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Role of Urania as a Promoter of Supported Rhodium in the Catalyzed Steam Dealkylation of Toluene

The steam dealkylation of alkylbenzenes, usually carried out either over Ni or Rh, has been a subject of many investigations (*1–4*). In an effort to improve overall catalyst performance, we have recently found that Rh–Al_2O_3 promoted by urania was most prominent for commercial use (*5*). We intend, in the present note, to clarify the role of urania through a few diagnostic studies.

The reaction was studied with a conventional flow apparatus. The reactor, 2.5-cm i.d. and 45-cm length, was made of stainless steel. Catalysts were prepared by impregnating extruded γ-Al_2O_3 with an aqueous solution of platinum-group metal chlorides and uranyl nitrate. After drying, the catalysts were calcined at 450°C and reduced *in situ* at 450°C in a stream of H_2 for 2 hr. The surface area of the reduced catalysts, as determined by low temperature N_2 adsorption, was in the range 180–190 m^2/g.

Summarized in Table 1 are the results of the steam dealkylation of toluene. Under the conditions used, the following activity sequence was established among unpromoted platinum-group metal catalysts: Rh > Pt > Pd, Ir ≫ Ru (a–i). The catalytic behavior of Rh and Pd, as compared with Pt and Ir, was characterized by the formation of gaseous products consisting of fairly large amounts of CO. The observed product patterns can be qualitatively interpreted in terms of the following two overall reactions:

$$C_6H_5CH_3 + H_2O \rightarrow C_6H_6 + CO + 2H_2 \quad \text{(steam dealkylation)},$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad \text{(CO shift reaction)}.$$

Over Rh and Pd, the steam dealkylation may be assumed to proceed much more rapidly than the shift reaction. CO is thus accumulated, and the adsorbed CO in turn inhibits further dealkylation from taking place smoothly. The assumption is in accord with allied observations hitherto reported. It has been known, for example, that CO is strongly adsorbed on Rh even under conditions at which the steam dealkylation takes place (*6*). Over Pt and Ir, on the contrary, the relative rate of the two reactions may be such that CO is effectively removed from the surface. It can be said, on the basis of the above interpretation, that the intrinsic activity of Rh and Pd for the steam dealkylation is considerably higher than that indicated by the sequence already mentioned. Enhanced activity, in fact, is ensured by the catalyst composed of Rh–Pt (*7*).

Included also in Table 1 are the results to show more directly that the removal of CO is important for the intrinsically active metals to exhibit their full activities. A marked increase in the activity accompanied by a decreasing amount of CO production, without deteriorating benzene selectivity even at higher conversion levels, was attained with Rh promoted by UO_3 (j, k). Thus, Rh–UO_3 was found to be about three times as active as unpromoted Rh and to have a much longer catalyst life. Since UO_3 alone was shown not to be active for the steam dealkylation, the promoting effect of UO_3 may be attributable to its

TABLE 1

Steam Dealkylation of Toluene[a]

No.	Catalyst[b]	Reaction temperature (°C)	Toluene conversion[c] (mol%)	Benzene selectivity[c] (mol%)	Gas production rate (Nl/hr)	Composition of gaseous product (mol%)			
						H_2	CO_2	CO	CH_4
a	Rh(0.3)	420	22.2	89.2	2.67	70.4	21.2	6.9	1.5
b	Rh(0.3)	450	45.3	89.6	5.07	68.4	20.1	8.3	3.2
c	Pd(0.3)	470	14.3	101.4	1.03	72.6	18.8	7.8	0.8
d	Pd(0.3)	500	22.0	98.9	1.76	71.8	19.8	7.2	1.2
e	Ir(0.3)	470	13.1	96.9	1.04	68.0	24.2	1.7	6.0
f	Ir(0.3)	500	26.5	93.9	2.29	66.0	24.4	1.9	7.7
g	Pt(0.3)	470	29.7	99.6	2.05	69.0	24.4	0.8	5.8
h	Pt(0.5)	450	20.6	99.0	1.50	68.9	25.2	0.0	5.5
i	Ru(0.3)	470	0.8	73.0	0.15	69.9	18.9	11.2	0.0
j	Rh(0.3)-UO_3(1.0)	420	62.5	90.9	7.01	70.0	24.5	2.1	3.3
k	Rh(0.3)-UO_3(1.0)	450	92.7	88.0	9.46	64.6	22.9	4.8	7.7
l	Pd(0.3)-UO_3(1.0)	420	11.7	101.8	0.89	75.0	23.5	1.5	0.0
m	Pt(0.5)-UO_3(1.0)	450	18.2	99.9	1.40	72.0	25.0	0.0	3.0

[a] LHSV(toluene = 0.67 ml/ml (catalyst)/hr; H_2O/toluene = 6 mol/mol.

[b] Figures in parentheses indicate percentage by weight based on γ-Al_2O_3 support.

[c] Toluene conversion = $(X + Y)$; benzene selectivity = $X/(X + Y)$; where X is percentage of toluene converted to benzene and Y to gaseous products by the benzene-ring cracking reaction with H_2O or H_2.

ability to catalyze the shift reaction. The proposed view is in accord with the fact that UO_3 also promoted Pd but not Pt (l, m). Inefficiency of UO_3 in the latter is conceivable since the shift reaction is already fast over unpromoted Pt.

The effect of CO admixed with toluene in the feed was also studied, and the results are summarized in Table 2. When unpromoted Rh was used as catalyst, the rate of the reaction decreased and a considerable portion of the added CO was recovered in the gaseous products. The rate was restored when the supply of CO was terminated. In sharp contrast, the rate remained unchanged, and added CO was almost completely converted to CO_2, when Rh-UO_3 was used. Although details are not given in the present note, it was made clear by a supplementary experiment that the reaction of CO with steam was quite fast over Rh-UO_3 even at 370°C.

TABLE 2

Effect of CO on Steam Dealkylation[a]

Catalyst[b]	Reaction temperature (°C)	Toluene feed rate (mol/hr)	CO feed rate (mol/hr)	Benzene in liquid product (mol%)	Composition of gaseous product (mol%)			
					H_2	CO_2	CO	CH_4
Rh(0.3)	470	0.047	—	27.1	72.0	15.9	11.2	0.9
Rh(0.3)	470	0.047	0.037	14.7	56.2	19.1	24.7	trace
Rh(0.3)-UO_3(2.0)	430	0.047	—	41.3	75.6	22.1	1.5	0.9
Rh(0.3)-UO_3(2.0)	430	0.047	0.042	38.3	67.2	31.1	0.6	1.1

[a] H_2O feed rate, 0.278 mol/hr.

[b] Figures in parentheses indicate percentage by weight based on γ-Al_2O_3.

The promoted Rh was subjected to a X-ray diffraction study using Ni-filtered Cu radiation, but no diffraction lines appeared except those pertaining to γ-Al_2O_3 support. Therefore, a model sample composed of 23 wt% Rh–77 wt% UO_3 was tested for the same study. The original sample reduced by H_2 at 450°C gave diffraction lines at the 2θ-values of 28.3, 32.8, 47.2, and 56.0. The lines were identified as being due to UO_2 based on agreement with those listed by ASTM. Upon steaming at 450°C, however, lines due to UO_2 disappeared and converted completely to those of $UO_{2.9}$. The values of 2θ observed were 21.4, 26.2, 34.1, 43.7, 46.4, 51.7, 53.9, and 58.7 in the range 20–60; also in agreement with the ASTM compilation for $UO_{2.9}$. These latter lines were again reduced to those of UO_2 at 450°C either by toluene or by CO. In this latter instance, CO, CO_2, and CH_4 were formed from toluene, and CO_2 from CO. In the course of the above treatment, Rh remained in its metallic form.

Based on the discussions presented, the role of urania in the Rh–UO_3 catalyst for the steam dealkylation can be described in terms of the following three distinct steps. UO_2 first dissociatively adsorbs H_2O and thereby changes its oxidation state to $UO_{2.9}$. The ambient oxygen in the latter then reacts with the hydrocarbon fragment adsorbed on Rh to form CO. CO is further oxidized to CO_2, and at the same time UO_2 emerges. The function of urania as such a redox medium should rest on the ease with which it forms oxygen-deficient nonstoichiometric compounds ranging from UO_2 to $UO_{2.9}$. The oxidation state of U up to U_3O_8, rather than $UO_{2.9}$, has been suggested by Dowden (*8*). But the occurrence of U_3O_8, if at all, does not alter our view on the role of urania.

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