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Metal–Support Interaction in Automotive Exhaust Catalysts: Rh–Washcoat Interaction

In our previous study of γ-alumina-supported Rh catalysts (*1*), it was shown that dispersibility, adsorption capacity, and thermal stability of Rh are greatly affected by the γ-alumina support. High dispersion was easily obtained on samples of low Rh loading [<2.5 μmol Rh/m^2 (BET)], but dispersed Rh was unstable to heat treatment in air at 873°K or higher because of a strong Rh–γ-Al_2O_3 interaction resulting in diffusion of Rh oxide into the support. Some automotive exhaust catalysts are supported on ceramic monoliths which possess mechanical strength and thermal resistance but little surface area for dispersion of active ingredients. This ceramic support is covered with a "washcoat," a thin layer of porous and refractory material to increase the surface area of the support. This work compares the effect of three washcoat materials, γ-Al_2O_3, α-Al_2O_3, and ZrO_2, on the CO chemisorption capacity, thermostability, and catalytic activity for the H_2–NO reaction of Rh on a monolithic support.

EXPERIMENTAL

The catalyst samples were prepared on Corning monoliths made of cordierite material ($Al_4Mg_2Si_5O_{18}$) with 47 passageways per square centimeter. This ceramic support was coated with a thin layer (about 10 wt% after drying) of γ-Al_2O_3. (Dispal-M, Continental Oil Co.) or ZrO_2 (Zircar Powder, Zircar Products, Inc.) and dried at 373°K, and some of the γ-Al_2O_3 washcoated monoliths were subjected to a 1423°K heat treatment for 2 hr. X-Ray diffraction examination of these samples showed the presence of α-Al_2O_3. The washcoated monoliths were impregnated with aqueous $Rh(NO_3)_3$ solution, dried at 393°K, and reduced in flowing H_2 at 673°K for 2 hr. Rh loading was analyzed by the conventional X-ray fluorescence method and by the inductive coupled plasma (ICP) technique. Both methods gave good agreement.

The volumetric adsorption measurements were performed in a conventional constant-volume apparatus equipped with a quartz spiral Bourdon Gauge (Texas Instruments) on samples which had been reduced by flowing H_2 at 673°K for 2 hr (*1*). Equipment and procedure for the activity measurements are described in Ref. (*2*). Catalyst samples (1.9 × 1.3 cm) were placed in a flow reactor with a vertical quartz tube 127 cm long and 1.9 cm in diameter encased in a 54000 Linderg Hevi-Duty tubular furnace. A pulse-flame apparatus (*2*) was used in the deactivation experiments. In this apparatus, isooctane fuel containing Pb, P, and S was burned in a pulsed flame to generate a simulated exhaust gas stream (corresponding to about 30 simulated miles per hour) which fed into a reactor containing the catalyst. The analytical section of the apparatus consists of detectors for NO (chemiluminescence, Leco Corp.), O_2 (fuel cell type, Teledyne), CO (NDIR, Beckman), and hydrocarbon (FID, Beckman).

RESULTS AND DISCUSSION

1. The Adsorption Capacity of Rh

Total CO adsorption isotherms were measured at 298°K on reduced fresh Rh catalysts with three different washcoats. These samples were subsequently outgassed at 298°K for 0.5 hr and then a reversible CO adsorption isotherm was taken. The difference between the total and the reversible uptake was taken as the

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irreversible adsorption of CO on Rh. These results are summarized in Table 1. Because of the large reversible adsorption of CO on the washcoated support, only the irreversible part of adsorption was used to calculate the adsorption capacity, CO_{ir}/Rh, i.e., the number of CO molecules adsorbed per surface Rh atom. In these catalysts, the Rh loading is far below the saturation concentration of 2.5 μmol Rh/m^2(BET) and all Rh oxide should be completely dispersed (*1*). The high ratio of CO_{ir}/Rh (>1) on Rh/γ-Al_2O_3 indicates the presence of a doubly adsorbed CO species (*3*, *4*). This ratio decreases as the washcoat changes in the order

$$Rh/\gamma\text{-}Al_2O_3 > Rh/\alpha\text{-}Al_2O_3 > Rh/ZrO_2. \quad (1)$$

Two possible interpretations can be given for the decrease of the CO adsorption capacity as the washcoat changes. One is the decreased dispersibility of Rh on α-Al_2O_3 and ZrO_2 due to the lower surface area of these washcoats. The other is that the stability of the adsorbed CO depends strongly on the washcoat material. If the first interpretation is correct, then the CO adsorption capacity of Rh/α-Al_2O_3 should be about the same as that of Rh/ZrO_2 since the surface area of these two washcoats is about the same. The large difference in CO adsorption capacity between Rh/α-Al_2O_3 and Rh/ZrO_2 does not support this interpretation. Furthermore, the Rh loading in all three samples is far below the saturation concentration of Rh in the dispersed phase (*1*) so the Rh in these three samples should be completely dispersed. The second interpretation is supported by Solymosi *et al.* (*5*) who report that the support material has a large effect on the stability of the adsorbate. The weaker CO adsorption on Rh/ZrO_2 may well result from the large reversible adsorption of CO on ZrO_2 (Table 1) and the consequent higher repulsive force of the adsrobed CO molecules on Rh/ZrO_2.

2. *The Thermal Stability of Rh as Measured by CO Adsorption*

A single sample of each of the three catalysts was subjected to a series of calcination–reduction cycles at several successive calcination temperatures: (i) calcination in flowing air for 5 hr, (ii) reduction in flowing H_2 at 673°K followed by CO adsorption at 298°K, and (iii) reduction in flowing H_2 at 823°K followed by CO adsorption at 298°K. The results in Fig. 1 indicate that thermal stability of Rh on these three washcoats during heat treatment in air at temperatures from 773 to 1073°K increases in the order

$$Rh/\gamma\text{-}Al_2O_3 < Rh/\alpha\text{-}Al_2O_3 < Rh/ZrO_2. \quad (2)$$

Yao *et al.* (*1*) attributed the loss of accessible Rh on γ-Al_2O_3 after oxidative heat treatment at 873°K to the diffusion of Rh oxide

TABLE 1

CO Chemisorption On Reduced Rh Catalysts

Washcoat material	BET area (m^2/g)	Rh loading		CO_{re}[a] (μmol/m^2 BET)	CO_{ir}[b] (μmol/m^2 BET)	CO_{ir}/Rh
		wt%	μmol/m^2 (BET)			
γ-A_2O_3	16.1	0.014	0.084	0.07 (0.068)	0.11	1.3
α-A_2O_3	2.7	0.017	0.61	0.25	0.68	1.1
ZrO_2	2.4	0.010	0.40	0.78 (0.77)	0.33	0.8

[a] CO_{re} = Reversible part of adsorption. It includes the adsorption on the support shown in the parentheses.

[b] CO_{ir} = Irreversible part of adsorption.

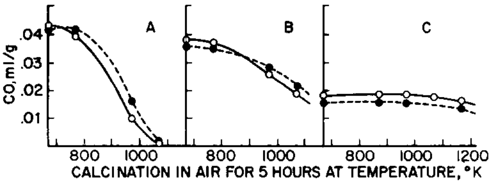

FIG. 1 The effect of calcination in air on (A) 0.014 wt% Rh/γ-Al_2O_3, (B) 0.017 wt% Rh/α-Al_2O_3, and (C) 0.010 wt% Rh/ZrO_2. ——, Samples reduced at 673°K; ---, samples reduced at 823°K.

into the γ-Al_2O_3 support. The dissolved Rh oxide interacts strongly with γ-Al_2O_3 and can be reduced only at temperatures >773°K. Results from this further indicate that during heat treatment in H_2 at 823°K the CO accessibility of Rh which was lost during the oxidative heat treatment at 773°K is completely restored. The Rh accessibility lost in the oxidative heat treatment at 973°K is only partially restored but that lost at 1173°K is not restored (Fig. 1A). For the Rh/α-A_2O_3 catalyst, the diffusion of Rh oxide into α-A_2O_3 is not indicated at 773°K, but is indicated at 973 and 1073°K. Part of the Rh accessibility is restored by the reductive heat treatment at 823°K. For the Rh/ZrO_2 catalyst, no diffusion of Rh was found even after the oxidative heat treatment at 1173°K for 5 hr. The reductive heat treatment at 823°K generally lowered the Rh area by 10–15% indicating sintering. After the oxidative heat treatments at 873 and 973°K, the Rh accessibility upon reduction at 673°K was found to have returned to the original value, indicating a redispersion. Although such sintering in reductive heat treatment and subsequent redispersion in oxidative heat treatment have not been reported before on supported Rh catalysts, similar phenomena were found on supported Pt catalysts (*6–8*).

3. The Effect of the Washcoat on the Catalytic Activity of Rh

For the NO–H_2 rection, catalytic activity measurements at a space velocity of 60,000 hr^{-1} were made on Rh catalysts as a function of temperature before and after heat treatment in air at 1223°K for 1 hr. Activity is defined as the total NO conversion to three main products: N_2 N_2O, and NH_3. The net NO conversion is the ratio of the unfixed nitrogen compounds, N_2 and N_2O, to the total NO conversion, i.e., $(N_2 + N_2O)/(N_2 + N_2O + NH_3)$. The results in Table 2 show that all three fresh catalysts give maximum total NO conversion in the temperature range 573–823°K. But the net NO conversion increases as the washcoat is changed from γ-Al_2O_3 to α-Al_2O_3 to ZrO_2.

The heat treatment of the catalysts in air at 1223°K sharply decreases total NO conversion of the Rh/γ-Al_2O_3 catalyst, moderately decreases it on the Rh/α-Al_2O_3 catalyst, and has little effect on the Rh/ZrO_2 catalyst. Thus, the effect of the washcoat on thermal stability of Rh described in Eq. (2) is supported by a total NO conversion measurement. The large loss of activity on the Rh/γ-Al_2O_3 catalyst is attributed to the larger Rh/γ-Al_2O_3 interaction and to the diffusion of Rh oxide into γ-Al_2O_3 during oxidative heat treatment.

Although total NO conversion over the three fresh catalysts is similar, net conversion of NO over the Rh/γ-A_2O_3 catalyst is very low. Net NO conversion increases as the washcoat is changed from γ-Al_2O_3 to α-Al_2O_3 to ZrO_2. Oxidative heat treatment at 1223°K for 1 hr improved the net NO conversion significantly over both Rh/γ-Al_2O_3 and Rh/α-Al_2O_3 catalysts. Similar improvement of net NO conversion was reported by Schlatter and Taylor (*9*) for a γ-Al_2O_3-supported pelleted Rh catalyst. We attribute the improvements of net NO conversion over Rh/γ-Al_2O_3 and Rh/α-Al_2O_3 after oxidative heat treatment at 1223°K to a change in surface structure of the washcoat possibly due to the diffusion of Rh oxide into γ-Al_2O_3 and α-Al_2O_3 during the heat treatment. On the other hand, because of the absence of Rh oxide diffusion in Rh/ZrO_2 catalyst no similar improvement is observed.

TABLE 2

Effect Of Precalcination in Air on Catalytic Activity and Selectivity of the Rh Catalysts in NO–H_2 Reaction[a]

Washcoat	γ-A_2O_3				α-A_2O_3				ZrO_2			
Rh loading	0.014 wt%				0.017 wt%				0.010 wt%			
Heat treatment in air	Fresh		1223°K 1 hr		Fresh		1223°K 1 hr		Fresh		1223°K 1 hr	
	Total (%)	Net (%)	Total (%)	Net (%)	Total (%)	Net (%)	Total (%)	Net (%)	Total (%)	Net (%)	Total (%)	Net (%)
T(°K)												
573	97	—	20	18	97	73	50	40	98	72	77	67
623	100	26	68	38	100	42	95	50	100	48	94	44
673	100	16	82	13	100	28	91	39	100	—	96	41
723	100	16	75	32	100	37	90	53	99	43	94	42
773	100	32	48	27	100	49	88	60	98	58	93	50
823	100	—	21	14	100	—	80	60	96	56	91	51

[a] Feed gas = 0.3% H_2 and 0.1% NO in N_2.

PRACTICAL IMPLICATIONS

In the above study of the Rh–washcoat interaction ZrO_2 and α-Al_2O_3 washcoat show resistance to thermal deactivation. Since the BET area of ZrO_2 and α-Al_2O_3 washcoats was five to seven times lower than that of γ-Al_2O_3 washcoat (Table 1) it was necessary to compare the chemical resistance of these catalysts for Pb, P, and S in fuel. Experiments were carried out in a pulse-flame reactor with isooctane fuel containing either 6 mg Pb/gallon (certification fuel) or 60 mg Pb/gallon with 0.8 mg P/gallon and 0.03 wt% S (*10*). The results showed that using a fuel containing a ten times excess of lead over the certification fuel, the Rh/α-Al_2O_3 and Rh/ZrO_2 catalysts show significantly higher deactivation compared with a Rh/γ-Al_2O_3 catalyst after 15,000 simulated miles of pulsator aging. On the other hand, catalysts were substantially less deactivated when tested for durability with fuel containing a certification level of lead. These results indicate that the catalysts prepared on thermally stable washcoats may be compatible only with fuels of low lead level (Pb $<$ 6 mg/gallon).

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