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Preparation of Red Organic Pigment with Phenylated Silica Gel as Core

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Synopsis. The silanols on the surface of silica gel were chlorinated and a phenyl group was introduced onto the silica gel ($\geq$Si–C_6H_5) by phenylating with phenyllithium. The surface group was derived to a structure similar to Sudan I by nitration, reduction, diazotization, and coupling (with 2-naphthol). The prepared pigment showed approximately the same color as Sudan I, and had very good resistance to water.

We have studied the introduction of alkoxyl groups onto silica gel (as model powder), silica, and titanium oxide by treating with aromatic alcohols [C_6H_5–$(CH_2)_n$–OH], and succeeded in the preparation of red or yellow pigments with metal oxides as core, by deriving the surface alkoxyl group to a structure similar to Sudan I (azo dyestuff) or tartrazine (food color).[1–3] But the surface groups of pigments were lost with hydrolysis in boiling water, because the surface groups were alkoxyl groups.

In this paper, silica gel was used as the reaction model; the surface silanols were chlorinated and a phenyl group was introduced onto the surface of silica gel by the reaction with phenyllithium. Pigment with the same color as Sudan I was prepared by deriving the surface phenyl group to a structure similar to Sudan I, by nitration, reduction, diazotization, and coupling with 2-naphthol.

Experimental

Silica gel (Wakogel C-200) was used as in the previous reports.[1,2] Thionyl chloride and benzene (commercial guaranteed reagent grade) were used after purification.[4] Phenyllithium solution (in cyclohexane–diethyl ether) (Aldrich Chemical Company's reagent) and diethyl ether (anhydrous) (Dotite reagent) were used. Chlorination and phenylation were performed according to one of the methods reported by Wartmann and Deuel:[5] 20 g of silica gel dried sufficiently at 110 °C was added to the mixture of 500 g of benzene and 160 ml of thionyl chloride, and was chlorinated by refluxing under stirring for 3 h. Benzene and thionyl chloride were distilled out and then the chloride of the silica gel was dried under 20 Torr (1 Torr=133.322 Pa) at 60 °C for 2 h. And 700 ml of 0.5 mol/l phenyllithium solution (in the mixture of cyclohexane and diethyl ether) was dropped slowly under cooling by ice bath, and the silica gel was phenylated by heating at 40 °C under stirring for 1 h. After the phenylation, the contents were added into about 500 ml of methanol to decompose the excess phenyllithium which did not react, and were filtered, washed (with methanol, water, and acetone) and vacuum dried (50 °C); the resulting sample was called phenylated. Nitration,[1,2] reduction,[2] diazotization,[1,2] and coupling[1,2] methods were the same as the previous reports.[1,2] The samples of each stage were called nitrated sample, reduced sample, and pigmented sample (which was coupled after diazotization).

IR spectrum and ultimate analysis of carbon and nitrogen were measured for the confirmation of the structure of surface group and the investigation of the character of the surface. The methods and conditions of measurements were the same as in the previous report.[2]

Results and Discussion

An IR spectrum of silica gel treated with phenyllithium after chlorination was shown in Fig. 1. Silica gel treated with phenyllithium exhibits 1420 and 700 cm^{-1} bands which are attributed to Si–C_6H_5. The strength of a 950 cm^{-1} band corresponding to the surface silanols of silica gel[6] decreased slightly. So it was confirmed that the surface silanols were phenylated, and the surface phenyl group was bonded directly to silicon atom on silica gel, as reported by Wartmann and Deuel.[5] The number of introduced phenyl groups calculated by carbon content (Table 1) is 2.76×10^{20} g^{-1}.

Then the phenylated sample was nitrated, reduced, diazotized, and coupled with 2-naphthol to prepare the red pigmented sample. The surface groups were separated from the silica gel core at each stage; their

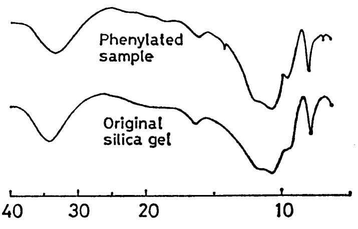

Fig. 1. IR spectra of original and phenylated silica gels.

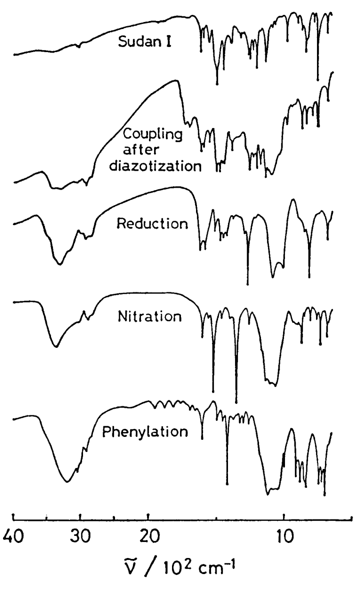

Fig. 2. IR spectra of the surface groups separated from the each sample.

IR spectra are shown in Fig. 2. The core silica gels of samples at each stage were dissolved with hot sodium hydroxide solution and the separated organic surface groups were extracted with ether. The ether extraction from the phenylated sample exhibits absorption bands in the neighborhood of 3000 (weak), 1600 (sharp), 1500 (weak), 1450 (weak), and 700 cm^{-1} (sharp) positions due to aromatic nucleus and also at 1420 (strong), 1120 (strong, shoulder), and 700 cm^{-1} (sharp) due to Si–C_6H_5. The bands at 3350 (broad) and 850 cm^{-1} (strong) are due to silanols and those at 1100—1000 cm^{-1} (strong) are due to Si–O–Si. After drying and calcination of the ether extraction part, white ash (SiO_2) remained. These results confirmed that the phenyl group is directly bonded to silicon atom, and that the Si–C bond in $\geqslant$Si–C_6H_5 was very stable and did not split even under a severe condition such as in a hot alkali treatment. The ether extraction from the nitrated sample was found to exhibit absorption bands at 1520 (strong) and 1340 cm^{-1} (strong) and 870 cm^{-1} (sharp) positions, the former two bands being due to aromatic nitro group and third one to C–N stretching vibration. This means that the nitro group was introduced on the surface phenyl group. In the extraction from the reduced sample, the bands of the nitro group disappeared and the bands due to aromatic primary amine newly appeared in 3450 (broad), 3350 (broad), 1620 (strong), and 1280 cm^{-1} (strong) positions. The spectrum pattern of pigmented sample which was prepared *via* coupling after diazotization agreed with the pattern of Sudan I. So it was presumed that the surface group was derived to a structure similar to Sudan I by the aforementioned procedure. The strong bands at 1100—1000 cm^{-1} positions, as stated for the phenylated sample, was absorption due to Si–O–Si. The results mean that the red pigment with silica gel as core can be prepared according to the reaction scheme shown in Fig. 3. The pigmented sample showed approximately the same red color as Sudan I, azo dyestuff.

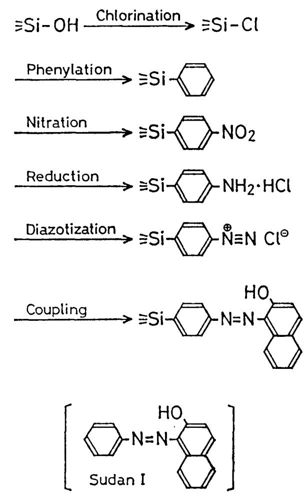

Fig. 3. Postulated reaction scheme.

Table 1. Results of ultimate analysis

Samples	C (%)	N (%)	N/C	
			Found	Calcd
Phenylated sample	3.31	0	—	—
Nitrated sample	3.38	0.55	0.16	0.19
Reduced sample	3.25	0.46	0.14	0.19
Pigmented sample	6.08	0.63	0.10	0.15

Results of the final analysis for the samples of each stage are shown in Table 1. Values found for the ratio of carbon and nitrogen contents (N/C) almost agreed with calculated values, but were slightly less than the calculated ones. So it was presumed that a small portion of the surface phenyl groups did not react in the further procedure and remained unchanged. The carbon and nitrogen contents of the pigmented sample did not show any decrease after refluxing in water for 5 h. And discoloration also did not occur at all after the refluxing. These results mean that the pigmented samples prepared by this procedure have great resistance to water.

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