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THE EFFECT OF γ -IRRADIATION ON THE ACIDIC PROPERTY OF SOLID NICKEL SULFATE

By

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Abstract

The effect of γ -irradiation on the acidity, the acid strength and the catalytic activity of solid nickel sulfate has been studied. It was found that the irradiation decreases the acidity at $4.8 \leq H_0 < 3.3$ of partially dehydrated nickel sulfate heat-treated at $150 \sim 450^\circ\text{C}$, but increases that at $3.3 \leq H_0 < -3$, while it does not change the acidity at acid strength $H_0 \leq -3$ of the same samples. Hydrated nickel sulfate with no heat-treatment which has no acidity becomes to show a definite acidity at $3.3 \leq H_0 < -3$ upon irradiation. Anhydrous form prepared by heat-treatment at 550°C did not change its acidic property by irradiation. The catalytic activity of nickel sulfate pretreated at 350°C for the depolymerization of paraldehyde was found to be unchanged by irradiation. From these results, the acidity change and creation of acid sites effected by γ -irradiation are considered due to the dehydration of hydrated water of nickel sulfate, as effected also by thermal treatment.

Introduction

It has been recently reported that the irradiation with γ -, x -, neutron-, or electron-ray changes the catalytic activity of solid acids such as alumina, silica-alumina and solid phosphoric acid for the isomerization of olefins,¹⁾ the polymerization of olefins and aldehydes²⁾, the cracking of hydrocarbons^{2,3)} and the dehydration of alcohols^{2,4)}. Increases in surface acidity upon irradiation which were observed in cases of silica-alumina,²⁾ silica⁵⁾ and kaolinite⁶⁾ have been correlated with their catalytic activity.²⁾ It is also reported that Lewis acid sites are formed on silica-alumina and zeolite catalysts by γ -ray irradiation⁷⁾.

Solid nickel sulfate, a new type of solid acid, whose acidic property is remarkably changed by heat-treatment is known to catalyze various acid-catalyzed reactions.⁸⁾ Since, however, no work has been made on the radiation effect on the acidic property or catalytic activity of the catalyst, the present work was initiated.

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Experimental

Nickel sulfate ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, guaranteed reagent of Wako Junyaku Co.) was put into a Hario glass tube and heated in an electric furnace at various temperatures ranging from 150 to 550°C for 3 hours and then cooled after sealing the tube. The 100~200 mesh powder was put together with calcium chloride as desiccant in a Hario glass ampoule as shown in Fig. 1 and irradiated with γ -ray of ^{60}Co at room temperature. The total dose was 5.76×10^7 r, the dose rate being 3×10^5 r/hr. Immediately after the irradiation, nickel sulfate samples were subjected to the measurement of acidity and catalytic activity.

The acidity (the number of acid sites) having an acid strength H_0 equal to or lower than the pK_a value of the indicator used were determined by using the amine titration method.⁹⁾ In the present work, nickel sulfate suspended in benzene was titrated with a solution of 0.1 N *n*-butylamine in benzene, using three indicators of different pK_a values; methyl red ($\text{pK}_a = +4.8$), dimethyl yellow ($\text{pK}_a = +3.3$) and dicinnamalacetone ($\text{pK}_a = -3$). The preparation method and purity of all reagents and indicators used are the same as those reported previously.¹⁰⁾ The titration was started in about 25 min after the completion of irradiation. Time required for the amine titration was 20~30 min in both cases of irradiated and non-irradiated samples.

The depolymerization of paraldehyde with irradiated nickel sulfate catalyst was studied by the same method as in the previous work.¹¹⁾ The reaction was carried out at 18.5°C with 50 ml of paraldehyde solution in benzene (0.0752 mol/l) and 1 g of catalyst and the amount of acetaldehyde formed by the reaction was determined by a bisulfite method.¹¹⁾

Results and Discussion

The effect of γ -irradiation on the acidic property of nickel sulfate heat-

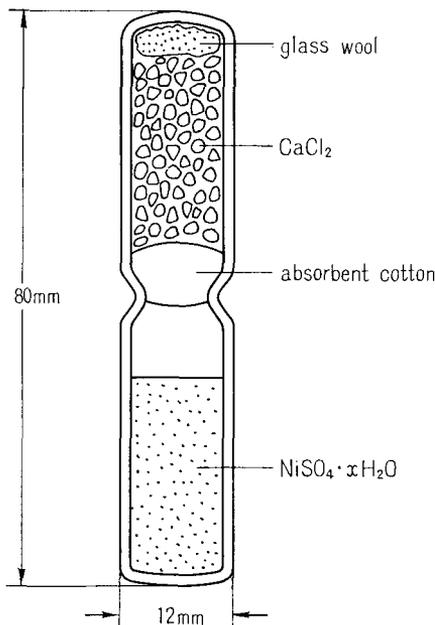


Fig. 1

The Effect of γ -Irradiation on the Acidic Property of Solid Nickel Sulfate

TABLE 1. Change of surface acidity of $\text{NiSO}_4 \cdot x\text{H}_2\text{O}$ by γ -irradiation

(total dose: 5.8×10^7 r)

Temp. of heat-treatment (°C)	Conditions	Acidity (<i>n</i> -butylamine titers), mmol/g		
		$4.8 \geq H_0 > 3.3$	$3.3 \geq H_0 > -3$	$-3 \geq H_0$
untreated	unirradiated	0	0	0
	irradiated	0.0002	0.0032	0
150	unirradiated	0.013	0.020	0
	irradiated	0.010	0.030	0
250	unirradiated	0.010	0.074	<0.0035
	irradiated	0.002	0.089	<0.0035
350	unirradiated	0.016	0.054	0.032
	irradiated	0.012	0.065	0.032
450	unirradiated	0.010	0.052	0
	irradiated	0.009	0.056	0
550	unirradiated	0.023	0	0
	irradiated	0.023	0	0

treated at various temperatures is shown in Table 1.

An untreated nickel sulfate ($\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ or $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$) which has not any acidity becomes to show definite acidity when it was irradiated. The appearance of the acid sites having acid strength between $H_0 = 3.3$ and -3 is remarkable as compared with those having weaker acid strength. However, γ -irradiation could not create the acid sites having high acid strength $H_0 \leq -3$.

The acidities at $4.8 \geq H_0 > 3.3$ of nickel sulfates heat-treated at $150 \sim 450^\circ\text{C}$ were found to decrease upon irradiation. The extent of the decrease is illustrated by solid circles in Fig. 2, the largest decrease being observed for the sample heat-treated at 250°C . On the other hand, the acidities at $3.3 \geq H_0 > -3$ of the same samples increased by irradiation as shown by open circles in Fig. 2, the highest increase being also observed for the same sample heat-treated at 250°C . These results of Fig. 2 seem to indicate that γ -irradiation changes the weaker acid site to the stronger one. The strong acid site having $H_0 \leq -3$ was not influenced by irradiation as shown in the fifth column of Table 1.

Since no effect of γ -irradiation was observed on the acidity of anhydrate of nickel sulfate heat-treated at 550°C , the radiation effect observed for hydrated

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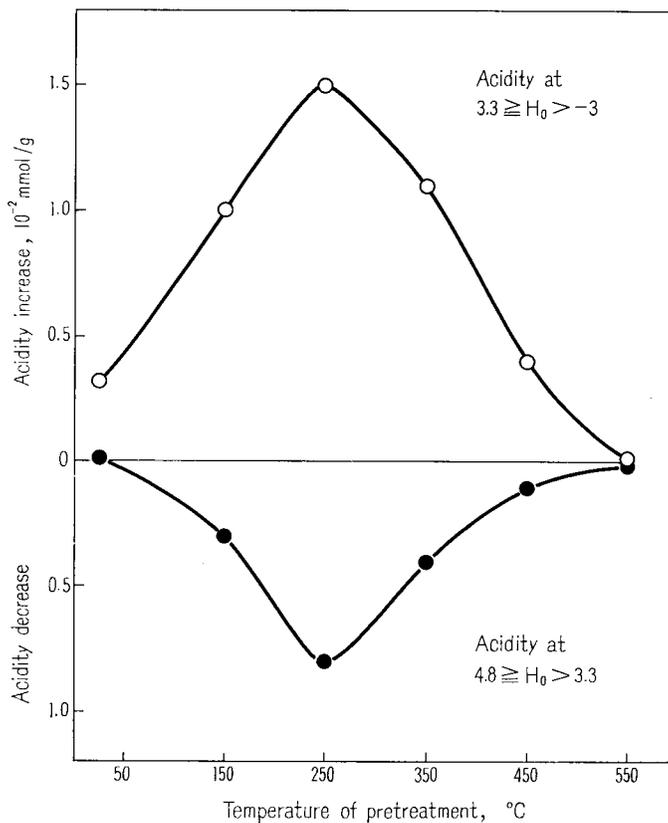


Fig. 2 Increase and decrease in acidity of $\text{NiSO}_4 \cdot x \text{H}_2\text{O}$ by γ -irradiation

or partially hydrated nickel sulfate is considered a kind of dehydration effect, although the results cannot be fully explained according to our model⁸⁾ for acid sites formed by dehydration with thermal treatment.

BARTER and WAGNER⁵⁾ reported that acid sites on silica gel formed by irradiation with electron-ray decayed at 25°C and half-time for the decay was about 2~3 hrs. In the present case of nickel sulfate, no decay of acid sites was observed even after 48 hours.

As mentioned above, radiation showed no effect on the acidity at $H_0 \leq -3$, but it might have caused any other change on surface structure of nickel sulfate, which may influence catalytic activity. In order to test this possibility, the depolymerization of paraldehyde, for which the effective strength of acid

The Effect of γ -Irradiation on the Acidic Property of Solid Nickel Sulfate

TABLE 2. Catalytic activity of γ -irradiated nickel sulfate for depolymerization of paraldehyde

Reaction temperature: 18.5°C, Concentration of paraldehyde: 0.0752 mol/l, Catalyst: 1.0 g of NiSO₄·xH₂O heat-treated at 350°C, whose acidity is given in Table 1

Catalysts	Reaction time, min	Amount of acetaldehyde formed per unit acidity mol/l, mmol of acid sites
unirradiated NiSO ₄ ·xH ₂ O	45	0.32 ± 0.015
irradiated NiSO ₄ ·xH ₂ O	45	0.33 ± 0.010

sites was clearly shown to be $H_0 \leq -3$,*) was carried out by using irradiated and unirradiated samples pretreated at 350°C. The results are shown in Table 2.

The catalytic activity of irradiated catalysts coincides with that of unirradiated ones within the limit of experimental error. The coincidence observed for both catalysts, on which the number of weaker acid sites is largely different, confirms again our previous conclusion concerning effective acid strength and further indicates the absence of radiation effect for the depolymerization reaction.

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*) This was shown by a poisoning experiment with a basic indicator of $pK_a = -3^{12)}$ and by an experiment examining correlation between the catalytic activity and the acidity at $H_0 \leq -3$.¹⁰⁾