

Transition metal pillared clay: 3. A para selective catalyst for nitration of chlorobenzene

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Abstract

Nitration of chlorobenzene has been studied at different temperatures using transition metal (Fe(III), Cr(III), Mn(III)) pillared clays as the catalysts. All the samples showed high para selectivity (up to 94%). The acid activated pillared clays calcined at 300°C showed higher activity than the nonactivated pillared clays which followed the order: iron oxide pillared acid-activated clay > chromium oxide pillared acid-activated clay > manganese oxide pillared acid-activated clay whereas the selectivity order is chromium oxide pillared acid-activated clay > manganese oxide pillared acid-activated clay > iron oxide pillared acid-activated clay.

Keywords: Transition metal pillared clay; Nitration; Chlorobenzene; Selectivity

1. Introduction

Most of the aromatic nitration reactions are generally performed with mixtures of nitric and sulfuric acids which give both ortho and para products close to the thermodynamic ratio of 2:1 [1]. However, addition of acetic anhydride to the mixture of nitrating agents results in high para selectivity even at low temperature [2,3]. But due to the present environmental concerns it would be highly desirable to use solid acid catalyst which will eliminate the problems in handling, storage and disposal of liquid acids. At the same time it can be recycled to reduce the cost of production.

Mononitrohalobenzenes, especially para-

nitrochlorobenzene are versatile intermediates for dyes, pharmaceuticals and perfumes [4]. So due to the commercial importance of the para products, it is desirable to improve the regioselectivity of the nitration reaction towards higher para products. In the last decade though, a lot of attempts have been made to find an efficient catalyst for the title reaction, each one has some or other disadvantages. Long reaction time and moderate yield are the major disadvantages in the nitration of halobenzene on clay supported copper nitrate (clay COP) [5] whereas low para-selectivity was obtained by Olah et al. [6] using Nafion-H as the catalyst. Subsequently fuming nitric acid and acetic anhydride were used in presence of clay COP [7] to improve the yield but the long reaction time still remained as the disadvantage. Masci [8,9] has obtained significant improvement in para selectivity by

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complexing the nitronium ion with crown ether. However, it is a highly expensive process which prohibits the large scale industrial applications. Recently improved selectivity was reported by Choudary et al. [10] using Fe^{3+} -montmorillonite (K10). According to them the selectivity was controlled by the Fe^{3+} ion present in the inter-layer of the clay matrix.

Although the thermal stability, acidity and shape selectivity of the pillared clays [11] are higher than the parent clays and ion-exchanged clays, no work has been carried out so far on

nitration reactions using these materials. So in the present study we have used pillared clays and acid-activated pillared clays with different oxide pillars (iron, chromium and manganese) to find out the effect of metal oxides on nitration of chlorobenzene.

2. Results and discussion

The total acidity (Table 1) and in particular Brønsted acidity of the acid-activated pillared

Table 1
Textural parameters of transition metal pillared clays calcined at different temperatures

Catalysts	Calcination temperature (°C)	S_{BET} (m^2/g)	Pore volume (ml/cm^3)	Basal spacing (Å)	Micropore diameter (Å)	Total acidity (mmol/g)
FePILC	110	95	—	22.4	—	530
FePILC	300	235	0.182	18.8	8.9	895
FePILC	500	284	0.24	18.0	8.5	700
CrPILC	110	98	—	22.0	—	520
CrPILC	300	241	0.232	18.3	8.5	900
CrPILC	500	286	0.245	17.8	7.9	680
MnPILC	110	97	—	21.1	—	525
MnPILC	300	252	0.217	18.0	8.7	905
MnPILC	500	280	0.235	17.1	8.4	670
FeAAPILC	110	101	—	22.4	—	—
FeAAPILC	300	220	0.215	18.4	9.4	950
FeAAPILC	500	273	0.254	17.8	8.6	770
CrAAPILC	110	108	—	21.5	—	810
CrAAPILC	300	242	0.254	17.9	9.3	940
CrAAPILC	500	270	0.273	17.5	8.9	710
MnAAPILC	110	109	—	20.4	—	730
MnAAPILC	300	241	0.251	17.7	8.9	955
MnAAPILC	500	268	0.275	16.8	8.4	720

Table 2
Nitration of chlorobenzene using transition metal pillared montmorillonite calcined at 300°C

Catalyst	Nitrating agent	P:O	P/O	Temp. (°C)	Time (min)	Yield (%)	Yield ^a (%)
Without catalyst	$\text{HNO}_3:\text{AC}_2\text{O}$	60:40	1.5	75	20	16	—
FeAAPILC	$\text{HNO}_3:\text{AC}_2\text{O}$	92:8	11.5	75	20	95	91
CrAAPILC	$\text{HNO}_3:\text{AC}_2\text{O}$	94:6	15.66	75	20	91	88
MnAAPILC	$\text{HNO}_3:\text{AC}_2\text{O}$	92:7.5	12.26	75	20	86	81
FePILC	$\text{HNO}_3:\text{AC}_2\text{O}$	92:8	11.5	75	20	85	81
CrPILC	$\text{HNO}_3:\text{AC}_2\text{O}$	94:6	15.66	75	20	83	79
MnPILC	$\text{HNO}_3:\text{AC}_2\text{O}$	93:7	13.28	75	20	79	76
FeAAPILC	$\text{HNO}_3:\text{AC}_2\text{O}$	92:8	11.5	RT	20	82	79
CrAAPILC	$\text{HNO}_3:\text{AC}_2\text{O}$	93:7	13.28	RT	20	74	70
MnAAPILC	$\text{HNO}_3:\text{AC}_2\text{O}$	92.5:7	13.21	RT	20	70	65

^a Experiment performed on 10th recycle of the catalyst.

clays (AAPILC) is higher than that of non-activated pillared clays (PILC). In order to compare the acidity with activity, both the pillared clays were used for nitration reactions and the results were presented in Table 2. The results of other workers on nitration of chlorobenzene were included in Table 3 for comparison purposes. It is seen from Table 2 that all the transition metal oxide pillared clays have high para selectivity (91%). Among all the samples FeAAPILC shows highest yield whereas MnPILC shows the lowest. In all the cases samples prepared from acid activated clays show higher yield than those of PILC. This indicates that the acidity of the catalyst plays the major role as far as the total yield is concerned. The difference in acidity between the PILC and AAPILC samples is mainly due to the difference in their Brønsted acid sites. So it can be concluded that the Brønsted sites play the key role in determining the activity of the catalyst. This observation is in contrast to Choudary et al., who have emphasised the role of Lewis acidity for higher yields [10].

The yields obtained using pillared clays calcined at different temperatures are presented in Fig. 1. The yields for 110 and 300°C calcined samples are nearly the same whereas they decrease drastically for 500°C calcined samples. The decrease in yield beyond 300°C is perhaps due to the loss of Brønsted acid sites. As most of the Brønsted acid sites are associated with the clay layers only, change in Brønsted acidity is less marked due to the change in oxide pillars [12,13]. However, it is marked that the total

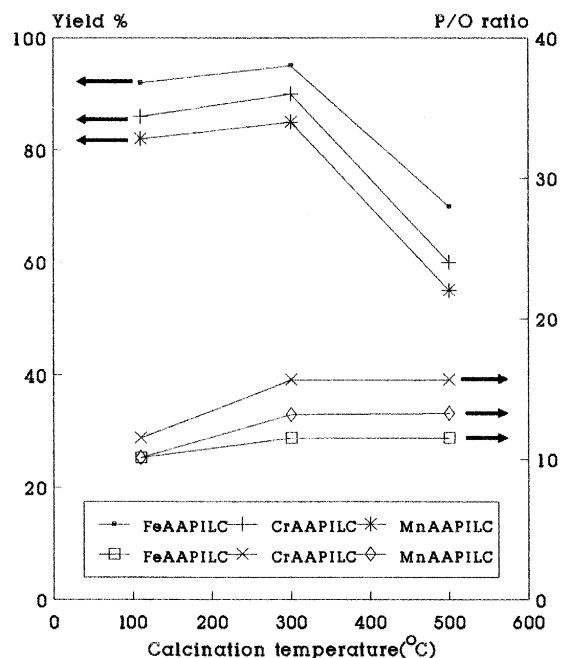


Fig. 1. Correlation of isolated yield and corresponding para/ortho ratio with calcination temperature of the catalyst.

yield varies with the change in metal oxide pillars following a trend: FeAAPILC > CrAAPILC > MnAAPILC. This shows the importance of metal oxide pillars in the nitration of chlorobenzene. But the trend for para selectivity for the same reaction is different which follows the order: CrAAPILC > MnPILC > FePILC. It is interesting to note that all the samples showed more than 91% para selectivity. This high para selectivity may be due to the presence of uniform micropores in the samples

Table 3
Nitration of chlorobenzene with various catalysts and nitrating agents

Catalyst	Nitrating agent	P:O	P/O	Temp (°C)	Time (min)	Yield (%)	Ref. No.
H ₂ SO ₄	HNO ₃	62:34	1.8	—	—	—	[1]
H ₂ SO ₄	HNO ₃ :AC ₂ O	90:10	9.0	0	15 h	—	[3]
Nafion-H	HNO ₃	61:38	1.6	100	—	87	[10]
Montmorillonite K10	HNO ₃ :AC ₂ O	80:20	4.0	80	15	68	[10]
Clay COP	Metal Nitrate	88:12	7.5	RT	48 h	73	[10]
Clay COP	HNO ₃ :AC ₂ O	85:13	6.54	RT	24 h	98	[5]
Cu ²⁺ -Montmorillonite K10	HNO ₃ :AC ₂ O	90:10	9.0	80	15	82	[7]
Fe ³⁺ -Montmorillonite K10	HNO ₃ :AC ₂ O	92:8	11.5	80	15	90	[6]

inside which most of the reaction takes place. The para/ortho ratio for FeAAPILC, MnAAPILC and CrAAPILC are 11.5, 13.28 and 15.66, respectively (Fig. 1). Though the micropore diameters are nearly the same for all the three samples (Table 1), there is a clear difference in their para selectivity which indicates that each transition metal oxide pillar may have a specific role towards para selectivity.

Total yield increases with increasing reaction temperature up to 75°C whereas the para selectivity more or less remains constant (Fig. 2). Only in case of CrAAPILC the para selectivity increases with increasing reaction temperature. However, in all the cases highest yield and selectivity is found at the reaction temperature of 75°C. It is seen from Fig. 3 that the para selectivity and yield increase with increase in catalyst amount up to 2 g and thereafter remains almost constant with further increase. The reusability of the catalysts is also studied and it is found that all the catalysts are reusable at least up to ten times having nearly the same

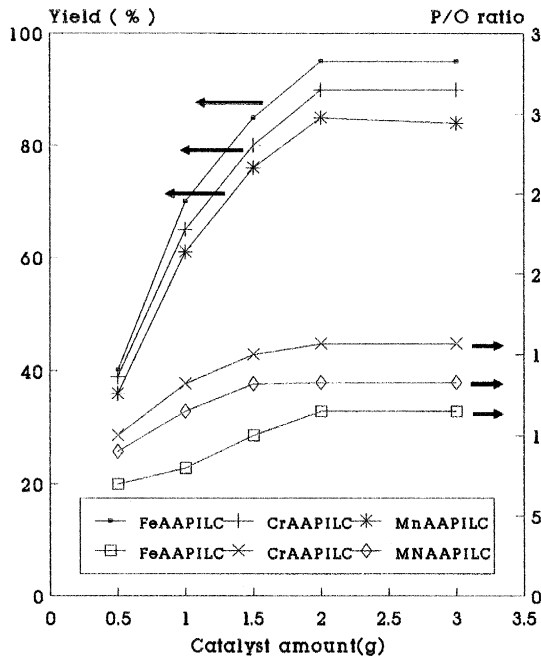


Fig. 2. Correlation of isolated yield and corresponding para/ortho ratio with the variation in catalyst amount.

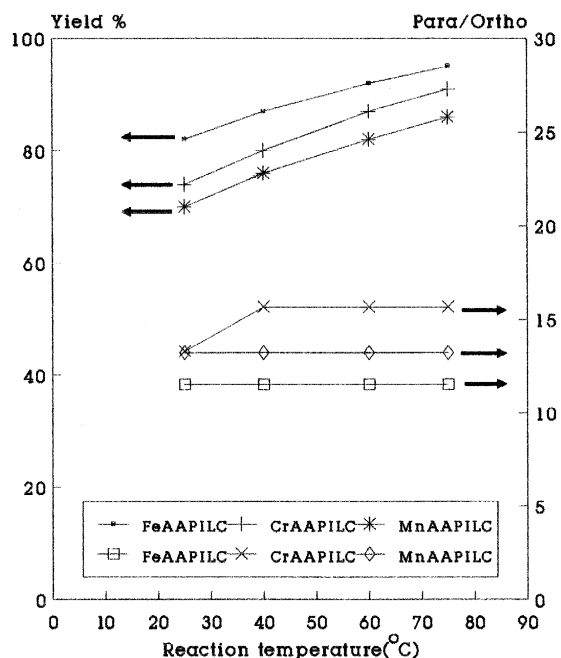
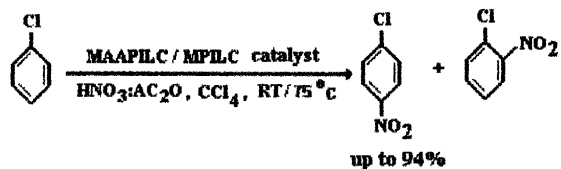


Fig. 3. Plot of isolated yield and corresponding para/ortho ratio at different reaction temperatures.

activity (Tables 2 and 3). This nitration of chlorobenzene can be represented schematically as follows:



3. Experimental

3.1. Materials

Na-montmorillonite (Mainburg, Germany) and acid activated montmorillonite were used as the starting materials for the preparation of pillared clays. Acid activation was carried out using sulfuric acid at 95°C for 15 h [14]. Accordingly the clay was treated with sulfuric acid

solution maintaining the solution to clay ratio of 20 ml g⁻¹ and acid to clay ratio (W/W) of 0.3. Then the acid activated clay was washed repeatedly to make it free from SO₄²⁻ and dried at room temperature. Trinuclear acetato complexes of Fe(III), Cr(III), Mn(III) prepared according to the reported methods [15–17], were used as pillaring agents.

3.2. Fe(III) pillared montmorillonite

Both Fe(III) pillared montmorillonite (FePILC) and pillared acid activated montmorillonite (FeAAPILC) were prepared at 25°C by stepwise ion exchange process using a trinuclear Fe(III) acetato complex as the pillaring agent. The detailed method of preparation was reported elsewhere [18]. The complex loaded materials were calcined at 110, 300 and 500°C for 4 h prior to further use.

3.3. Cr(III) pillared montmorillonite

Materials (CrPILC and CrAAPILC) were prepared from both the Na-exchanged montmorillonite as well as acid activated montmorillonite by stepwise ion exchange process at 25°C using trinuclear Cr(III) acetato complex as the pillaring agent. In each step 3 mmol of Cr(III)/g of clay was maintained in aqueous solution for 3 h under stirring condition and filtered. The same process was repeated 5 times and the final product was filtered, washed and dried at room temperature. The dried sample was calcined at 110, 300, 500°C for 4 h prior to further use.

3.4. Mn(III) pillared montmorillonite

Mn(III) pillared montmorillonite (MnPLIC) and Mn(III) pillared acid activated montmorillonite (MnAAPILC) were prepared by stepwise ion-exchange process using trinuclear manganese(III) acetato complex as pillaring agent in methanol solvent at 80°C. The detailed procedure was reported elsewhere [19].

All the materials were characterised by low

angle XRD and N₂ adsorption–desorption isotherms and the calculated textural parameters are presented in Table 1. Total acidities of the samples determined by spectrophotometric method [20] are also included in the same table.

3.5. Nitration procedure

A mixture of chlorobenzene (1.12 g, 10 mmol), acetic anhydride (3.0 ml), in 50 ml CCl₄ and required amount of catalyst were taken in a 100 ml three necked round bottomed flask fitted with a condenser and CaCl₂ guard tube. The reaction mixture was maintained at 75°C under stirring condition. Then about 0.5 ml (11 mmol) of fuming nitric acid was added dropwise to the reaction mixture and the reaction was allowed to continue for 20 min under the same condition. The reaction mixture was cooled, filtered and the residue was washed with the solvent. Then the filtrate was washed with water to remove acetic acid. The organic fraction of the filtrate was separated by separating funnel and concentrated under vacuum to get the final product. The nitration products were analysed by gas chromatograph (Sigma, India) on FID mode using 6 ft long SS column with 15% FFAP for their ortho and para fractions.

The temperature and amount of catalyst in the reaction were varied in order to find out the optimum conditions required to achieve the highest selectivity and yield.

4. Conclusions

Transition metal (Fe(III), Cr(III) and Mn(III)) pillared montmorillonite can be used as an effective catalyst for higher (> 91%) para selectivity in the nitration of chlorobenzene. Among all the samples CrAAPILC showed highest (94%) para selectivity whereas the acid activated pillared materials calcined at 300°C showed better activity. As far as yield and selectivity are concerned it followed the order: FeAAPILC > CrAAPILC > MnAAPILC and

CrAAPILC > MnAAPILC > FeAAPILC, respectively.

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