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Effects of Poisoning and Sintering on the Pore Structure and Diffusive Behavior of Platinum/Alumina Catalysts in Automotive Converters

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Fresh, sintered (heat treated) and lead poisoned spherical Pt/Al_2O_3 pellets were investigated by ultrahigh pressure mercury porosimetry measurements and by hydrogen–nitrogen static counterdiffusion. The relationship between the effective diffusivity of these pellets and their pore structure was analyzed using the random pore diffusivity model.

Poisoning and sintering were found to have opposing effects on the diffusivity. These effects may counterbalance each other in catalytic converters during the aging process so that it is possible that no net observable change in the diffusivity of H_2 in N_2 is recorded during diffusivity measurements on samples from these converters. These phenomena are interpreted in terms of the changes in the pore structure of the catalysts during poisoning and sintering.

NOMENCLATURE

D, D_K, D_{AB}, $D_{AB,eff}$	diffusivities, see text (cm²/sec)
M_A	molecular weight of species A (g/mole)
r	pore radii (frequency peaks) (cm, Å)
$\bar{r}$	integral averaged pore radii [see Eq. (1)] (cm, Å)
R	gas constant ($= 8.3144 \times 10^7$) (g cm²/sec²/mole/°K)
T	temperature (°K)
V	pore volumes (cm³/g)
ϵ	porosities
ρ	densities (g/cm³)

INTRODUCTION

It is generally recognized that diffusion resistances may significantly influence the conversion of hydrocarbons and carbon monoxide in oxidative automobile converters. For this reason, it was of interest to investigate how the diffusive behavior of the catalyst changes during its lifetime and whether these changes can be explained in terms of the pore structure of the aged catalysts.

The most frequently encountered aging phenomena in automobile converters can be characterized as thermal (sintering) and chemical (poisoning) processes. In this paper we deal with the sintering of the support itself and not that of the active catalyst. The sintering and poisoning experiments were carried out under controlled conditions to separate the effects of these two different catalyst aging modes on the diffusivity.

EXPERIMENTAL METHODS

A variety of experimentally poisoned and sintered catalyst samples was prepared by aging in reactors attached to conventional engine dynamometer installations with a 5735 cm^3 V8 engine as the source of exhaust and poisons. In addition, laboratory sintering experiments were conducted by heating the catalyst samples to high temperatures in the presence of air. Other catalyst samples were poisoned in the laboratory by impregnation with a lead acetate solution and heating to about 350°C in air. Subsequently, the pellets were exposed to a gaseous mixture of about 20% O_2, 1% SO_3, and 3% H_2O in N_2 at about 300°C. The SO_3 was generated by oxidizing SO_2 over a Pt/Al_2O_3 catalyst at 600°C. X-Ray diffraction analysis of the samples revealed the presence of PbO and $PbSO_4$ over the catalyst surface.

The catalyst pellets which filled the reactors had a mean radius of 0.159 cm. The impregnation was carried out by wetting the support with a large excess of an $H_2(PtCl_6)$ solution in water. Subsequent chemical analyses confirmed the platinum levels reported. The distribution of the Pt along the pellet radii was nonuniform (observed by electron microprobe), decreasing toward the center.

The static N_2–H_2 counterdiffusion measurements were carried out in an apparatus built in our laboratories, employing similar techniques to those described by Wicke and Kallenbach (*1*). The spherical catalyst pellets were mounted in flexible Tygon tubes as proposed by Weisz (*2*).

The mercury porosimetric measurements were carried out using a 60,000 psi (4081 atm) porosimeter. A wetting angle of 140° between the mercury and alumina was used in the conversion of pressure data to pore radii.

RESULTS AND DISCUSSION

Figure 1 shows a plot of the specific mercury penetration volume V (cm^3/g) against the logarithm of the pore radii r (Å).

The integral average radii of the micropores ($\bar{r}_{\text{micro}}$) and the macropores ($\bar{r}_{\text{macro}}$) were computed by graphical integration of the r–V curves. The most probable pore radii (r_{macro} and r_{micro}) were estimated from the appropriate inflexions of the V–ln r curves.

The properties of the catalysts were correlated with the effective diffusivity of H_2 in N_2 using the random pore model of Wakao and Smith (*3*). This model was

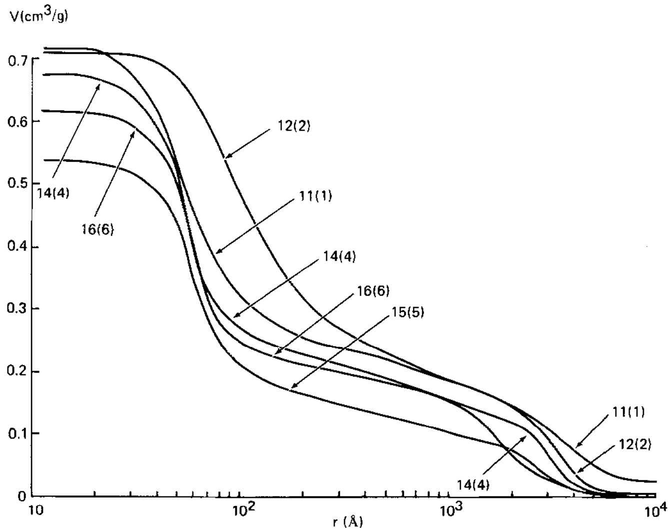

FIG. 1. Pore volume–pore radius data. The samples were poisoned in an experimental converter or sintered [sample 12 (2)] in the laboratory (see Table 1 for details).

used because it contains no adjustable parameters. The molecular diffusivity of H_2 in N_2 was calculated from the Slattery-Bird formula (*4*). Comparison of calculated and measured diffusivities reveal (Table 1) that both the trends and the absolute values of the calculated and measured effective diffusivities agree well for the catalysts investigated in this work. Thus, the random pore model correlates the pore structure of our catalysts with the effective diffusivities rather well.

Inspection of Fig. 1 and Table 1 reveals some interesting features of the effects of sintering (high temperature treatment) and poisoning on the pore structure and diffusive behavior of these catalysts. It is especially interesting to observe that sintering has a tendency to shift the micropore distribution curve toward larger radii, leaving the micropore volume intact. Increasing levels of poisoning appear to change the micropore volumes while the most probable value of the micropore radii remain unaffected.

Both sintering and poisoning have the same effect on the macropores: they tend to shift the distribution peaks toward smaller radii. The macropore volumes remain essentially unchanged during this process, but it appears [sample 15 (5)] that the macropore volume decreases significantly for heavily poisoned catalysts.

The influence of all these pore structure changes on the effective diffusivity of H_2 in N_2 is shown in Table 1. While sintering alone increases the effective diffusivity, smaller levels of poisons leave it essentially intact. That is, initially only the micropore volumes appear to be filled by the poisons, and the effective diffusivity does not decrease significantly during this process since it largely depends on the macroporous structure. However, the effective diffusivity rapidly decreases if the accumulated poison level is so high that it also begins to obstruct the macropores.

Electron microprobe analysis of the catalysts poisoned in experimental automotive converters showed that the poisons accumulate near the surface of the catalyst pellets. Thus, the measured pore size distributions and diffusivities represent some kind of an average between the poisoned and unpoisoned sections of the catalyst pellets. We also investigated catalyst pellets which were poisoned in the laboratory by lead impregnation and subsequent partial sulfatization as described earlier. This resulted in a nearly uniform distribution of lead across the radius of the pellet. As Table 2 and Fig. 2 indicate, the behav-

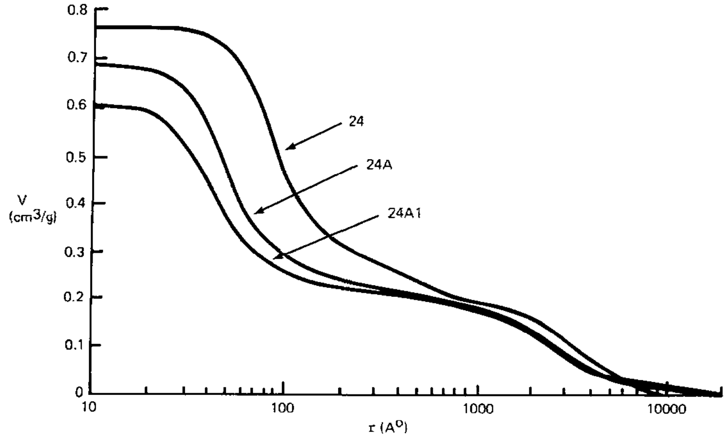

FIG. 2. Pore volume–pore radius data. The samples were lead sulfate poisoned in the laboratory (see Table 2 for details).

TABLE 1

SINTERED AND POISONED CATALYSTS; THE POISONING WAS CARRIED OUT IN AUTOMOTIVE CONVERTERS

Catalyst[a]	History	V_{ma} (cm^3/g)	V_{mi} (cm^{3}g)	Integral av $\bar{r}_{ma}$ (Å)	Integral av $\bar{r}_{mi}$ (Å)	Frequency peaks r_{ma} (Å)	Frequency peaks r_{mi} (Å)	ϵ_{ma}	ϵ_{mi}	ρ_{solid} (g/cm^3)	ρ_{pellet} (g/cm^3)	Random pore $D_{H_2-N_2}$ (cm^2/sec)	Measured $D_{H_2-N_2}$[b] (cm^2/sec)
0.1% Pt/Al$_2$O$_3$ 1(1)	Fresh (calcined 5 hr, 500°C)	0.210	0.503	3945	102.1	4300	58	0.198	0.475	2.89	0.944	0.086	0.082 0.089 0.078 0.086
0.1% Pt/Al$_2$O$_3$ 12(2)	Sintered (24 hr, 1000°C in air)	0.200	0.508	3112	178.8	3700	100	0.200	0.507	3.40	0.998	0.111	0.111 0.111 0.113
0.1% Pt/Al$_2$O$_3$ 14(4) RR-13	Poisoned (34 hr, 560°C, 0.6% Pb, 0.11% P)	0.190	0.483	2580	68.5	3600	55	0.199	0.507	3.57	1.049	0.070	0.081 0.077 0.091
0.1% Pt/Al$_2$O$_3$ 16(6) RR-10	Poisoned (46 hr, 560°C, 11.1% Pb, bottom of bed)	0.195	0.420	2061	76.7	1850	58	0.219	0.472	3.63	1.123	0.066	0.091 0.077 0.086
0.1% Pt/Al$_2$O$_3$ 15(5) RR-10	Poisoned (46 hr, 560°C, 14.1% Pb, top of bed)	0.130	0.407	2290	87.8	2800	58	0.155	0.486	3.32	1.222	0.052	0.063 0.062 0.068

[a] Average pellet radius: 0.159 cm.

[b] The numbers reflect measurements on individual pellets of 0.178 cm radius and were repeatable to about ±2%.

TABLE 2
CATALYSTS POISONED IN THE LABORATORY BY LEAD IMPREGNATION

No.	Catalyst	Poison	V_{ma} (cm^3/g)	V_{mi} (cm^3/g)	Integral av		Frequency peaks		ϵ_{ma}	ϵ_{mi}	ρ_{solid} (g/cm^3)	ρ_{pellet} (g/cm^3)	Random pore $D_{H_2-N_2}$ (cm^2/sec)	Measured $D_{H_2-N_2}$ (cm^2/sec)	
					$\bar{r}_{ma}$ (Å)	$\bar{r}_{mi}$ (Å)	r_{ma} (Å)	r_{mi} (Å)							
24	0.1% Pt/ Al_2O_3	Fresh	0.220	0.540	3910	108.0	4000	96	0.212	0.520	3.58	0.962	0.091	0.092	0.092
														0.089	0.088
24A	0.1% Pt/ Al_2O_3	9.8% Pb 0.1% S	0.221	0.460	3720	75.1	3300	59	0.232	0.485	3.72	1.054	0.078	0.083	0.089
														0.083	0.084
24Al	0.1% Pt/ Al_2O_3	10.1% Pb 0.5% S	0.210	0.395	3200	66.0	3000	53	0.248	0.460	4.04	1.180	0.074	0.084	0.083
														0.094	0.091

ior of these lead impregnated catalysts is similar to catalysts poisoned in automotive converters. Thus, the lead appears to deposit first in the micropores and causes only minor changes in the macropore structure.

We conclude then that sintering and poisoning have an opposite influence on the effective diffusivity. Since these processes coincide during the operation of typical automotive converters, not much change in the effective diffusivity should be observed during a good part of the catalyst's life. Indeed, Dwyer and Morgan (*5*) reported that no significant changes in the diffusive behavior of a base metal/alumina catalyst could be observed after the catalyst was poisoned by lead in an oxidative catalytic converter. As a matter of fact, their published data show a slight increase in the measured effective diffusivity which we feel can be interpreted in the light of the mechanisms proposed here.

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