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Low-temperature catalytic combustion on Pt / SO_4^{2-} / ZrO_2 and Pd / SO_4^{2-} / ZrO_2 catalysts

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Low-temperature combustion of various organic compounds on Pt/SO_4^{2-}/ZrO_2 and Pd/SO_4^{2-}/ZrO_2 was studied. For these organic compounds, especially saturated hydrocarbons, the combustion activities of Pt/SO_4^{2-}/ZrO_2 are higher than those of Pt/Al_2O_3. Pt/SO_4^{2-}/ZrO_2 combustion catalysts can be used in a wide range of space velocity and oxygen content. The catalytic activity is enhanced with an increase of Pt loading from 0.1 to 1.0 wt%. The superacidity of the support material is responsible for the improvement in activity rather than an increase in catalyst surface area or metal dispersion. Pd/SO_4^{2-}/ZrO_2 are less active than Pt/SO_4^{2-}/ZrO_2.

Keywords: low-temperature catalytic combustion; sulfated zirconia; Pt and Pd catalysts; superacidity

1. Introduction

Solid superacids are a new type of catalytic materials with acid strengths stronger than 100% H_2SO_4. Their potential of use as catalysts for selective hydrocarbon isomerization and chlorination at low temperature and other clean chemical processes has aroused enthusiasm among scientists recently [1–10]. Precious metal catalysts, such as platinum and palladium supported catalysts, are highly active for catalytic combustion of hydrocarbon and other organic exhausts. It has been reported that low-temperature catalytic combustion activity of propane can be enhanced by increasing the acid strength of the support [11]. When studying the temperature programmed desorption of basic organic molecules on solid superacids, it was also noticed that pyridine, aromatics, ethers and esters oxidize readily on solid superacid catalysts, so these compounds are not suitable to use as probe molecules for acidity measurements [12]. In the present work, the low-temperature catalytic combustion of various organic compounds on platinum supported sulfated zirconia catalysts was studied. The substitution of alumina by sulfated zirconia as a support increased the catalytic activities of the platinum catalyst considerably. This beneficial effect was discussed taking into account the experimental data on support characteristics and metal dispersion of the catalysts. The activities of palladium on sulfated zirconia for low-temperature combustion were compared with those of platinum on the same support material.

2. Experimental

Aqueous ammonia was added dropwise to a solution of $ZrOCl_2 \cdot 8H_2O$. The precipitate was filtered, dried, followed by immersing in a 0.5 M H_2SO_4 aqueous solution for 30 min. The sulfated sample was then filtered and dried at 110°C. The predried sulfated zirconia was impregnated with an aqueous solution of H_2PtCl_6 or $PdCl_2$, then followed by drying at 110°C and calcining in dry air at 650°C for 3 h. The obtained catalysts are labeled as Pt/SZ and Pd/SZ. Pt/Al_2O_3 catalyst was prepared by impregnating γ-Al_2O_3 with an aqueous solution of H_2PtCl_6, then followed by drying at 110°C and calcining in dry air at 400°C for 3 h.

The BET surface area of the catalysts was measured on a Micromeritics ASAP 2000 system under liquid N_2 temperature using N_2 as the adsorbent. The acid strength of the supports was measured by a modified Hammett indicator method [13] and *n*-butane isomerization as a probe reaction [14]. The dispersion of platinum or palladium was measured by the CO pulse-adsorption method. After the catalyst was reduced in flowing H_2 at 350°C for 3 h, CO pulses were injected into the catalyst bed at room temperature until the quantity of the exit CO pulse reached a steady value. The dispersion of platinum or palladium was calculated from the total CO

Table 1
Hexane oxidation activities of the samples

Sample	Atmosphere	Hexane conversion (%)			
		150°C	200°C	250°C	300°C
SZ	air	0	4.2	8.9	13.5
	N_2	0	0	0	0
Al_2O_3	air	0	0	6.3	11.2
	N_2	0	0	0	0
0.5% Pt/SZ	air	8.2	78.2	99.3	100
	N_2	0	0	0	0
0.5% Pt/ Al_2O_3	air	0	15.4	34.9	81.0
	N_2	0	0	0	0

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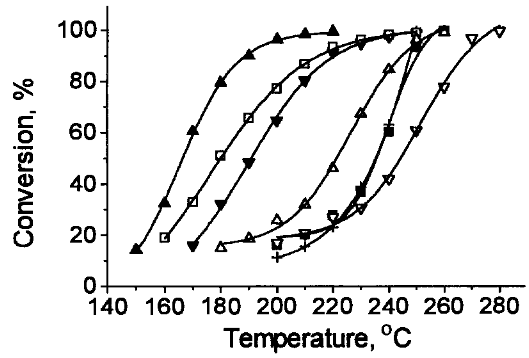

Fig. 1. Combustion activities of Pt/SZ for various organic compounds. (▲) Heptane, (▼) cyclohexane, (■) toluene, (+) benzene, (△) acetone, (▽) ethyl acetate, (□) hexane.

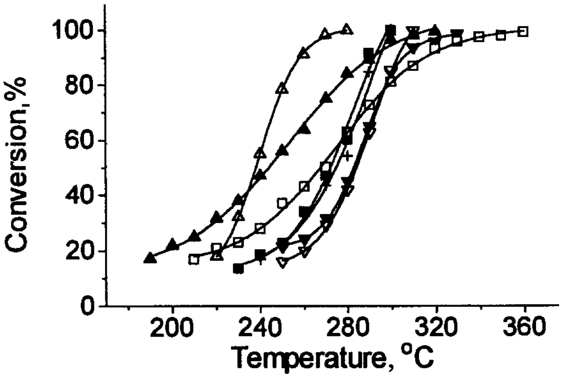

Fig. 2. Combustion activities of Pt/Al_2O_3 for various organic compounds. (▲) Heptane, (▼) cyclohexane, (■) toluene, (+) benzene, (△) acetone, (▽) ethyl acetate, (□) hexane.

uptake by assuming a stoichiometry of $[CO]/Pt_s = 1$ or $[CO]/Pd_s = 1$.

Catalytic tests were conducted by using a conventional continuous flow reaction apparatus. 0.67 ml of catalyst (40–60 mesh) was mixed with quartz powder in the ratio of 1 : 5 to prevent a local increase of temperature. Organic compounds were led through the catalysts by air or a mixture of air and nitrogen under the space velocity (GHSV) of 2700–5400 h^{-1} and the content of organic compounds in the raw gas was 29.5 g/m^3 creating a net-oxidizing atmosphere. The catalyst was pretreated in a flow of H_2 at 350°C for 3 h, and then in a flow of air at 550°C for 2 h. The reaction products were analyzed by using a gas chromatograph 30 min after the bed temperature attained the predetermined value measured by a thermocouple directly installed at the center of the catalyst bed.

3. Results and discussion

The oxidation of hexane on SZ, Al_2O_3, 0.5% Pt/SZ and 0.5% Pt/Al_2O_3 in air and N_2 under space velocity of 2700 h^{-1} was tested, and the results are given in table 1. Hexane is not oxidized on all the samples in N_2, indicating that the oxidizing property of the supported sulfate ions could not be responsible for the oxidation reaction. The conversions of hexane on SZ and Al_2O_3 in air are rather low in comparison with those of the Pt supported samples. As is now well known, noble metals like platinum on the catalyst surface may activate the dioxygen molecules and promote the catalytic oxidation cycle.

As shown in figs. 1 and 2, the activities of 0.5% Pt/SZ and 0.5% Pt/Al_2O_3 for the combustion of various organic compounds under the space velocity of 2700 h^{-1} and oxygen content of 21 vol% were increased as the reaction temperature was raised gradually. The temperatures of 95% conversion (T_{95}) were read out from the curves to compare the combustion activities of the catalysts for different organic compounds. They are listed in table 2. The T_{95} of all the organic compounds on 0.5% Pt/SZ are lower than those on 0.5% Pt/Al_2O_3, demonstrating that the former catalyst is more active in the combustion reaction than the latter. The activities of the two catalysts vary from compound to compound in a different way. For Pt/SZ, T_{95} decreases in the order of ethyl acetate > toluene > benzene = acetone > cyclohexane > hexane > heptane, while for Pt/Al_2O_3 the order changes to hexane > cyclohexane > ethyl acetate > heptane > benzene = toluene > acetone. This shows that the Pt/SZ catalyst is more favorable for the combustion of saturated hydrocarbons. The maximum difference in T_{95} between the two catalysts (105°C) is observed in the combustion of heptane, and the minimum (10°C) in the combustion of acetone.

Hexane, toluene and ethyl acetate were selected as the representative reactants to examine the effects of space velocity and oxygen content on the catalytic activity of 0.5% Pt/SZ in a net-oxidizing atmosphere. The results are listed in table 3. In all the three cases the oxidation activities of 0.5% Pt/SZ do not change very much when the space velocity is raised from 2700 to 5400 h^{-1}. The maximum rises in T_{95} are 10 and 20°C at oxygen

Table 2
Combustion activities of Pt/SZ and Pt/Al_2O_3 catalysts

Catalyst	T_{95} (°C)						
	heptane	hexane	cyclohexane	benzene	toluene	acetone	ethyl acetate
0.5% Pt/SZ	195	225	230	250	255	250	270
0.5% Pt/Al_2O_3	300	325	310	295	295	260	305

Table 3
Effects of space velocity and oxygen content on the activity of 0.5% Pt/SZ

Compound	Space velocity (10^3 h^{-1})	T_{95} (°C)	
		21 vol% O_2	11 vol% O_2
hexane	2.7	225	225
	4.1	225	235
	5.4	235	245
toluene	2.7	255	285
	4.1	255	285
	5.4	265	295
ethyl acetate	2.7	270	270
	4.1	270	270
	5.4	280	280

Table 4
Effects of noble metal loading on the catalytic activity

Catalyst	Pt or Pd (wt%)	T_{95} (°C)		
		hexane	toluene	ethyl acetate
Pt/SZ	0.1	255	295	290
	0.3	235	275	280
	0.5	225	255	270
	1.0	205	245	260
Pd/SZ	0.5	345	265	305
	1.0	340	250	295

contents of 21 vol% (reactant/O_2 mol ratio = 0.034–0.037) and 11 vol% (reactant/O_2 mol ratio = 0.065–0.070), respectively. Toluene oxidation on the 0.5% Pt/SZ catalyst is relatively more susceptible to the change of oxygen content in the reactants than the other two compounds. Its T_{95} is elevated by 30°C as the oxygen content is reduced by one half. The tolerance on space velocity and oxygen content of Pt/SZ shows that it can be a good and versatile combustion catalyst for exhaust gases with low content of organic compounds.

The combustion of hexane, toluene and ethyl acetate on Pt/SZ catalysts with different metal loadings was investigated under the space velocity of 2700 h^{-1} and oxygen content of 21 vol% as well. As shown in table 4, the activities of Pt/SZ are enhanced with an increase of Pt loading from 0.1 to 1.0 wt%, but the activity increase seems to slow down when the Pt loading is above 0.5 wt%. Palladium is often a more desirable precious metal component of combustion catalysts as compared to platinum because of cost and availability. The combustion activities of Pd/SZ catalysts with metal loadings of 0.5 and 1.0 wt% were measured. The T_{95} of the organic compounds, especially hexane, on Pd/SZ are evidently higher than those on Pt/SZ, showing that on sulfated zirconia Pd is as usual less active than Pt for the catalytic combustion of organic compounds. However, Pd/SZ catalysts are still more active than Pt/Al_2O_3 for the combustion of toluene, and as active as Pt/Al_2O_3 for the combustion of ethyl acetate.

The acid strength determined by Hammett indicator method and rate constant of *n*-butane isomerization reaction at 25°C of the supports, specific surface area and metal dispersion of the catalysts were measured. The results are given in table 5. Although the surface area of the 0.5% Pt/Al_2O_3 catalyst is about 2.5 times as high as that of the 0.5% Pt/SZ catalyst, and the number of Pt surface atoms on 0.5% Pt/Al_2O_3 is about 5 times as high as that on Pt/SZ, the combustion activities of Pt/Al_2O_3 for the organic compounds are evidently lower than those of Pt/SZ, especially for saturated hydrocarbons. This can only be explained by the difference in acid strength of the supports. It may suggest that the superacidity of the sulfated zirconia support strengthens the adsorption and activation of the organic molecules on the catalyst, and hence facilitates the low-temperature combustion reaction. According to Olah's carbocation chemistry [15], the organic compounds are probably protonated by the solid superacid as an initial step of the reaction, and the complete oxidation of the carbocation intermediates takes place afterwards. In addition, palladium is more easily dispersed on sulfated zirconia than platinum, and the number of Pd surface atoms on Pd/SZ is much higher

Table 5
Properties of various catalysts

Catalyst	Support acid strength		Pt or Pd (wt%)	Surface area (m^2/g)	Dispersion (%)	Surface atoms Pt or Pd (10^{18}/g)
	H_0	*n*-C_4 isomerization [a] ($k_1 \times 10^3/h^{-1}$)				
Pt/SZ	−16.0	10.8	0.1	119	41	1.2
			0.3	112	13	1.2
			0.5	114	12	1.9
			1.0	101	10	3.1
Pd/SZ	−16.0	10.8	0.5	122	19	5.4
			1.0	103	15	8.5
Pt/Al_2O_3	+4.8	0	0.5	314	63	9.7

[a] Data from ref. [14]: SO_4^{2-}/ZrO_2 (650°C), $H_0 \leqslant -16.0$, $k_1 = 10.8 \times 10^{-3}$ h^{-1}, SO_4^{2-}/ZrO_2 (700°C), $H_0 \leqslant -13.8$, $k_1 = 3.69 \times 10^{-3}$ h^{-1}, SO_4^{2-}/ZrO_2 (800°C), $H_0 \leqslant -12.7$, $k_1 = 0.87 \times 10^{-3}$ h^{-1}.

than the number of Pt surface atoms on Pt/SZ, but Pd/SZ catalysts are inferior to Pt/SZ catalysts in combustion activity because Pd is probably less effective than Pt on the activation of the dioxygen molecules.

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