Light Fastness Properties of Acid Dye and Mesoporous Ca-Aluminosilicate Composite

Masashi Shibata,* Hajime Hotta, Toshiyuki Suzuki, Sabine Valange,† and Zelimir Gabelica†
Kao Corporation, Tokyo Research Laboratory, Sumida-ku, Tokyo 131-8501
†*ENSCMu, Groupe Securite et Ecologie Chimiques, 3, Rue A. Werner, F-68094, Mulhouse Cedex, France*

(Received August 9, 1999; CL-990698)

Light-fastness properties of composites involving mesoporous Ca aluminosilicate substrates (MCM-41 structure) and acid dye (Lithol Rubine B) were examined. High surface area Al-MCM-41 materials synthesized in the presence of Ca^{2+} ions yielded the dye composites with the highest light fastness qualities, when compared to Ca^{2+} ion-exchanged Al-MCM-41 aluminosilicates, to non composite pigment or to smectite - dye composites.

Many investigations have been carried out to improve light-fastness properties of azo dyes. Major research was devoted to find appropriate conditions leading to an efficient anchoring of dyes in/on various inorganic substrates. The most widely used inorganic materials to elaborate such dye composites were clay minerals, e.g. smectites[1,2] or hydrotalcite.[3] Although it was reported that dye - smectite composites show higher stability against light fading than the sole dye molecule,[2] further improvement of such systems is still desirable for practical industrial uses.

In this preliminary work, we have examined the ability of MCM-41 type mesoporous aluminosilicate materials to behave as efficient dye supports. In particular, we have investigated the light-fastness properties of mesoporous Ca aluminosilicate - acid dye (Lithol Rubine B, 3-hydroxy-4-((4-methyl-2-sulfophenyl) azo)-2-naphthalenecarboxylic acid) composites. The effects of the mesophase crystallinity and of its modification by Ca^{2+} cations were examined. Ca^{2+} ions are expected to behave as connectors between the acid dye and the inorganic substrate[4] and it is speculated that the way they are introduced into the substrate mesopore volume or absorbed onto their external surface could play an essential role.

Three MCM-41 mesoporous materials have been prepared according to previously published recipes[5] involving the use of tetramethylorthosilicate as silica source, Al or Al - Ca nitrates and cetyltrimethylammonium bromide as surfactant agent. The as-synthesized phases were calcined in static air, typically at 750 °C, in order to remove completely the surfactant molecule from their pore volume. Sample A is a high surface mesoporous aluminosilicate that was further ion-exchanged with 10% $CaCl_2$, with the idea to insert calcium as dispersed Ca^{2+} counter ions to the framework negative charges induced by the presence of Al. After exchange, the sample was washed with water until no more Cl^- ions were detected. Sample B is also a high surface MCM-41 material prepared using the same experimental conditions, from a solution containing both Ca and Al nitrates, expecting that calcium could integrate the mesoporous framework in a different way. Sample C is identical to sample B but calcined in air at 1000 °C. Its low BET surface area strongly suggests a collapse of the

Table 1. Properties of some Ca- bearing MCM-41

Sample (code)	Introduction of Ca^{2+}	Gel comp. (atom %)[a]			Final comp. (atom %)[b]			BET surface area (m^2/g)
		Al	Ca	Si	Al	Ca	Si	
A	ion-exchange	4.0	-	96.0	3.8	1.1	95.1	1093
B	during synthesis	2.0	2.0	96.0	1.9	2.2	95.9	1061
C	during synthesis	2.0	2.0	96.0	1.8	2.1	96.1	149

[a] From ingredients [b] Determined by ICP analysis

Table 2. Color fade of the various dye composites after 14 h sunlight exposure

Sample (code)	Substrate	Post dye adsorption treatment	Amount of ads. dye / wt%	Color change (fade) (ΔE^a)
LR/A	Sample A	washed	5.2	5.9
LR/B	Sample B	washed	8.1	3.7
LR/C	Sample C	washed	6.5	6.1
LR/D	Sample B	unwashed	not determined	7.9
Commercial pigment[b]	-	-	-	7.7
LR/smectite	Ca^{2+} ion-exchanged smectite	washed	not determined	6.9

LR: Lithol Rubine B. [a] $\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$ [b] Calcium salt of Lithol Rubine B from Kishi Kasei Co.

mesoporous structure. Table 1 gives some chemical properties of the three samples.

Dye and MCM-41 composites were prepared by stirring the different Ca aluminosilicate samples in a 0.5% Lithol Rubine B (from Kishi Kasei Co.) aqueous solution for 6 h at ambient temperature. The obtained dye composites were dried at ambient temperature and thoroughly washed with water (except sample D, that was left unwashed). The amount of dye in each sample was evaluated by measuring the weight loss upon recalcination at 550 °C (Table 2).

The dye composites were applied onto the paper surface with a paint brush. All the papers exhibited the same color strength (Godlove's A value = 55 [6]). The painted papers were then exposed to the sunlight for 14 h. The color change (fade) of the papers after the exposure was recorded on a Minolta CR-300 colorimeter. The total UV-vis. irradiation energy after the sunlight exposure was 1542 kJ/m^2. Color changes of the dye composites (ΔE values) after exposure are reported in Table 2. It is understood that a sample showing a smaller ΔE value has a higher stability against fading.

Among all the MCM-41 - dye composites, sample LR/B showed the smallest ΔE value. While sample A (Ca^{2+} ion-exchanged sample) involved about the same surface area as sample B, ΔE value of sample LR/A was higher than that of sample LR/B. Sample LR/C, involving a low surface area, also showed a higher ΔE value than its analog sample LR/B that involves a high surface area. Finally, the unwashed sample LR/D showed a lower stability than its washed analog (LR/B), although it contained a larger amount of dye. It suggests that most of the dye was left weekly adsorbed (impregnated) on the surface of sample LR/D and hence more easily decomposed by sunlight than the more strongly bound dye interacting with Ca^{2+} ions mostly existing in the mesopore volume of sample LR/B. Interestingly, the commercial pigment, which is basically the aggregate of Ca salt of Lithol Rubine B, also shows a large ΔE value (7.7, thus similar to the value recorded on sample LR/D, both being far larger than in the case of other washed MCM-41 - dye composites, samples LR/A, LR/B and LR/C). The composite involving the same dye and the Ca^{2+} ion-exchanged smectite, which is one of the typical dye composites known to possess high anti photo fading properties,[2] shows a superior stability than the commercial pigment but inferior to that of sample LR/A. This experiment demonstrates that the Ca^{2+} ion-exchanged aluminosilicate MCM-41 is a better support than any clay type material for an efficient dye fixing.

From this first series of experiments, it is evident that both a high surface area (compare samples LR/B and LR/C) and the introduction of Ca^{2+} ions onto the MCM-41 substrate during the synthesis step (compare samples LR/A and LR/B) are the prerequisite conditions for a MCM-41 - dye composite to show an efficient resistance to fading. A high surface area of the substrate could play a positive role, possibly by allowing more dye molecules to get adequately positioned (anchored) to the aluminosilicate framework through the Ca^{2+} ions. A close comparison of the Ca contents, amounts of adsorbed dye and ΔE values for samples LR/A and LR/B indicates that the light-fastness properties could be proportional to the amount of appropriately fixed dye, that in turn depends on the amount of Ca^{2+} in the MCM-41 substrate. Indeed, low Ca concentrations would suppose a low concentration of adsorbed dye that would eventually lead to a low stability of the composite, as proposed in the literature.[7] In that respect, the exchange method appears less efficient in bringing Ca^{2+} ions into/onto the MCM-41 substrate than the direct synthesis in the presence of Ca^{2+} ions, despite the fact that enough framework Al is available for a more extended exchange (sample A).

The properties of azo dyes against photo fading are known to be affected by various factors[7] and the detailed mechanism explaining the stability improvement of the dye - MCM-41 composites has not been clarified so far. One of the possible mechanisms is that the active site of the dye molecule could be protected from the triplet oxygen, similarly to cyclodextrin - dye composites.[8] Note that particle size of the dye aggregate[7] in/on MCM-41 substrate and equilibrium of azo-hydrazone tautomerism[9] could also be important factors which affect the light-fastness properties.

References and Notes

1 Y. Kubo and Y. Nakayama, *Shikizai Kyokaishi*, **69**, 578 (1996).
2 M. Horino, Japanese Patent 53-113036 (1978).
3 Y. Kubo and M. Tsuji, *Shikizai Kyokaishi*, **69**, 667 (1996).
4 M. Horino, Japanese Patent 55-133462 (1980).
5 Z. Gabelica, J.M. Clacens, R. Sobry, and G. Van den Bossche, *Stud. Surf. Sci. Catal.*, **97**, 143 (1995).
6 I.H. Godlove, *Am. Dyestuff Report*, **43**, 685 (1954).
7 H. Zollinger, in "Color Chemistry," VCH Verlag, Weinheim (1987).
8 K. Enmanji and T. Ando, *Nippon Kagaku Kaishi*, **1987**, 1078.
9 E. F. Saad, E. A. Hamed, and A. El-Faham, *Spectrosc. Lett.*, **29**, 1047 (1996).