial shifting of the Rh signal from the scan line, with respect to the catalyst particle SEM image (Figs. 1a,b,c,d, upper images), such a phenomenon may be due to two effects: (i) some unavoidable slight tilting and roughness of the cut chromia surfaces, due to the softness of the embedding resin and to the hardness of α -chromia, respectively; and (ii) the weakness of the Rh signal. In linear scanning, a sufficiently high (signal/background) ratio could be obtained only if the electron beam was properly widened, therefore leading to a partial shift of the image. Furthermore, except maybe for RKC1, the concentration of rhodium at the surface of the particles seemed very similar in all the catalysts and, in any case, the precious metal appeared to be located mainly within the chromia particles. However, both the size of the Rh crystallites and the form in which rhodium was present within the support particles remained undetermined.

An analysis by TEM then followed in an

attempt to answer at least the former question. Many specimens of each catalyst were prepared, by suspending the powder in ethyl alcohol, with the help of an ultrasonic stirrer, and by putting a drop of the suspension on a film of Formvar, deposited on a thin metal network. The results of TEM analysis, typically reported in Fig. 2, showed that, apart from RKC1 (Fig. 2a), the Rh crystallites were of similar size and they were visible in comparable amount in all the catalysts (Figs. 2b,c,d). A progressive diffusion of increasing amounts of rhodium into the crystal lattice of the support, when increasing the concentration of the precious metal, was then suspected.

To obtain deeper insight into this, an EPR analysis was performed to compare the unpaired spin electron signal of our catalysts with that given by the pure support. EPR spectra were recorded on samples prepared by placing ca. 0.5 g of powder within a 20-cm long, 4 mm in diameter glass sampling tube and heating at 720 K for 2 h in slowly flowing helium. After cooling in flowing gas, the tube was sealed at both ends and placed into the spectrometer cavity, thermostated to 293(\pm 2) K. The results are collected in Fig. 3. Pure chromia showed a relatively strong signal (Fig. 3a). The signal of RKC1 catalyst was considerably weaker (Fig. 3b) and that of other catalysts (Figs. 3c,d,e) practically vanished. Notice that instrument sensitivity (gain) had to be increased by an order of magnitude to record these latter spectra.

It is known (10, 11) that pure α -chromia in powder form and below its Curie temperature (311 K) produces only a weak resonance absorption signal in the antiferromagnetic region. The relatively strong signal, given by our support, is probably due to the presence of submicrocrystals, not sufficiently ordered to give the α -chromia structure. Such a partially disordered structure is likely to have originated during the preparation of the support when the amorphous chromium hydroxide gel is transformed into α -chromia by heat treat-

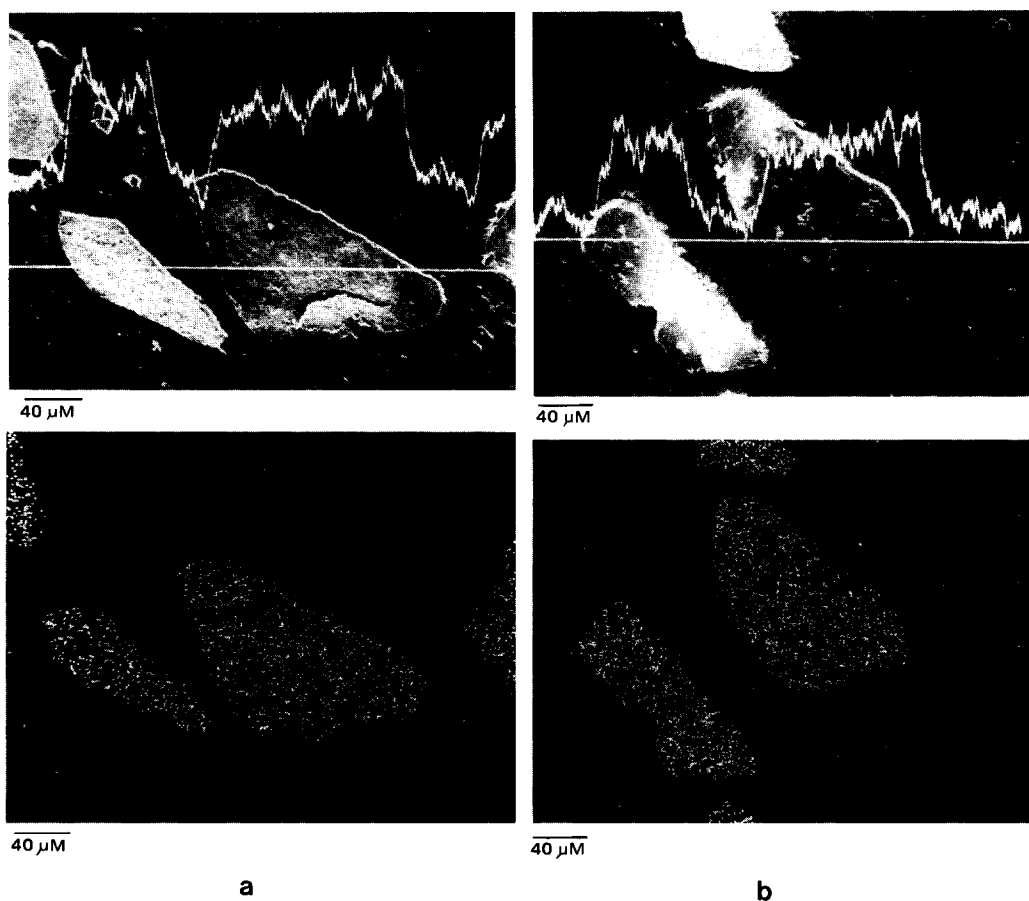


FIG. 1. SEM-EPMA micrographs of RKC1 (a), RKC2 (b), RKC3 (c), and RKC4 (d) catalysts. Upper micrographs: SEM image with $RhL\alpha$ crossing line EPMA trace; lower micrographs: $CrL\alpha_1$ EPMA map.

ment (4, 5). The weakening of the EPR signal with increasing rhodium concentration could then be due to the presence of Rh^{3+} ions diffusing within the lattice of the support during the calcination step, following the impregnation with aqueous $RhCl_3$. A similar behavior has been observed in $Rh/\gamma-Al_2O_3$ (12), in which a relatively bulky ion (Rh^{2+} , ionic radius 0.86 Å) diffused within the $\gamma-Al_2O_3$ (Al^{3+} ionic radius 0.50 Å). In our case the diffusion and the accommodation of the foreign ion within the chromia matrix are likely to be much easier, owing to the practically identical values of the Cr^{3+} and Rh^{3+} ionic radii (0.69 and 0.68 Å, respectively). Indeed, as previously mentioned, no alteration of our $\alpha-Cr_2O_3$ X-ray

Debye pattern was recorded in any of our catalysts, even at the highest rhodium concentration. In addition, the diffusion of Rh^{3+} is probably favored also by the presence of the structural imperfections in the $\alpha-Cr_2O_3$ crystal lattice, formerly cited. The vanishing of the EPR signal in higher concentration catalysts could be due to a "reconstruction" effect, conferred by the Rh^{3+} guest-ions on the disordered submicrocrystals of our chromia. The Rh^{3+} ions are not reduced to Rh^0 in the conditions of our H_2 treatment step (4), due to the stabilizing effect of the crystal field forces and in such a state they have no direct catalytic activity on the TSD reaction.

The ratio of Rh^{3+} ions diffusing into the

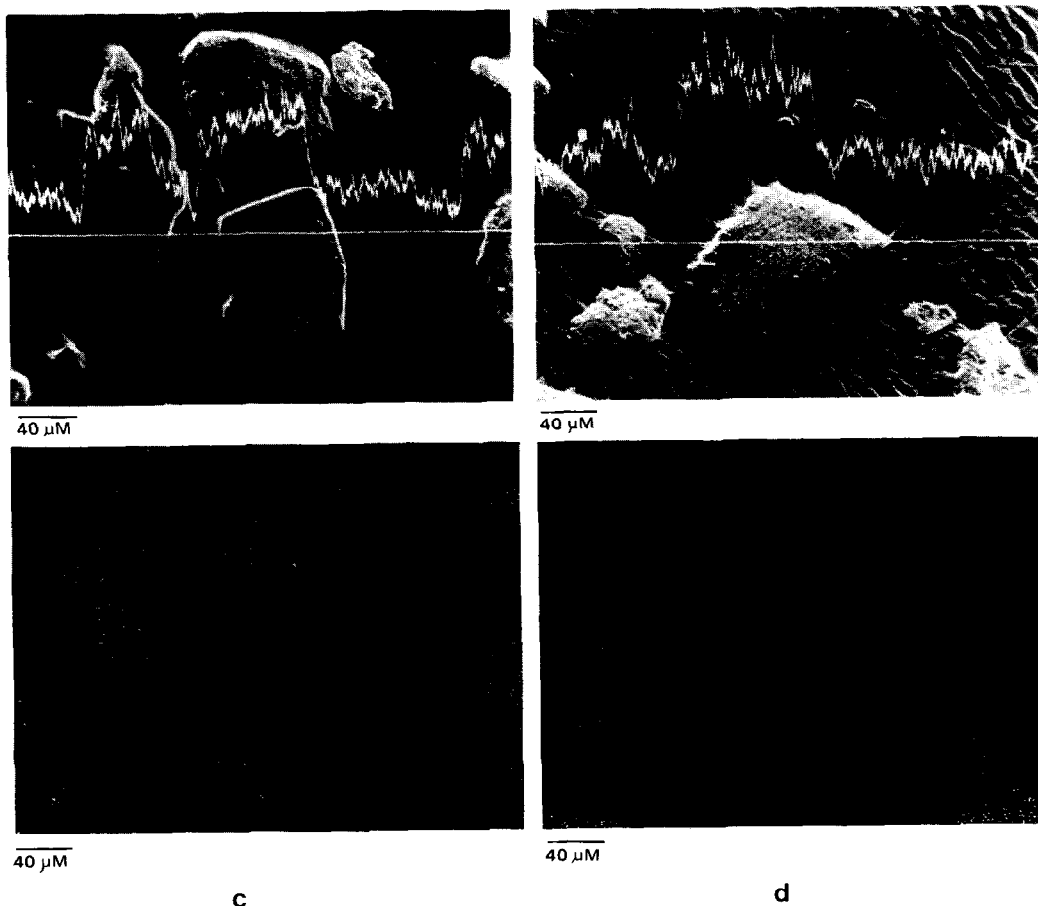


FIG. 1—Continued.

support lattice to those reducing to Rh⁰ at the support surface clearly depends on the ratio of the diffusion rate to the reduction rate. The latter, depending substantially only on temperature, should be the same for all catalysts; the former depends also on initial Rh³⁺ concentration at the support surface. As a consequence, in RKC1 most of the Rh³⁺ ions are reduced to Rh⁰, the Rh³⁺ surface concentration being quite low. On the other hand, in RKC2, RKC3, and RKC4 the higher the initial surface concentration of Rh³⁺, the larger the amount of diffusing Rh³⁺ ions. The last hypothesis is confirmed by the substantially unchanging concentration of exposed Rh with increasing rhodium content of the catalyst (Table 1 and Figs. 1, 2).

As to the decrease in selectivity to benzene with increasing Rh loading, we noticed that this was connected essentially with the growing in importance of cracking reactions, as evidenced by the increasing formation of gaseous byproducts. Such an effect may be ascribed to a progressive lowering of the rate of desorption of the useful aromatic intermediate from the metal surface. The longer the adsorbed species lies on the catalyst, the higher the probability of being cracked. The steam dealkylation reaction requires the presence of water derivatives, namely hydroxyl groups, on, or near to, metallic centers. Hydroxyl groups very probably form on support centers and then migrate to metallic sites. Therefore, the progressive modification of the chromia

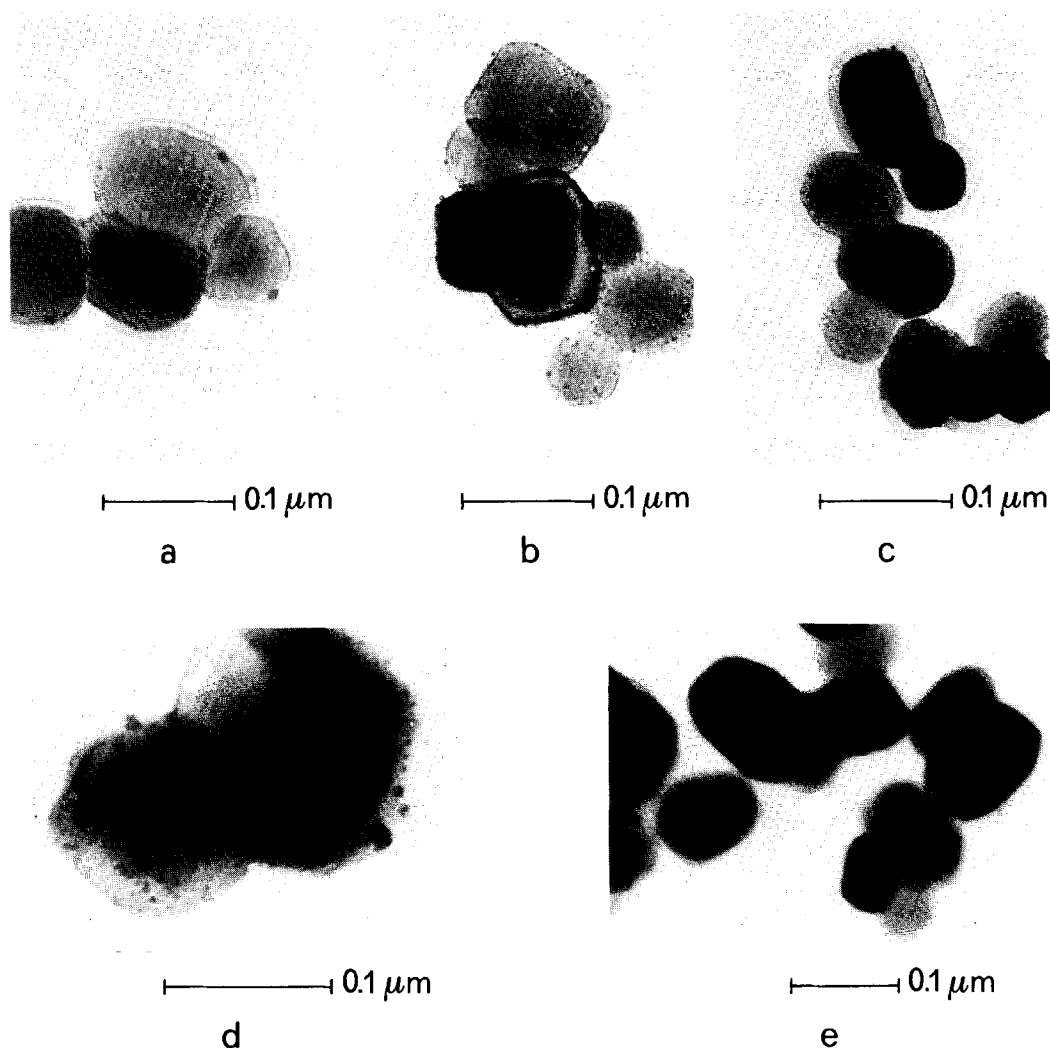


FIG. 2. TEM micrographs: (a) RKC1 (magnification: 220,000), (b) RKC3 ($\times 220,000$), (c) RKC4 ($\times 220,000$), (d) RKC2 ($\times 280,000$), (e) pure support ($\times 180,000$).

matrix, conferred by the presence of dissolved Rh^{3+} ions, could reflect on the rate of either water dissociation or hydroxyl surface migration, thus modifying the ratio of steam dealkylation over cracking rates. This confirms that chromia should be considered as a true cocatalyst, more than merely as a support, in the TSD reaction.

CONCLUSIONS

The results may be summarized as fol-

lows. (i) The maximum exploitation of the precious metal in K-promoted $\text{Rh}/\text{Cr}_2\text{O}_3$ catalyst for TSD corresponds to a concentration of rhodium lower than ca. 0.8 wt%. (ii) A higher concentration is not only useless, but even detrimental, due to the increasing of reaction selectivity to unwelcome byproducts. (iii) The loss in exploitation of the precious metal seems not to be due to the increasing in size of surface Rh crystallites, but instead is likely to be ascribable to a progressive diffusion of the precursor Rh^{3+} ions within the chro-

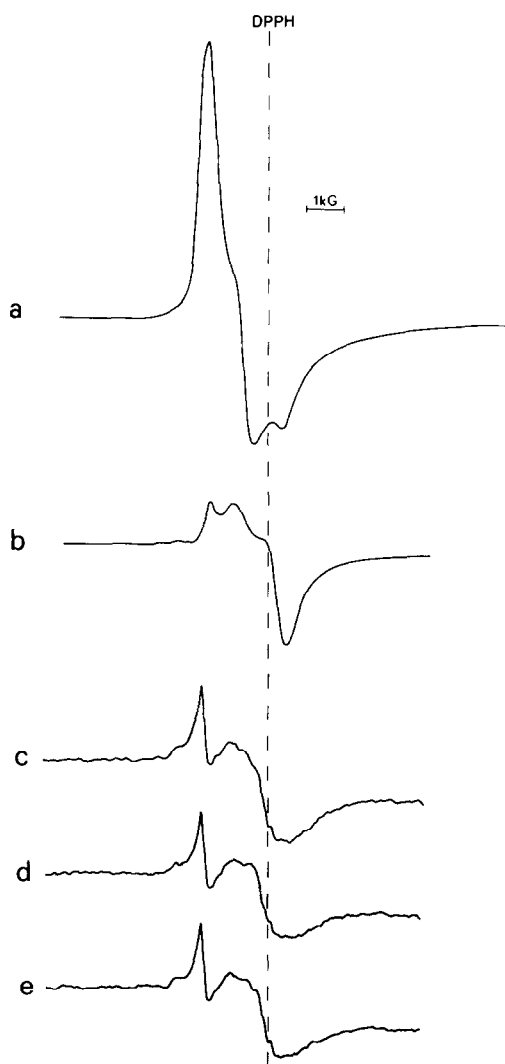


FIG. 3. EPR spectra (293 K): (a) pure support (receiver gain 2.5×10^3), (b) RKC1 (2.5×10^3), (c) RKC2 (2.5×10^4), (d) RKC3 (2.5×10^4), (e) RKC4 (2.5×10^4).

mia lattice, where they are stabilized by crystal field forces. (iv) The presence of increasing amounts of Rh³⁺ ions within the

chromia lattice could also be the cause of the progressive decrease of reaction selectivity to benzene.

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REFERENCES

1. Beltrame, P., Ferino, I., Forni, L., Marongiu, B., and Torrazza, S., *Chim. Ind. (Milano)* **62**, 401 (1980).
2. Acres, J. K., Bird, A. J., Jenkins, J. W., and King, F., in "Catalysis" (C. Kemball and D. A. Dowden, Eds.), Vol. 4, p. 1. Chem. Soc., London, 1981.
3. Harrison, B., Heffer, J. P., and King, F., in "Proceedings, 7th International Congress on Catalysis, Tokyo, 1980" (T. Seiyama and K. Tanabe, Eds.), p. 768. Kodansha-Elsevier, Tokyo, 1981.
4. Beltrame, P., Ferino, I., Forni, L., and Torrazza, S., *J. Catal.* **60**, 472 (1979).
5. Baker, F. S., Carruthers, J. D., Day, R. E., Sing, K. S. W., and Stryker, L. J., *Discuss. Faraday Soc.* **52**, 173 (1971).
6. Beltrame, P., Ferino, I., Forni, L., and Torrazza, S., *Chim. Ind. (Milano)* **60**, 191 (1978).
7. Figueras, F., Fuentes, S., and Leclercq, C., in "Growth and Properties of Metal Clusters" (S. Bourdon, Ed.), p. 525, Elsevier, Amsterdam, 1980.
8. Buyanova, N. E., Karnaukhov, V. B., Koroleva, N. J., Kulishkin, N. T., Rybak, V. T., and Fene-lonov, V. B., *Kinet. Catal.* **16**, 636 (1975).
9. Azaroff, L. V., and Buerger, M. J., "The Powder Method in X-Ray Crystallography." McGraw-Hill, New York, 1958.
10. Trounson, E. P., Bleil, D. F., Wangsness, R. K., and Maxwell, L. R., *Phys. Rev.* **79**, 542 (1950).
11. Poole, C. P., and McIver, D. S., "Advances in Catalysis," Vol. 17, p. 223. Academic Press, New York, 1967.
12. Yao, H. C. and Shelef, M., in "Proceedings, 7th International Congress on Catalysis, Tokyo, 1980" (T. Seiyama and K. Tanabe, Eds.), p. 329. Kodansha-Elsevier, Tokyo, 1981.