

$$(f) \int \phi_{v, \sigma}^* \phi_{v, \sigma} d\tau = \langle v|2\rangle = \sum_i C_{2i} \langle v|i\rangle$$

$$= C_{20} \langle v|0\rangle + C_{21} \langle v|1\rangle + C_{22} \langle v|2\rangle + \dots$$

$$(g) \int \phi_{i, \sigma}^* \phi_{v, \sigma} d\tau = \langle 2|v\rangle = \sum_i C_{2i} \langle i|v\rangle$$

$$= C_{20} \langle 0|v\rangle + C_{21} \langle 1|v\rangle + C_{22} \langle 2|v\rangle + \dots$$

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Lead Tolerance of Noble Metal Catalysts for CO Oxidation

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Lead tolerance of Pt/Al₂O₃ catalysts was evaluated for CO oxidation depending on the properties of the alumina supports and base metals added as promoter. Among the four different alumina supports, the support with a large macropore volume (0.45cc/g) and 5% Ce has shown the best resistance to lead poisoning. Most of the base metals added to the Pt-catalysts were found to be ineffective for improving lead resistance, but boron has shown an excellent lead tolerance, although it decreases the initial catalytic activity.

Introduction

The major cause of catalyst deactivation in the automobile systems using leaded gasoline is poisoning by lead. Although the lead deactivation has recently been reviewed by several authors,¹⁻⁴ its detailed mechanism was not completely understood. Some of the important aspects of lead poisoning known by experiments are that among the single component metal catalysts, Pt-catalyst is most resistant to lead poisoning and a considerable fraction (10-30%) of the lead in the fuel consumed is deposited on the catalyst as lead sulfate or phosphate in major. Such a coating of lead salts on the catalyst surface cause poor mass transfer properties³ resulting in decrease of its activity. Furthermore, experiments have shown only a small changes in the macropore volume of the support Al₂O₃, while a remarkable decrease in the micropore volume was observed.⁵

In this paper we present the results of the attempts to prepare lead-tolerant catalysts for CO oxidation by impregnating platinum into modified γ -Al₂O₃ supports with dif-

ferent properties and by promoting the Pt-catalyst using various base-metals.

Experimental

Preparation of Pt-catalysts supported on γ -Al₂O₃.

Pt-impregnated catalysts were prepared using four different kinds of γ -Al₂O₃ pellets of 2-8mm in diameter obtained from Rhone-Poulenc. Their characteristic properties are shown in Table 1.

In order to load platinum an aqueous solution of H₂PtCl₆·6H₂O with pH adjusted to 2.5±0.5 using HCl solution was impregnated on the alumina supports. An exact amount of the Pt-solution containing 0.2% Pt of the alumina support was taken into a round-bottom flask together with the dried alumina pellets and then evaporated to dryness in a rotary evaporator at 85°C. The catalyst was dried at 150°C in oven and then calcined for 4 hours at 550°C. The catalyst was then reduced under hydrogen atmosphere for 2 hours at 550°C before use.

Preparation of Base Metal-Promoted Pt-Catalysts.

To increase the catalytic activity and durability of the Pt-catalysts some base metals such as B, Mn, V, Sn, Fe and Cr were selected and incorporated to the Pt-catalysts as was described in the literatures.⁶⁻¹⁵ In case of boron, a dilute aqueous solution of boric acid (3%) was impregnated onto Pt-loaded alumina as was mentioned in the above, and then the boron-promoted Pt-catalyst was calcined at 600°C for one hour resulting in retention of 0.2% B₂O₃ on the catalyst.

On the other hand, the other transition metals were impregnated before platinum loading. Aqueous solutions of MnCl₂·4H₂O, SnCl₄·5H₂O, Fe(NO₃)₃·9H₂O and Cr(NO₃)₃·9H₂O containing exact amounts of metals to be loaded were used for impregnation on alumina, drying and calcining processes followed and then platinum was loaded on each of these transition metal oxide catalyst in the same way as above-mentioned. For vanadium loading the incipient method was employed: an exact amount of V₂O₅ was dissolved in an aqueous ammonia solution of an exact volume corresponding to the measured pore volume of the alumina support to be taken, and this solution was added dropwise to the support. The dried and calcined catalyst was then loaded with platinum.

Lead-poisoning.

In order to save time and to control the amount of poison, the catalysts prepared in the above were poisoned artificially in the laboratory using lead acetate or nitrate solution according to the methods in the literature.^{5,15} The catalysts prepared in the above were impregnated with a lead nitrate or acetate solution containing a desired amount of lead, dried for one hour at 150°C and calcined for 4 hours at 480°C. The lead oxide thus obtained was converted to lead sulfate by being exposed for 12 hours to an air mixture of about 1% SO₃, which was generated by oxidizing SO₂ over Pt/Al₂O₃ catalyst at 500°C. The amount of lead poisoning was controlled at 0.5% of the support in all cases, which was found to be appropriate for comparisons in this study.

Evaluation of Catalytic Activities.

The activities of fresh and poisoned catalysts were evaluated using a composite gas reactor system in the laboratory schematically shown in Figure 1. An appropriate gas mixture was obtained by controlling the rotameters (Matheson) connected to component gas cylinders. A typical composite gas used for the evaluation was composed of 2.2 vol % CO, 4.4 vol % O₂, 9.5 vol % CO₂ and 83.9 vol % N₂, which is similar to the compositions of auto-exhaust gases at the stage of engine start-up. This composite gas was fed into the reactor surrounded by an electric furnace automatically temperature-controlled. The temperature of the catalytic bed was directly measured by a thermometer recorded. The

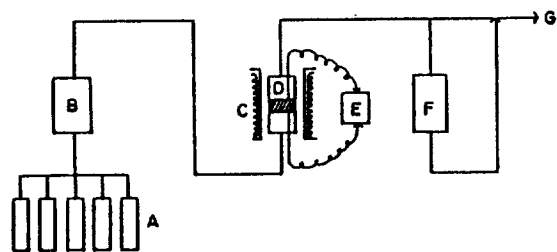


Figure 1. A schematic diagram of a composite gas reactor system. A, rotameters; B, gas mixer; C, electric furnace; D, reactor with a catalytic bed; E, thermometer; F, gas chromatograph; G, outlet.

reacted gas mixtures were analyzed by a Hewlett-Packard Model 5732A Gas-chromatograph. The amounts of catalysts for each charge was approximately 3g and the flow rate of the composite gas was adjusted to be in the range 12,000-19,000 hr⁻¹ of GHSV.

The surface areas and the amounts of hydrogen adsorption of the Pt-catalysts were measured by standard methods using BET apparatus.

Results and Discussion

The Effect of Properties of γ -Al₂O₃ Support on Lead Poisoning.

In general, the catalytic activities of fresh metal catalysts are concerned with the number of active sites and with surface area of the catalyst, but their durability largely depends on the chemical, and physical properties of the support material.

The activities for CO oxidation by fresh catalysts containing the same amount of platinum (0.2 wt%) on different γ -Al₂O₃ supports were shown in Figure 2. The activities of the fresh Pt-catalysts depending on the different aluminas are shown to be similar in the figure as expected from more or

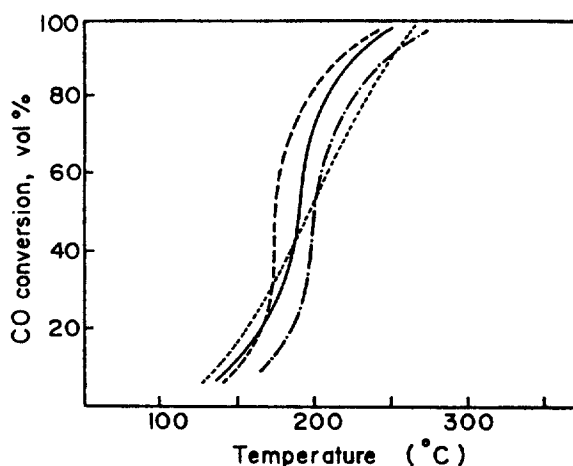


Figure 2. Activities of fresh Pt-catalysts on alumina supports A (—), B (— · —), C (— · · —), and D (— · —) depending on reaction temperatures.

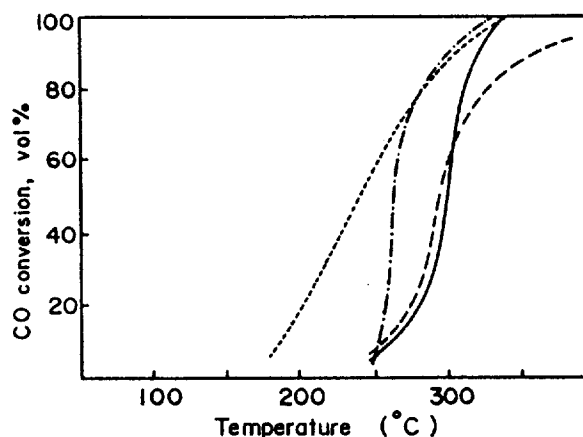


Figure 3. Activities of Pb-poisoned Pt-catalysts on alumina supports A (—), B (— · —), C (— · · —), and D (— · —).

less the same measured surface areas given in Table 2. However, the temperature profiles of the catalyst activities exhibit noticeable differences in detail. For instance, the CO conversion by the Pt-catalyst on support C is less dependent on temperature than by others. These small differences in activities of the fresh catalysts for CO conversion shown in the figure seem to be due to the different properties of the supports as is seen in Table 1.

However, the lead-poisoned catalysts have shown remarkable changes in activities on CO conversion and the effect of the properties of supports on their activities are more clearly seen in Figure 3 and in Table 2. The CO conversion temperatures of the Pb-poisoned catalysts on support A and D (Figure 3) are shifted in overall more than 100°C to the higher than those of the fresh catalysts on the same supports (Figure 2). On the other hand, the poisoned catalyst on support C has shown only moderate shift of less than 50°C. The activities of fresh and poisoned catalysts designated by temperatures of 50% CO conversion are compared directly in Table 2 along with the data of their surface area and hydrogen adsorptivity measured. It is seen in the table that the Pt-catalyst on support A with no macropore is most severely poisoned by lead, as its surface area and hydrogen adsorptivity are both drastically decreased. The support B and C have the same macropore volume, but the support C contains 5% Ce, which seems to improve the lead resistance as shown both in Figure 3 and in Table 2.

However, the results on support D indicate that added rare-earth metals can not improve lead resistance without a significant macropore volume, although rare earth elements are generally known to be effective in platinum catalysis. The general tendency of more drastic decreases of hydrogen adsorptivity of the Pb-poisoned catalysts in Table 2 may be attributed to the deposition of Pb metal atoms on the active

Pt-sites other than their plugging action on the micropores of the support.

In conclusion, the properties of the support play important role in improving lead tolerance, and the support material with large macropore volume and the rare earth element added seems to be most promising.

The Effect of Base Metal on Lead Poisoning.

It is known that some of the transition metal oxides are not only good oxidation catalysts themselves but also promote catalytic activities of noble metal catalysts.⁶⁻¹⁴ Therefore, several base metals were selected and added as promoter to the platinum catalysts in order to examine their effect on lead poisoning. However, surprisingly, the results have shown no significant improvement. The activities both of fresh and poisoned Pt-catalysts promoted by base metals are listed in Table 3 in terms of 50% CO conversion temperatures. It is seen in the table that regardless of the properties of the supports the base metals do not show promoting effects neither in fresh nor poisoned Pt-catalysts. The general tendency of higher temperatures of 50% CO conversions by poisoned Pt-catalysts promoted by base metals compared with those by poisoned Pt-catalysts without promoter (Table 2) seems to imply that the base metals added may act as poison rather than promoter probably through a chemical interaction. Such a result is surprising since the base metals were impregnated on the γ -Al₂O₃ support before platinum loading as was mentioned in the experimental section. On the other hand, the non-transition element boron which was added after Pt-loading has shown an interesting feature: Although the activities of fresh boron-added Pt-catalysts on Support C and

Table 1. Properties of γ -Al₂O₃ Pellets

	A	B	C	D
Bulk density (g/cc)	0.67	0.45	0.48	0.47
Surface area (m ² /g)	83	96	106	87
Macropore volume				
>0.1 μ (cc/g)	0	0.15	0.15	0.05
>1 μ (cc/g)	0	0.30	0.30	0.15
Total pore volume (cc/g)	0.65	1.0	1.0	0.9
Rare earth metal			5% Ce	2% Nd/La

Table 2. Activities of fresh and Pb-poisoned 0.2% Pt-catalysts Supported on Different Aluminas

Supports	Pb-poisoning content (wt%)	Surface area (m ² /g)	Amount of H ₂ -adsorbed (μ mole/g)	Temperatures(°C) for 50% CO conversion
A	—	83	7.2	188
A	0.5	48	2.1	296
B	—	96	8.4	200
B	0.5	84	3.8	263
C	—	106	8.4	190
C	0.5	91	4.7	238
D	—	87	6.8	175
D	0.5	67	4.2	294

Table 3. Activities of 0.2% Pt-catalysts Promoted by Base Metals on Different Aluminas

Supports	Transition metal /contents (wt%)	Poisoning Pb contents (wt%)	Temperatures(°C) for 50% CO conversion
A	Cr ₂ O ₃ /0.5	—	213
		0.5	284
B	Cr ₂ O ₃ /0.5	—	200
		0.5	264
C	B ₂ O ₃ /0.2	—	260
		0.5	279
	SnO ₂ /1.0	—	222
		0.5	295
	Fe/0.5	—	190
		0.5	302
Mn/0.5	—	240	
	0.5	308	
D	Cr ₂ O ₃ /0.5	—	175
		0.5	295
	B ₂ O ₃ /0.2	—	280
		0.5	291
	SnO ₂ /1.0	—	236
		0.5	312
	Fe/0.5	—	215
		0.5	305
	Mn/0.5	—	238
		0.5	304
Cr ₂ O ₃ /0.5	—	205	
	0.5	293	
V ₂ O ₅ /1.0	—	220	
	0.5	292	

D (in Table 3) are lower than those of Pt-catalysts without boron on the same supports (in Table 2), the both boron-promoted catalysts exhibit high tolerance against lead poisoning. The exact role of these base metals in the catalysis is not understood yet, but boron seems to be a promising candidate promoter for lead tolerant catalyst if the initial activity can be raised.

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Calculation of the Dipole Moments for Square Pyramidal Complexes

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Modified technique in calculating the dipole moments for square pyramidal complexes has been developed and then the dipole moments for bisacetylacetonato(oxo)vanadium(IV) complexes are calculated, adopting this approach. The calculated dipole moments for bisacetylacetonato(oxo)vanadium(IV) in benzene and bisacetylacetonato(oxo)vanadium in dioxane solutions are in agreement with the observed values. The calculated dipole moments of bisacetylacetonato(oxo)vanadium(IV) in dioxane solution is slightly higher than that of bisacetylacetonato(oxo)vanadium(IV) in benzene. Such a result may suggest that bisacetylacetonato(oxo)vanadium(IV) interact with dioxane molecule to form bisacetylacetonato(oxo)vanadium(IV)-dioxane adduct. This calculated dipole moments are also in agreement with the experimental results.

Introduction

Over the twenty years, a great deal of interest has been focussed on the measurement of the dipole moments for transition metal complexes in investigating their geometric structure in inert or aprotic solvent solutions.^{1,2} A method for calculation of the electric dipole moments for molecules containing rotating polar groups has been proposed by Gilman,³ modifying the vector method of Wilcox⁴ and the mean square moments for organic molecules containing a single rotatable polar group as well as one or more fixed groups were calculated to obtain information for the absence of free rotation. Recently this method was applied to the calculation of the dipole moments for $CL_nSn(CH_2CL)_{4-n}$ type complexes.⁵ The vector method of Wilcox and Gilman can only be applied to the calculation of the dipole moments for the molecules with both fixed and rotating polar groups. To overcome such the shortcoming, a new approach in calculating the dipole moments for transition metal complexes has been proposed. This approach was however applied to calculate the dipole moments for octahedral, square planar and tetrahedral complexes.

To determine the theoretical dipole moments for square pyramidal complexes such as bisacetylacetonato(oxo)vana-

dium(IV), we may modify the previous three assumptions,⁶ which has been made to attempt to calculate the dipole moments for transition metal complexes, as follows;

(1) The only valence electrons of ligands, which take part in valence bond with the central metal ion, are assumed to be contributed to the nuclear part of the dipole moments for transition metal complexes.

(2) The atoms that bond directly with the metal ions and are located at the end of the ligands are assumed to be the dominant contribution to the dipole moment for transition metal complexes. We therefore adopt the modified linear combination of valence basis sets of the transition metal and ligands.

The purpose of this work is to perform example calculations of the dipole moments for square pyramidal complexes, adopting the modified two assumptions. As far as we are aware, no attempt has been made to determine the theoretical dipole moments for square pyramidal transition metal complexes.

Theory

For example calculation of the dipole moments for square