Reductive N-acylation of nitroarenes by Fe^{3+}-montmorillonite

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Abstract

Reductive N-acylation of nitroarenes to anilides in moderate to good yields in the presence of carboxylic acid anhydrides using a recyclable heterogeneous catalyst, Fe^{3+}-montmorillonite, prepared from inexpensive materials is achieved in a single pot.
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1. Introduction

Anilines and anilides are industrially important intermediates for several pharmaceuticals, agrochemicals and dyes. The classical route practiced in industry for the production of anilines involves the reduction of nitroarenes employing stoichiometric amounts of iron powder in the presence of hydrogen source, protic acid HCl or acetic acid [1,2]. These processes encounter the problem of the disposal of a large amount of ferric salts generated during the reaction. Although the direct use of molecular hydrogen for reduction of nitroarenes is an expensive endeavor, several processes for the manufacture of aniline via reduction of nitrobenzene employing copper on silica in vapour phase, palladium/platinum on carbon catalysts both in the vapour phase and liquid phase are operating in the industries [1]. Although, iron carbonyls have been used extensively in the reductive acylation of nitroarenes using variety of reducing agents [3–6], these reactions suffer from serious limitation of using expensive reagents in more than stoichiometric quantities. In the effort to devise the catalytic reaction, a desired option, expensive platinum, rhodium and ruthenium complexes are used in catalytic amounts in the reductive acylation of nitroarenes to obtain anilides using carbon monoxide at high pressure or $CO–H_2O$. These reactions invariably used either high pressure or excessive bases or both [7–9]. Recyclable heterogeneous catalysis is particularly attractive because it allows the production and ready separation of large quantities of products using small amounts of catalysts. Recently, reduction of nitroarenes was carried out in the presence of iron(III) oxide hydroxide using expensive hydrazine hydrate as a reducing agent [10–14]. We have recently reported hydrogen processing by Fe^{3+}-exchanged montmorillonite [15] using water/carboxylic acids as the proton source.

Wide use of iron complexes in the reductive acylation of nitroarenes as exemplified above, promotive effect of montmorillonite in the redox reactions [16] and availability of both these materials at cheaper cost motivated us to choose Fe^{3+}-montmorillonite in the present studies.

We report in this letter a novel synthesis of anilides from nitroarenes employing reusable Fe^{3+}-exchanged on mesoporous montmorillonite K10 in catalytic amounts using carboxylic acid anhydrides as acylating agents in liquid phase at atmospheric pressure and $180\,°C$ in good yields for the first time (Scheme 1).

2. Experimental

2.1. Catalyst preparation

Montmorillonite K10 obtained from Fluka was used directly without any pretreatment. Metal exchanged montmorillonite, Fe^{3+}-montmorillonite, Fe^{3+}-zeolite-Na-Y and Fe-pillared clay (Fe-PILC) were prepared according to the literature procedures [17–19]. The analysis of the metal content in the catalysts was carried out as reported by Vogel [20] and found to be 2.44% of exchanged iron, by weight in Fe^{3+}-montmorillonite.
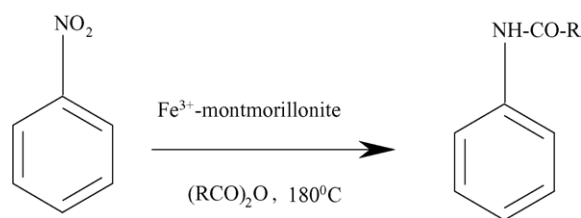
Scheme 1. Reductive N-acylation of nitrobenzene using Fe^{3+}-montmorillonite.

2.2. Methods of characterization

The samples of the reaction mixture were collected in regular intervals and analyzed by Nucon gas chromatography on 1/8 in. of SS (2 m) OV-17 packed column with FID detector using nitrogen as a carrier gas using *n*-decane as an internal standard. The gas samples were collected during the reaction using balloon arranged on the top of the reflux condenser and analyzed on a POROPAK-Q column at 50 °C using hydrogen as a carrier gas.

3. Catalytic reactions

3.1. Typical procedure

A mixture of carboxylic acid anhydride (40 mmol) and catalyst (0.5 g) was stirred in a 50-ml two-necked R.B. flask sealed with rubber septum and fitted with a reflux condenser under nitrogen atmosphere. After obtaining the reaction temperature (180 °C), nitroarene (10 mmol) was added slowly for 15 min and continued the reaction. After completion of the reaction (monitored by GC), the reaction mixture was filtered to separate the catalyst and washed the catalyst with distilled acetone for four to five times. The reaction mixture was taken in 50 ml of ethyl acetate and washed with 5% sodium bicarbonate solution to remove unreacted carboxylic acid anhydride. The reaction mixture was concentrated under vacuum and the crude product was purified by column chromatography using ethyl acetate:hexane (1:5) as eluant to get pure product.

3.2. Results and discussion

All the catalysts were evaluated for the reductive N-acylation of nitrobenzene with propionic anhydride to the correspond-ing anilides and the results are shown in Table 1. Fe^{3+}-montmorillonite catalysts are found to be superior over other catalysts, while Fe^{3+}-Na-Y-zeolite shows poor activity. Although acidic strength is high in Fe-PILC, Fe^{3+}-montmorillonite shows higher activity than other two. The higher activity is because of the Fe^{3+} in the exchanged form in Fe^{3+}-montmorillonite and the montmorillonite is regarded as a best support for redox reactions. On the other hand, in the Fe-PILC, the iron hydroxyl oxide-clusters are propped up the interlayers of the montmorillonite, where in direct contact of Fe^{3+} with the support is minimized. The molar ratio of acid anhydride to nitrobenzene required to obtain optimum yields is 4. The optimum reaction temperature is >180 °C and no reaction is noticed at lower temperatures. No reaction is observed with acetic anhydride at its reflux temperature. Interestingly, the reductive acylation of nitrobenzene proceeds smoothly with higher carboxylic acid anhydrides affording good yields (entries 1c–e, Table 2). The rate of the reaction is slow when higher homologues of carboxylic acid anhydrides were used. As the carbon chain increases, the formation of by-products decreases. Buoyed with these results, various nitroarenes were subjected to the reductive acylation with propionic anhydride to afford moderate to good yields and selectivity. The catalyst is used for three cycles, which shows a slight decrease in activity. The formation of usual by-products such as aniline, *p*-nitro propiophenone and *N,N*-disubstituted carboxylic amide is noticed in minor quantities.

Evolution of a small amount of CO and large amount of CO_2 as detected by GC–MS during the successful reductive acylation of nitrobenzene using propionic anhydride as acylating agent and essentially no reaction using propionic acid as acylating agent indicate that the source for the evolved carbon oxides is the acid anhydride. The inactivity of the calcined Fe^{3+}-montmorillonite, devoid of water in a separate experiment (entry 1b, Table 2) conducted under similar conditions and the display of activity with the Fe^{3+}-montmorillonite as synthesized suggest that the evolved CO reacts with water present in the Fe^{3+}-montmorillonite (water gas shift reaction) and water formed during the reductive acylation reaction produce hydrogen to initiate and sustain the reduction of the nitroarenes, respectively (Scheme 2). In our reaction, we have not observed the formation of alcohol. It is transformed into an ester.

Table 1
Reductive N-acylation of nitrobenzene with different catalysts using propionic anhydride as acylating agent

Entry	Catalyst	Total acidity (μmol/g)	Time (h)	Conversion (%)[a]	Selectivity (%)[a]		
					Amide	Amine	Others
1	Fe^{3+}-montmorillonite	337	18	85, 79[b]	91, 85[b]	4	5
2	Fe-PILC	398	16	74	88	6	6
3	Fe^{3+}-Na-Y-zeolite	168	16	25	85	10	5
4	K10-montmorillonite	310	12	10	95	3	2
5	$FeCl_3$	–	24	–	–	–	–
6	$FeSO_4$	–	24	–	–	–	–

[a] By GC analysis.
[b] Third cycle.

Table 2
Reductive N-acylation of nitroarenes catalyzed by Fe^{3+}-montmorillonite

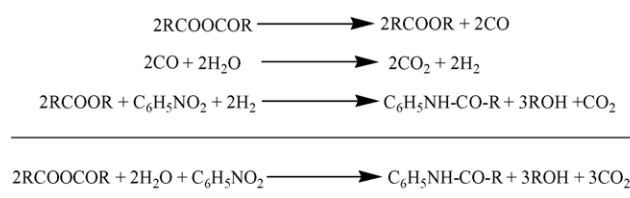| Entry	Substrate	Acylating agent/solvent	Time (h)	Conversion (%)	Selectivity (%)		
					Amide	Amine	Others
1a	Nitrobenzene	Propionic acid[a,b]	6	80[a], 90[b]	90[a], 95[b]	10[a], 5[b]	–
b		Propionic anhydride	18, 24[c]	85, 0[c]	91	4	5
c		Butyric anhydride	18	80	96	–	4
d		Valeric anhydride	18	85	98	–	2
e		Hexanoic anhydride	18	88	98	–	2
2	*p*-Nitroanisole	Propionic anhydride	14	72	86	11	3
3	*p*-Chloronitro benzene	Propionic anhydride	16	42	86	9	5
4	*p*-Bromonitro benzene	Propionic anhydride	14	50	85	10	5
5	*p*-Nitro toluene	Propionic anhydride	14	67	90	6	4
6	*o*-Nitro toluene	Propionic anhydride	14	74	90	5	5
7	1-Nitro naphthalene	Propionic anhydride	14	60	92	6	2

[a] In the presence of H_2.

[b] In the presence of CO and H_2.

[c] Catalyst calcined at 300 °C for 6 h.

The successful reduction of nitrobenzene to anilide in 70% yield at 10 atm of hydrogen and 10 atm of mixture of hydrogen and CO (5 atm of CO + 5 atm of H_2) using Fe^{3+}-montmorillonite in presence of propionic acid (entry 1a, Table 2) reinforces that the hydride is responsible for reduction.

All these results rule out the possibility of direct reduction of nitro group with the carbon monoxide [7]. The redox reaction involving the relay of two electrons from carbon monoxide to form hydrogen or hydride similar to the one proposed for $Fe(CO)_5$ system [21–26] is catalyzed in the present systems by Fe^{3+}-montmorillonite presumably via a transient Fe^{3+}/Fe^{2+} redox cycle. The evidence for such involvement of the Fe^{2+}/Fe^{3+} redox cycle in the reductive acylation of nitroarenes mediated by propionic anhydride in the present system is provided by the XPS of the Fe $3p_{3/2}$ of the Fe^{3+}-montmorillonite and used catalyst (Fig. 1) which show two lines at 712 and 715 eV using a curve resolver corresponding to the binding energies of the Fe^{2+} and Fe^{3+} oxidation states, with the increase of former's concentration from fresh to used catalyst. The XPS of C 1s in the used catalyst shows one extra line (other than carbon impurity) at 288.58 eV corresponding to Fe–COOH as is evident from the loss of mass fragment ion ($m/z = 44$, CO_2) in the TG-DTA-MS (Fig. 2). The production of hydrogen (hydride) in the water gas is effected by a strong base (OH^- ions) [21–26]. The present reaction is probably initiated by the Fe^{2+}–OH formed by the dissociation of $Fe^{3+}(H_2O)_n$ of the montmorillonite [16]. The influence of montmorillonite support in the reductive acylation of nitroarene is further established, when no activity is

observed in the set of the separate reactions conducted using either stoichiometric amounts of $FeCl_3$–propionic anhydride in place of Fe^{3+}-monmorillonite–propionic anhydride (entries 5 and 6, Table 1).
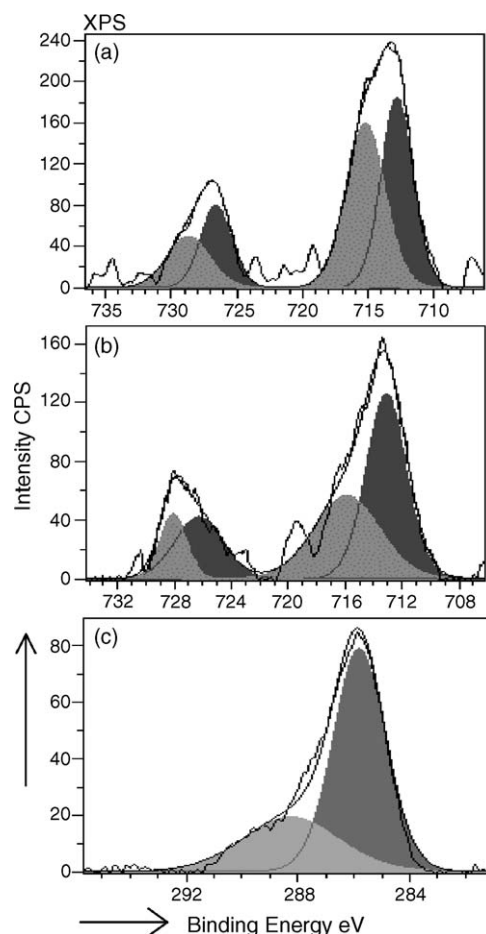

Fig. 1. Fe $3p_{3/2}$ and Fe $3p_{1/2}$ XPS of (a) fresh, (b) used catalyst and (c) XPS of C 1s of the used catalyst.
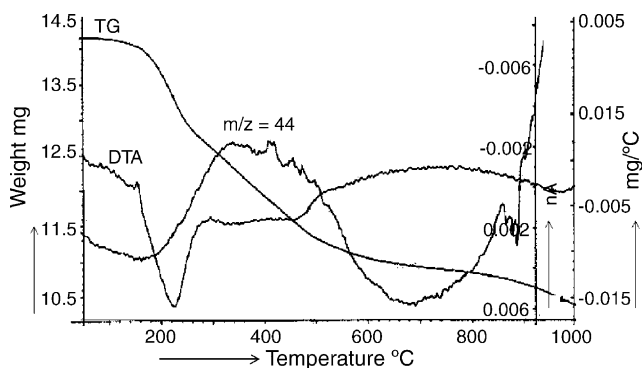
$$2RCOOCOR \longrightarrow 2RCOOR + 2CO$$
$$2CO + 2H_2O \longrightarrow 2CO_2 + 2H_2$$
$$2RCOOR + C_6H_5NO_2 + 2H_2 \longrightarrow C_6H_5NH\text{-}CO\text{-}R + 3ROH + CO_2$$

$$2RCOOCOR + 2H_2O + C_6H_5NO_2 \longrightarrow C_6H_5NH\text{-}CO\text{-}R + 3ROH + 3CO_2$$

Scheme 2. Proposed mechanism for reductive N-acylation of nitroarenes.

Fig. 2. TG-DTA-MS thermogram of used Fe^{3+}-montmorillonite.

4. Conclusion

In conclusion, the easily and cheaply available recyclable Fe^{3+}-montmorillonite catalyst offers a simple methodology for the reductive N-acylation of nitroarenes under atmospheric pressure using carboxylic acid anhydride as a source of carbon monoxide. Further Fe^{3+}-montmorillonite catalyst facilitated the water gas shift reaction at one atmosphere without using a strong base as an additive for the first time.

Acknowledgment

References

[1] A.W. Dawes, J. Werner, Kirk Othemer Encyclopedia of Chemical Technology, vol. II, fourth ed., Wiley, New York, 1992, pp. 355–376, and references therein.

[2] D.C. Owsley, J.J. Bloomfield, Synthesis (1977) 118.
[3] J.M. Landesberg, L. Katz, C. Olsen, J. Org. Chem. 37 (1972) 930.
[4] J.B.N. Guini Effa, B. Djebailli, J. Lieto, J. Pierre Aune, J. Chem. Soc., Chem. Commun. (1983) 408.
[5] P.L. Gauss, S.W. Gerritz, P.M. Jeffries, Tetrahedron Lett. 29 (1988) 5083.
[6] M. Yamashita, S. Yamamura, R. Suemitsu, The Science and Engineering Review of Doshisha University, vol. 20, 1979, pp. 147–152, and references therein.
[7] Y. Watanabe, Y. Tsuji, T. Kondo, R. Takeuchi, J. Org. Chem. 49 (1984) 4451.
[8] E.M. Nahmed, G. Jenner, Tetrahedron Lett. 32 (1991) 4917.
[9] K. Nomura, J. Mol. Catal. A 130 (1998) 1–28, and reference therein.
[10] M. Lauwiner, P. Rys, J. Wissmann, Appl. Catal. A: Gen. 172 (1998) 141.
[11] M. Benz, A.M. Van der Kraan, R. Prins, Appl. Catal. A: Gen. 172 (1998) 149.
[12] M. Benz, R. Prins, Appl. Catal. A: Gen. 183 (1999) 325–333.
[13] T. Miyata, Y. Ishino, T. Hirashima, Synthesis (1978) 834.
[14] N.R. Ayyangar, A.G. Lugade, P.V. Nikrad, V.K. Sharma, Synthesis (1981) 640.
[15] B.M. Choudary, M.L. Kantam, K.V.S. Ranganath, K.K. Rao, Angew. Chem. Int. Ed. 117 (2005) 322.
[16] P. Laszlo, Science (1987) 1473.
[17] P. Laszlo, A. Mathy, Helvetica. Chim. Acta 70 (1987) 577.
[18] E.G. Rightor, M.S. Tzou, T.J. Pinnavaia, J. Catal. 130 (1991) 29.
[19] B.M. Choudary, K.L. Matusek, L. Guczi, J. Catal. 122 (1990) 320.
[20] A.R Vogel, Text Book of Quantitative Inorganic Analysis, third ed., 1982, p. 287.
[21] K. Higuchi, M. Onaka, Y. Izumi, Bull. Chem. Soc. Jpn. 66 (1993) 2016.
[22] K. Cann, T. Cole, W. Slegeir, R. Pettit, J. Am. Chem. Soc. 100 (1978) 3969.
[23] M. Torrent, M. Sola, G. Frenking, Organometallics 18 (1999) 2801.
[24] D.J. Darensbourg, B.J. Baldwin, J.A. Froelich, J. Am. Chem. Soc. 102 (1980) 4688.
[25] A.D. King, R.B. King Jr., D.B. Yang, J. Am. Chem. Soc. 102 (1980) 1028.
[26] J.C. Bricker, C.C. Nagel, S.G. Shore, J. Am. Chem. Soc. 104 (1982) 1444.