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Green and efficient diazotization and diazo coupling reactions on clays

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Abstract

Diazotization and diazo coupling reactions of sodium sulfanilate dihydrate and *para*-diazonium benzene sulfonyl azide with aromatic phenols over eco-friendly clay catalysts are described. These inexpensive, noncorrosive and reusable catalysts were found to exhibit bifunctional catalytic properties for diazotization and diazo coupling reactions. No considerable decreases in the efficiency of the catalysts were observed after four cycles of operation. The new method totally avoids the use of acids, alkalies and toxic solvents in diazotization and diazo coupling reactions.

Keywords: Azo dyes; Diazotization; Diazo coupling; Clays; Green chemistry

1. Introduction

Azo dyes are compounds that contain azo groups linked to methine or aromatic sp^2-hybridized C-atoms. The formation of diazotizing reagent starts with protonation of nitrous acid under strongly acidic conditions, and azo coupling carried out at low temperature in the presence of nucleophilic coupling components, the reactivity of a nucleophilic substrate increases with increasing basicity phenolates and amines [1]. These conventional acid–base catalyzed processes are effective for the near quantitative formation of the desired products. But the main limitation of such synthetic processes is their environmental incompatibility. The acidic and basic effluents from the laboratory and industry produce permanent damage to the environment and disturb the ecological balance [2]. In recent years, clay based catalysts are reported to be effective for performing many of the acid–base catalyzed organic reactions in a better, environmentally benign manner [3,4]. Recently, we reported new azoic dyes containing (1H)-tetrazol and imidoyl azide group [5]. As part of our ongoing research program for exploring the bifunctional catalytic properties, we herein describe a new process for diazotization and diazo coupling reactions using clay based layered silicates as a catalyst toward the synthesis of azo dyes.

2. Results and discussion

This pape\r describes the facile and modified synthesis of azo dyes (this method previously has been reported under acidic and basic conditions) [6] without using conventional acid or base in the presence of clays. In the present synthesis, the sodium sulfanilate or 4-aminobenzene sulfonyl azide was first made into a paste with clay catalyst and it was then cooled to 0–5 °C, as shown in Scheme 1.

This clay mixture was then diazotized with dilute $NaNO_2$ solution. The diazonium–clay complex formed was subsequently coupled with phenols, naphthols and an aromatic amine. The sodium sulfanilate azo dye formed was separated from the catalyst by extracting it into water or alcohol and sulfonyl azide azo dye was separated from the catalyst by extracting it into acetone and from where it was recovered by removal of the solvent under vacuum. The generality of the process is proved by performing the reaction with all the three catalysts, with sodium sulfanilate or 4-aminobenzene

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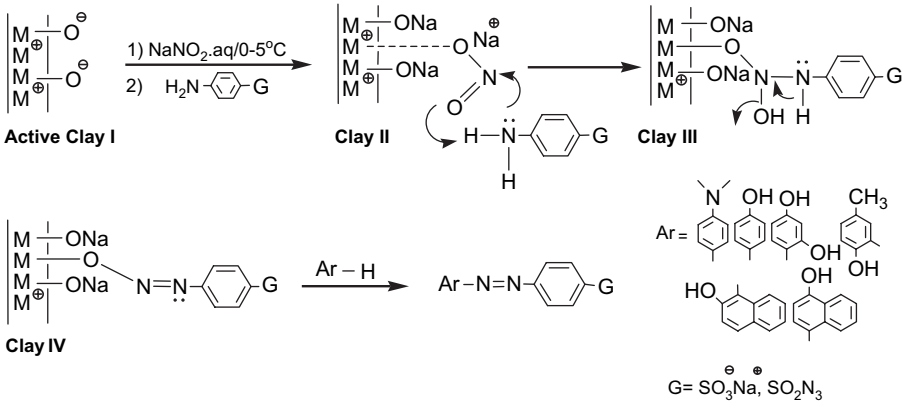
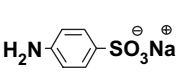
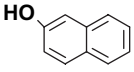
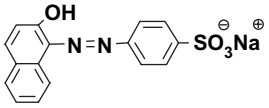
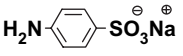
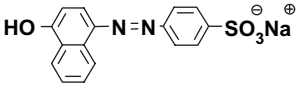
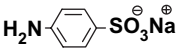
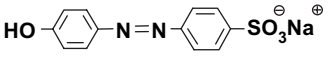
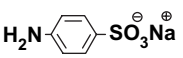
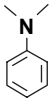
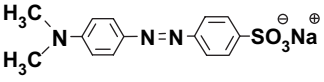
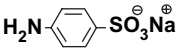
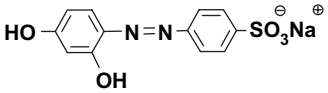
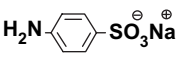
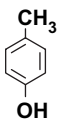
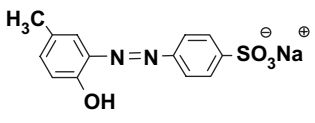


Scheme 1.

sulfonyl azide and with coupling agents. After the formation of the diazonium–clay complex, the edge hydroxyls of the clay platelets are believed to get converted into –ONa species by consuming the Na ions from $NaNO_2$ solution used for diazotization. This –ONa species helps to maintain the pH of the medium neutral or slightly alkaline for a quantitative coupling of the diazonium ion with the coupling agent. In almost all the cases, the isolated yields of the pure products were found to be near quantitative as outlined in Tables 1 and 2. Control reactions were carried out with the same reagents in the presence of mineral acids like HCl and bases by following the conventional procedure for comparing the yields. All substrate yields for sodium sulfanilate dyes are in the range of 60–85% and for sulfonyl azide dyes in the range of 30–60%. The yields found to be slightly less than the same obtained from the present mineral acids process. Recycling of the catalysts was also investigated. For this purpose, the catalysts after the removal of the azo dyes were washed several times with acetone and dried at 110 °C in an air oven for 1 h. These oven-dried samples were then calcined at 450 °C for 3 h in a furnace and used for performing the reactions. This process was repeated 4 times and no considerable decreases in the yield of the azo dyes were observed. The results obtained for the recycling reactions are given in Tables 3 and 4. The mechanism for diazotization and diazo coupling reactions is depicted in Schemes 1 and 2. This mechanism was proposed

Table 1
Diazotization and diazo coupling reactions of sodium sulfanilate dehydrate with some aromatic phenols over bentonite, kaolin and K10

Azo dyes	Amine	Coupling agent	Product	%Yield		
				K10	Bentonite	Kaolin
1[a]				85	75	80
2[a]				80	70	75
3[b]				80	74	78
4[c]				85	77	79
5[b]				65	60	62
6[d]				70	60	65

The structure of all dyes were reported previously in Refs. (a) [6a], (b) [6b], (c) [6c], and (d) [6d].