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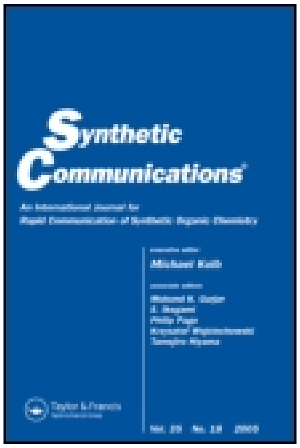

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Modified Clays as Efficient Acid-Base Catalyst Systems for Diazotization and Diazocoupling Reactions

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Modified Clays as Efficient Acid–Base Catalyst Systems for Diazotization and Diazocoupling Reactions

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Laboratory (CSIR), Kerala, India

ABSTRACT

Diazotization and diazocoupling reactions of aniline and its substituted derivatives with phenol and other aromatic amines over ecofriendly clay catalysts is described. This inexpensive, noncorrosive and reusable catalysts were found to exhibit bifunctional catalytic properties for these reactions. No considerable decrease in the efficiency of the catalysts were observed after five cycles of operation. The new method totally avoids the use of acids and alkalies.

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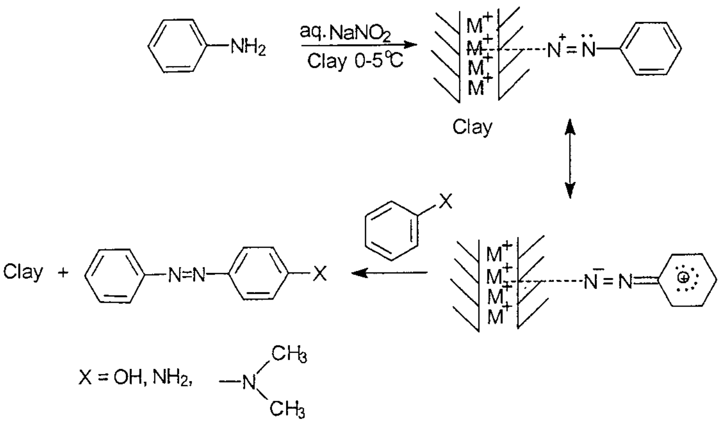
Key Words: Diazotization; Diazocoupling; Bifunctional; Clays; Green.

Diazotization and diazocoupling reactions are important class of organic reactions, which are currently performed with mineral acids and alkalies as catalysts.[1,2] 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.[3] 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.[4,5] As part of our ongoing research programme for exploring the bifunctional catalytic properties of clay based layered silicates, here we describe a new process for diazotization and diazocoupling reactions in which acidic and basic catalysts are required in a sequential manner.

We have studied the performance of three clay based catalysts denoted as KK, GB and K10 for the said reactions. Out of this, KK and GB are procured from local sources and belong to kaolinite and bentonite variety respectively. K10 is procured from Aldrich and used as such.

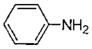
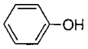
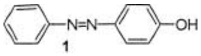
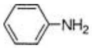
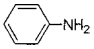
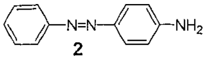
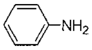
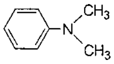
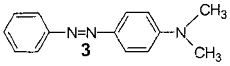
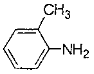
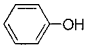
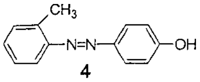
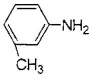
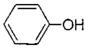
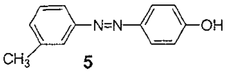
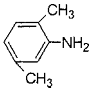
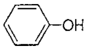
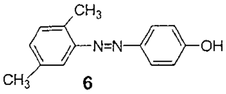
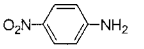
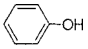
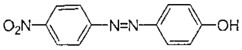
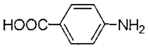
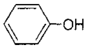
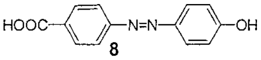
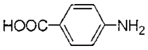
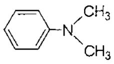
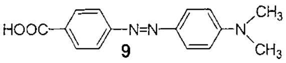
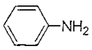
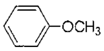
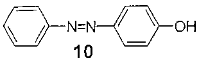
In the present synthesis, the amine was first made into a paste with clay catalyst and it was then cooled to 0°C (Sch. 1). This amine clay mixture was then diazotized with dil. $NaNO_2$ solution.



Scheme 1.

The diazonium-clay complex formed was subsequently coupled with phenol or amine. The azo dye thus formed was separated from the catalyst by extracting it into alcohol or 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 and with different amines and coupling agents. In almost all the cases, the isolated yield of the pure products were found to be near quantitative (Table 1). A notable high yield of the azo coupled product was obtained in the case of a weakly basic amine like *p*-nitro aniline, which gave >80% yield for the dye in the present synthesis (Entry 7, Table 1).

Table 1. Diazotization and diazocoupling reactions of aniline and its substituted derivatives with phenol and aniline over KK, GB and K10.

Entry	Amine	Coupling agent	Product	% Yield*		
				K.K.	G.B.	K10
1			 1	97	99	91
2			 2	94	94	88
3			 3	96	97	92
4			 4	94	98	94
5			 5	96	96	91
6			 6	92	95	89
7			 7	88	90	81
8			 8	93	95	89
9			 9	91	91	90
10			 10	80	81	80

*Isolated pure products.

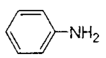
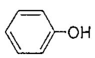
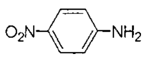
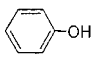
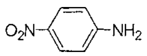
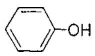
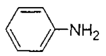
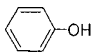
Control reactions were carried out with the same reagents in the presence of mineral acids like HCl and bases by following the conventional procedure for comparing the yields. All substrates except *p*-nitro aniline yielded the corresponding dye in the range of 75–80% and are found to be slightly less than the same obtained from the present clay based process. For *p*-nitro aniline, the conversion was found to be $< 50\%$.

Recyling ability of the catalysts were also studied. 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 5 times and no considerable decrease in the yield of the azo dyes were observed. The results obtained for the recycling reactions of aniline and phenol is given in Table 2.

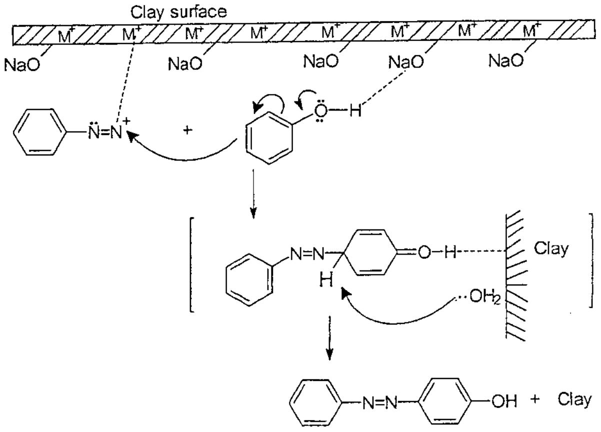
A plausible mechanism proposed for the present method is given in (Sch. 2). After the formation of the diazonium-clay complex, the edge hydroxyls of the clay platelets are believed to get converted into –ONa species by consuming the Na^+ ions from $NaNO_2$ solution used for diazotization. This –ONa species 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 conclusion, we have developed a highly efficient 'green' methodology for diazotization and diazocoupling reactions by employing clay catalysts with better recycling options and totally avoids the use of acids, alkalies and toxic solvents.

Table 2. Results of the recycling reactions with GB and KK.

Catalyst	Amine	Coupling agent	% Yield*				
			0 cycle	I cycle	II cycle	III cycle	IV cycle
G.B.			99	99	97	97	97
G.B.			90	90	89	89	89
K.K			88	88	88	85	85
K.K.			97	96	96	95	95

*Isolated pure products.



Scheme 2.

EXPERIMENTAL

General

The montmorilonite K10 clay catalyst was procured from Aldrich Chemicals and used as such. The kaolinite clay used for the preparation of catalyst (K.K.) was collected from the diagentic clay deposits of Quilon district, Kerala, India. The bentonite clay used for the preparation of catalyst (G.B.) was procured from Ashapura mines of Gujarat State, India. The amines were procured from E-Merck (India) Limited and used as such. Azo dyes formed were systematically characterized by GC–MS, ^{1}H NMR and IR spectral analyses.

Preparation of the Kaolinite Clay Catalyst KK

The raw clay was first subjected to coning and quartering to obtain a sample which is representative of the bulk. This was then subjected to slacking to remove soluble impurities and is then sieved using −350 mesh. The fine grained clay particle obtained was dried and powdered. It was then calcined at 550°C (metakaolinization) for 4 h. The metakaolinized sample was then activated with 2 M HCl in the solid to liquid ratio 1:4 (400 mL 2 M HCl for 100 g clay) for a period of 45 min and filtered. It was then washed thoroughly with distilled water for removing chloride ions and dried in an air oven at 110°C for 2 h.

Then acid activated clay was again calcined at 400°C for a period of 3 h and used for the reaction. SiO_2 55.8%, Al_2O_3 25.69%, Fe_2O_3 2.24%, TiO_2 1.93%, Na_2O 0.08%, K_2O 0.26%, Loss on ignition (LOI) 8.45%, Ho 0.03 mmol/g and Surface area (B.E.T.) 53.634 m^2/g.

Preparation of Bentonite Clay Catalyst GB

The bentonite clay (GB) was collected from Ashapura mines of Gujarat State, India and purified by adopting the same procedure mentioned above for KK. The −350 fractions collected was dried and calcined at 450°C for 4 h and used as such for reaction. SiO_2 56.19%, Al_2O_3 15.56%, Fe_2O_3 7.59%, TiO_2 0.79%, CaO 5.68%, MgO 4.98%, Loss on ignition (LOI) 14.2%, Ho 0.043 mmol/g and Surface area (B.E.T.) 98.30 m^2/g.

Representative Procedure for Diazotization and Diazocoupling Reactions

In a typical experiment, 4.67 g of (0.05 mol) of aniline was adsorbed on 8 g of clay (KK) catalyst and cooled to 0°C. To this, 4.34 g (0.1 mol) of $NaNO_2$ in 15 mL H_2O was added dropwise for a period of 1 h. After the addition of $NaNO_2$, 4.67 g (0.05 mol) of phenol was added to this ice cold diazonium clay complex and was brought to room temperature with constant stirring and kept at room temperature for 1 h. The reaction mixture was then repeatedly extracted into alcohol. The alcohol extracts evaporation under vacuum afforded **1**.

Selected data for **1**: IR(KBr cm^{-1}): 1625 (–N=N–), 3400 (OH), UV (λmax nm) 415. ^{1}H NMR ($CDCl_3$/DMSO, 300 MHz). δ9.8 (s, 1H, –OH), 8.1–8.4 (m, 4H, phenyl), 7.3–6.9 (m, 5H, phenyl), GC–MS OV 101, Rt 10.57 min *m*/*z*. 198 (M^+) **2**. (IR KBr cm^{-1}) 1621 (–N=N–) 3425 (NH_2), UV (λmax nm) 420, ^{1}H NMR ($CDCl_3$/DMSO 300 MHz): δ3.8 (s, 2H, –NH_2), 8.1–8.3 (m, 4H, phenyl), 7.2–6.9 (m, 5H, phenyl), GC–MS OV 101 Rt 10.53 min *m*/*z* 197 (M^+). **3**. IR(KBr cm^{-1}): 1625 (–N=N–), UV (λmax nm) 420, ^{1}H NMR ($CDCl_3$/DMSO) δ2.96 (s, 6H, $2 \times CH_3$), 6.72–7.36 (m, 9H, $2 \times C_6H_5$), GC–MS OV 101, Rt 12.77 min; *m*/*z* 225 (M^+). **4**. IR(KBr cm^{-1}): 1625 (–N=N–), 3411 (OH), UV (λmax nm) 415. ^{1}H NMR ($CDCl_3$/DMSO) δ2.1 (s, 3H, CH_3), 9.8 (s, 1H, –OH), 8.1–8.3 (m, 4H, phenyl), 7.1–7.4 (m, 4H, phenyl), GC–MS OV 101, Rt 11.22 min; *m*/*z* 212 (M^+). **5**. IR(KBr cm^{-1}) 3400–3450 (OH), 1621 (–N=N–), 1510, 1340 (NO_2), UV (λmax nm) 270, 390. ^{1}H NMR δ8.1–8.3 (m, 4H, phenyl), 6.7–7.36 (m, 4H, nitrophenyl), GC–MS OV 101, Rt 11.30 min; m/z 243 (M^+).

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