Korean J. of Chem. Eng., 8(3), 177-182 (1991)

CHARACTERIZATION OF ALUMINA MODIFIED WITH SULFATE AND PHOSPHATE

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(*Received 9 May 1991 • accepted 5 June 1991*)

Abstract—The acidity and surface properties of alumina modified with sulfate (Al-S) and phosphate (Al-P) were characterized by IR, NH_3 TPD and 1-butene isomerization reaction. The Point of Zero Charge (PZC) of modified alumina and the amount of Mo anion adsorbed on modified alumina were measured. The PZC of modified alumina and the amount of Mo anion adsorbed on modified alumina decreased with increasing modifier content. Non-linear relationship between the PZC and Mo uptake in modified alumina was observed in Al-S and Al-P. The bonding mode of sulfate on alumina changed with increasing sulfate content. The Bronsted acid site appeared in alumina modified with sulfate of 10 wt%.

INTRODUCTION

Alumina has been used as a support for hydrodesulfurization (HDS) catalyst because of its stability and ability to disperse molybdate. The interaction between Mo and alumina exists when Mo was supported on alumina. The interaction between Mo and alumina occurs via a reaction between Mo anion and the basic (protonated) hydroxyl groups on the alumina surface during catalyst preparation [1-3]. Also it was shown that the molybdate adsorption on the alumina surface might occur by a reaction between the molybdate and basic surface hydroxyl groups, leading to the decomposition of the adsorbing molecules/ions and physisorption on coordinatively unsaturated site (cus) Al^{3+} sites [1, 2]. Therefore, it is thought that the interaction between Mo and alumina can be affected by the surface properties of alumina. There are many studies about the electrical properties of γ-alumina/electrolyte solution interface [3-7]. The electrical properties of the alumina surface can change by the pH of Mo solution, the temperature of Mo solution, and the kind of dopant [4]. There were several studies about the dopping effect of ions on the electrical properties of γ-alumina/Mo solution interface [7-10]. However, the effects of phosphate and sulfate anions on the electric properties of the alumina surface have not been systematically studied. In the present study, the surface properties of alumina modified with sulfate and phosphate were investigated by NH_3 TPD, IR and PZC measurement. 1-Butene isomerization reaction catalyzed over modified alumina was performed as a probe reaction. These surface properties of modified alumina will be used to explain the promoting effect of phosphate additive on the catalytic activities of Mo/Al_2O_3 and $CoMo/Al_2O_3$ in the HDS reaction.

EXPERIMENTAL

1. Modification of Alumina

γ-alumina (Strem Chem. Co.) was used for the preparation of modified alumina. The pore volume and surface area of pure alumina were 0.25 cm^3/g and 220 m^2/g, respectively. Modified alumina was prepared by impregnating aqueous solution of phosphoric acid (Hayashi Co.) or ammonium sulfate (Tokyo Kasei Co.) into pure alumina, drying at 393 K for 6 hr and calcining at 773 K for 6 hr. Al-M(x) denotes modified alumina where M represents the kind of element and x represents the content (wt%) of modifier, either PO_4 or SO_4. The surface areas of modified aluminas were listed in Table 1.

2. Temperature Programmed Desorption

0.1 g sample was loaded in quartz reactor. The sample was calcined at 773 K for 2 hr and then cooled to room temperature in N_2 (99.999%, Dongjin Co., Korea). After NH_3 was admitted for 0.5 hr in 30 cm^3/min, the sample was flushed with N_2 to remove physisorb-

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Table 1. The specific surface area of modified alumina

Support	Area(m^2/g)	Support	Area(m^2/g)
Al_2O_3	220	–	–
Al-P(1)	195	Al-S(1)	190
Al-P(3)	180	Al-S(3)	180
Al-P(5)	162	Al-S(5)	175
Al-P(10)	149	Al-S(10)	151

ed NH_3. TPD started at a rate of 10 K/min to 773 K. The effluent NH_3 was monitored by GC equipped with TCD (Varian Aerograph Co., model 920).

3. Point of Zero Charge (PZC) Measurement

The PZC of alumina support was determined by a drift method [8]. The pH's of several deionized waters were adjusted to various pH values with HNO_3 or NH_4OH. Samples of modified alumina (0.2 g) were poured into these solution (25 ml). The final pH's were measured after 24 h. The ΔpH as a difference between initial pH and final pH was obtained. Plots of ΔpH vs. initial pH of modified aluminas were made and the PZC's of modified aluminas were determined as the point at which a value of ΔpH was zero.

4. Measurement of Mo Uptake

To investigate the capability of modified alumina to adsorb Mo anion in solution, equilibrium adsorption experiments were performed in aqueous Mo solution of which Mo concentration and pH were 1 mg Mo/cm^3 and 6.0, respectively. 0.2 g of modified alumina was poured into 25 ml of aqueous Mo solution and was kept at 20℃ for 24 hr. The amount of Mo anion to adsorb on modified aluminas were determined by measuring a difference between initial and final Mo concentration in Mo solution. Mo concentration in solution was measured by AA (Atomic Absorption: Varian Aerograph Co., model 575).

5. IR

The IR spectra of the samples were recorded in transmittance mode with IR spectrophotometer (Bomem Inc., Michelson-102). The resolution was 4 cm^{-1} and the scan number was 64. Self-supporting wafer was prepared by pressing 15 mg powdered sample at 15000 psi and was loaded on a sample holder of *in situ* IR cell. After the sample was evacuated at 10^{-4} torr at 773 K for 2 hr and then cooled to room temperature in vacuum, the IR spectrum for calcined state was recorded. Pyridine was adsorbed on the wafer at 423 K for 1 hr and evacuated for 2 hr at 423 K and 10^{-4} torr. The IR spectra were then recorded at room temperature.

6. 1-Butene Isomerization

Atmospheric flow microreactor was used for 1-butene isomerization. 0.2 g of modified alumina was calcined at 773 K for 2 hr and then cooled to reaction temperature of 423 K in N_2. A flow rate of 1-butene was 20 cm^3/min. The catalytic activities in the 1-butene isomerization were measured after 1 hr of reaction. Reaction products were analyzed by GC (Varian Aerograph Co., model 5870) equipped with OV-101 column.

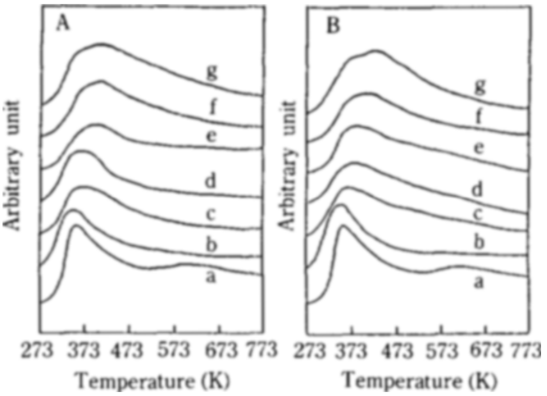


Fig. 1. NH_3 TPD spectra: (A) (a); pure alumina, (b); Al-S(1), (c); Al-S(2), (d); Al-S(3), (e); Al-S(4), (f); Al-S(5), and (g); Al-S(10). (B) (a); pure alumina, (b); Al-P(1), (c); Al-P(2), (d); Al-P(3), (e); Al-P(4), (f); Al-P(5), and (g) Al-P(10).

RESULTS

1. NH_3 TPD

Fig. 1 illustrates NH_3 TPD spectra for pure and modified alumina. A sharp peak at 373 K and a broad peak around 600 K were observed in NH_3 TPD of pure alumina. A broad peak around 600 K disappeared in the NH_3 TPD spectrum of Al-S(1). As the sulfate content increased to 10 wt%, the sharp peak at 373 K became broader and was shifted to around 423 K. The patterns of NH_3 TPD spectra of Al-P were similar to those of Al-S.

2. PZC and Mo Uptake Measurement

The PZC of pure alumina was 8.3 as shown in Fig. 2. The PZC of alumina modified with sulfate rapidly decreased to 6.1 when 1 wt% of sulfate was added and then slowly decreased to 3.4 with increasing sulfate content to 10 wt%. The PZC of alumina modified with phosphate, on the other hand, decreased slowly to 6.5 with increasing phosphate content to 10 wt%. The amounts of Mo uptake on modified alumina during equilibrium adsorption are shown in Fig. 3. The amount of Mo uptake on pure alumina was 4.02 Mo

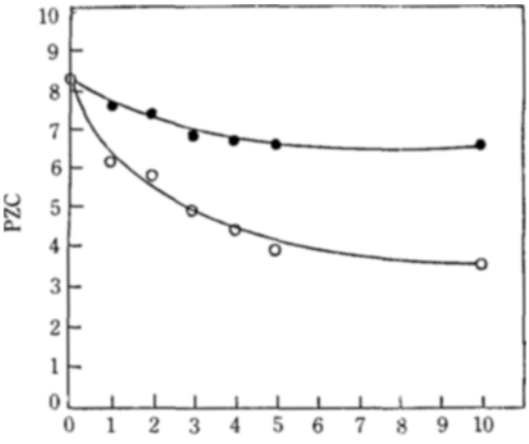


Fig. 2. The PZC's of modified alumina: (a) Al-S (○) and (b) Al-P (●).

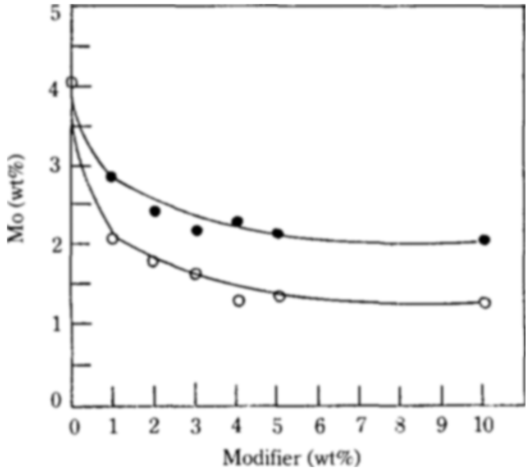


Fig. 3. The amount of Mo uptake on modified alumina: (a) Al-S (○) and (b) Al-P (●).

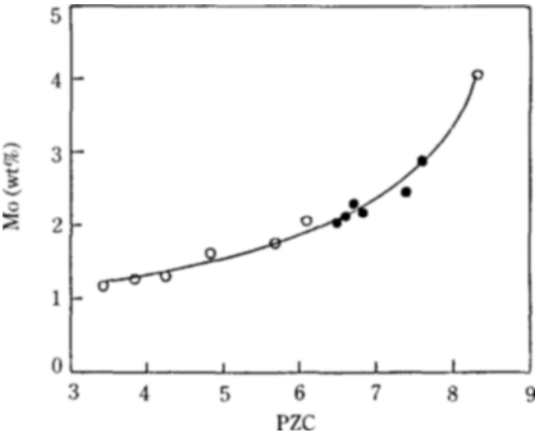


Fig. 4. Plot of the PZC vs. the amount of Mo uptake: (a) Al-S (○) and (b) Al-P (●).

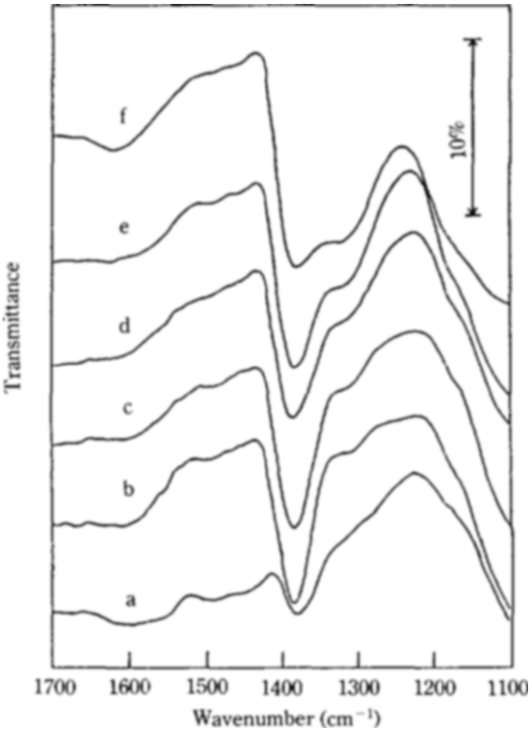


Fig. 5. IR spectra of alumina modified with sulfate: (a) Al-S(1), (b) Al-S(2), (c) Al-S(3), (d) Al-S(4), (e) Al-S(5) and (f) Al-S(10). Pretreatment condition: evacuated at 773 K and for 2 hr.

wt%. The amount of Mo uptake decreased with increasing modifier content, irrespective of sulfate or phosphate. Fig. 4 shows a relationship between the amount of Mo uptake and the PZC of alumina modified with sulfate and phosphate.

3. IR

The IR spectra of Al-S are shown in Fig. 5. An IR band at 1383 cm^{-1} was observed when Al-S(1) was calcined at 773 K, which can be assigned to the asymmetric stretching band of the S=O group [11-13]. Another IR band at 1330 cm^{-1} appeared and its intensity increased with increasing sulfate content.

Fig. 6 shows the IR spectra of pure alumina and Al-S when pyridine was adsorbed. When pyridine was adsorbed on pure alumina, there were three IR bands at 1446, 1490 and 1620 cm^{-1} which can be assigned to pyridine adsorbed on the Lewis acid site on alumina [14]. The IR band at 1594 cm^{-1} indicates physisorbed

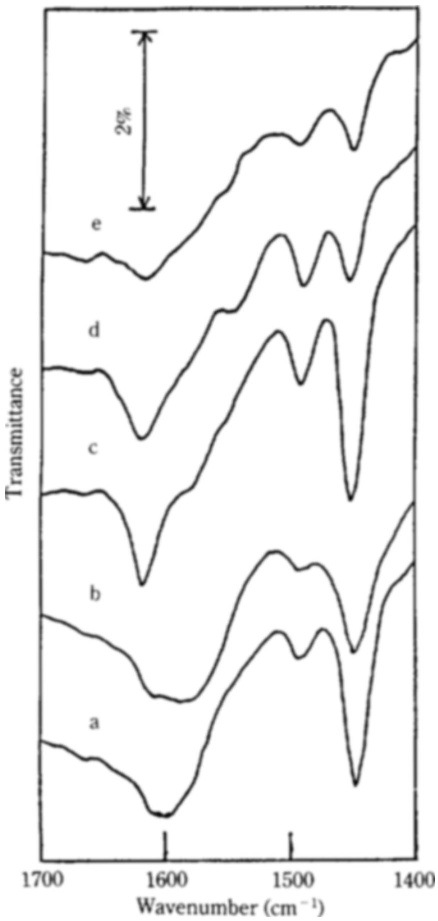


Fig. 6. IR spectra of pyridine adsorbed on modified alumina: (a) pure alumina, (b) Al-S(1), (c) Al-S(5), (d) Al-S(10), and (e) Al-P(10). Pretreatment condition: pyridine was adsorbed at 423 K for 2 h followed by the evacuation at the same temperature for 2 hr.

pyridine. The IR bands of pyridine adsorbed on Al-S(1) and Al-S(5) were similar to those on pure alumina. However, new IR band at 1549 cm^{-1} appeared in Al-S(10), indicating the presence of pyridine adsorbed on the Bronsted acid site [14, 15]. The IR spectrum of pyridine adsorbed on Al-P(10) was similar to that adsorbed on alumina as shown in Fig. 6(e). IR band at 1549 cm^{-1} which was observed in Al-S(10) did not appear in Al-P(10).

4. 1-Butene Isomerization

Fig. 7 and 8 show the activities and selectivities of 1-butene isomerization reaction catalyzed over Al-S and Al-P. The conversion in 1-butene isomerization reaction on pure alumina was 0.22%. The conversion slowly increased at a low content of modifier and more rapidly at a higher content. The conversions on Al-S were larger than those on Al-P. The selectivity (the mole ratio of cis-2-butene to trans-2-butene in product) in pure alumina was 3.5. The selectivities decreased to 0.8 and 1.9 with increasing sulfate and phosphate content to 10 wt%, respectively. The effect of calcination temperature on isomerization is shown in Table 2. Conversions on modified aluminas [Al-P(4) and Al-S(4)] decreased as the calcination temperature increased from 773 K to 1073 K, while the maximum conversion was obtained at 973 K with pure alumina.

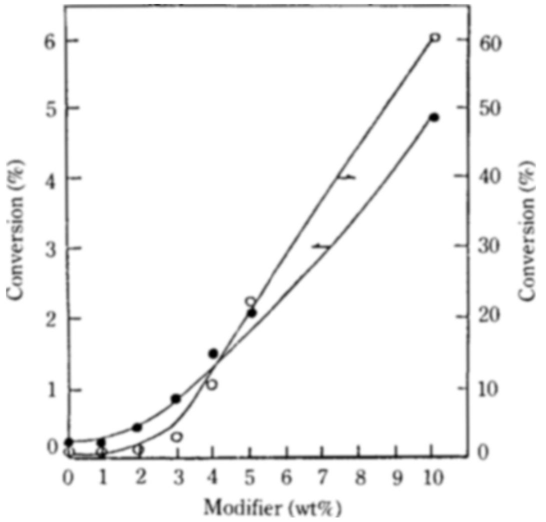


Fig. 7. Catalytic activity in 1-butene isomerization: (a) Al-S (○) and (b) Al-P (●).

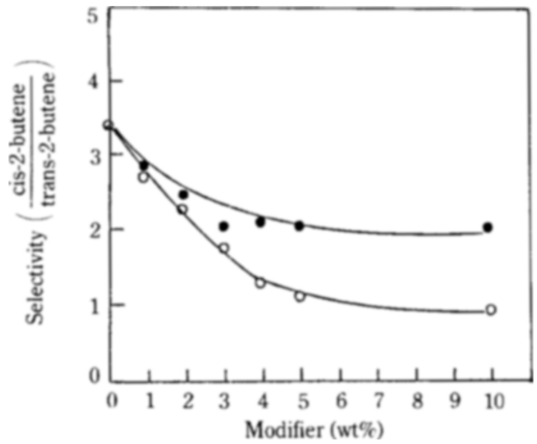


Fig. 8. The selectivity (mole ratio of cis-2-butene to trans-2-butene in products): (a) Al-S (○) and (b) Al-P (●).

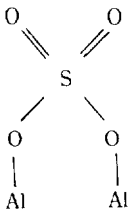
Table 2. Conversion of 1-butene isomerization catalyzed over modified aluminas at various calcination temperatures

Calcination temperature (K)	Conversion (%)		
	Al_2O_3	Al-S(4)	Al-P(4)
773	0.22	10.31	0.89
873	0.25	9.39	0.73
973	0.33	8.82	0.64
1083	0.32	8.83	0.53

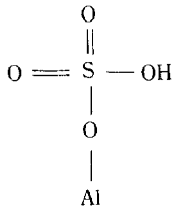
DISCUSSION

1. Bonding Mode of Sulfate

When alumina was modified with sulfate, two IR bands at 1383 and 1330 cm^{-1} were observed in Fig. 5. The intensity of an IR band at 1330 cm^{-1} increased with increasing sulfate content. The former band is assigned to the asymmetrical stretching band of the S=O group [11-13]. The IR band at 1330 cm^{-1} is characteristic of the partially double bond of the S=O group [11-13]. The IR band at 1330 cm^{-1} was related to the S=O group associated with H_2O or surface hydroxyl groups [11, 16]. The IR band at 1330 cm^{-1} appeared at relatively high sulfate content without adding water in our IR spectra, which shows that the bonding mode of sulfate can be affected according to the sulfate content. The sulfate is multidentately [11, 12, 17] bonded to the alumina surface modified with a low sulfate content [I]. The amount of hydroxyl group on the alumina surface decreases as the sulfate content increases. Therefore, the amount of monodentately-bonded sulfate [II] increases with increasing sulfate content.



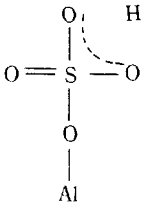
[I]



$O{=}S({=}O)({-}OH){-}O{-}Al$

[II]

The monodentately-bonded sulfate has a free S-OH group. The S=O group in the sulfate is known to have an electron inductive property, which induces the electron density from the environment of the S=O group [12, 13]. Therefore, the monodentately-bonded sulfate might change to [III] which has the character of partially double bond of the S=O group. The appearance of the IR band at 1330 cm^{-1} might be explained by the bonding mode [III].



[III]

The IR band appeared at 1549 cm^{-1} when pyridine was adsorbed on Al-S(10) as shown in Fig. 6. This band has been assigned to the Bronsted acid site [14, 15]. The Bronsted acid site can originate either from the hydroxyl group in sulfate or from the hydroxyl group on the alumina surface. The amount of the hydroxyl groups on the alumina surface decreases with increasing sulfate content, because the hydroxyl group on the alumina surface was consumed via a reaction with the hydroxyl group in sulfate. Therefore, it is more likely that the Bronsted acid site in Al-S(10) originated from the hydroxyl group in sulfate (mode [III]).

2. The Electrostatic Model

According to the electrostatic model [18], anions in aqueous solution are attracted and bound electrostatically to the positively charged oxide surface when the pH of the solution is below the PZC of oxide. The PZC of the support has been used for the estimation of Mo anion uptake on alumina doped with fluoride or magnesium [11, 12]. A linear correlation between the PZC value and the amount of Mo uptake was observed when the alumina surface was doped with fluoride or magnesium. However, a linear relationship was not observed in our Al-S and Al-P as shown in Fig. 4. This phenomenon can be explained as follows. Different bonding modes between modifier and alumina results in the different configuration of the hydroxyl groups on the alumina surface. Fluoride is monodentately adsorbed on alumina surface [11] while sulfate or phosphate can be adsorbed multidentately [8, 11, 19, 20]. The bonding mode can also changed from multidentate to monodentate as the content of sulfate and phosphate increases. The IR study confirmed that the bonding mode of sulfate changed with the sulfate content in Fig. 5. As shown in Fig. 1, the amount of the acidic hydroxyl group in alumina modified with phosphate and sulfate increased with increasing amount of phosphate and sulfate. The acidic hydroxyl group such as P-OH or S-OH increased because the bonding mode of sulfate and phosphate changed from the multidentate bonding mode to the monodentate bonding mode with increasing modifier content. Also the modification of the alumina surface with modifier results in the decrease in the specific surface area of the support as shown in Table 1, which suggests that the adsorption site for Mo anion decreases for modified alumina with higher modifier content. As a result, the linear relationship between the PZC and the amount of Mo uptake in modified alumina was not observed.

3. 1-Butene Isomerization

The activity in the 1-butene isomerization reaction increased with increasing modifier content. The Bronsted acid site was observed in Al-S(10) as shown in Fig. 6. The presence of the Bronsted acid site indicates that the carbonium mechanism operated in 1-butene isomerization with Al-S. The carbonium mechanism and the carbanion mechanism preferentially produce trans-2-butene and cis-2-butene, respectively [15]. The decrease in the selectivity to cis-2-butene with increasing content of sulfate and phosphate, also indicates that 1-butene isomerization occurs by the carbonium mechanism rather than the carbanion mechanism in alumina modified with higher modifier content. The isomerization activity in Al-S with a sulfate content higher than 3 wt% rapidly increased, while slowly increased in Al-S with the sulfate content less than 3 wt%. This result indicates that the strong acidic sites, S-OH or P-OH, are more active than Al-OH. The conversion in 1-butene isomerization reaction catalyzed by Al-S(4) and Al-P(4) decreased with increasing calcination temperature, due to the destruction of S-OH and P-OH acid sites. In pure alumina the maximum conversion was observed at the calcination temperature (973 K), due to the increase in the Bronsted acidity of the hydroxyl groups on the alumina surface and to the increase of cus (coordinatively unsaturated site) Al^{3+} sites. The Bronsted acid site is an active site for Al-S with higher sulfate content, while both the Lewis acid site such as cus Al^{3+} and the basic site on pure alumina are considered to be an active site when 1-butene isomerization is performed on alumina [21, 22].

CONCLUSION

The PZC and the amount of Mo anion uptake on alumina modified with phosphate and sulfate decreased with increasing modifier content. The modification of alumina with phosphate and sulfate results in the decrease in the adsorption site for Mo anion. Nonlinear relationship between the PZC and the amount of Mo uptake was found. The bonding mode of sulfate on the alumina surface changed with increasing sulfate content. The Bronsted acid site appeared in alumina modified with a sulfate of 10 wt%.

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