



## NOTE

### Metal Ion-Exchanged Bentonites as Useful Solid Catalysts for Regioselective Nitration of Toluene

H. ZHANG<sup>1,2,\*</sup>, X. PENG<sup>1</sup> and S. ZHAO<sup>1</sup>

<sup>1</sup>Department of Chemistry, School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, P.R. China

<sup>2</sup>School of Physics and Chemistry, Henan Polytechnic University, Henan 454003, P.R. China

\*Corresponding author: Tel/Fax: +86 25 84315520; E-mail: xhpeng@mail.njust.edu.cn

(Received: 20 February 2012;

Accepted: 28 December 2012)

AJC-12630

Metal ion-exchanged bentonites were found to be efficient catalysts in regioselective nitration of toluene when using nitric acid as nitrating agent. Fifteen metal ion-exchanged bentonites were tested as catalysts toward a *para* position considerably. Out of a range of catalysts tried silver-supported bentonite appeared of higher regioselectivity of *ortho-para* ratio of 0.64 in an acceptable yield of 45 %. The possible recovery and reuse of catalyst suggest that system would be commercially viable.

**Key Words:** Bentonite, Toluene, Nitrotoluene, Regioselective nitration.

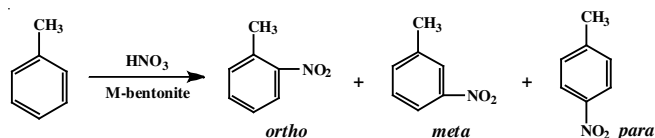
In recent years many selective aromatics nitrations have been carried out with the help of solid or solid-supported catalysts<sup>1</sup>. Smith and Fry<sup>2</sup> have used inorganic solids such as aluminum or proton exchanged large port modenite to catalyze nitration reactions of alkylbenzenes utilizing benzoyl nitrate as the nitrating agent. The reaction is highly *para* selective giving 67 % of 4-nitrotoluene isomer for toluene nitration in almost quantitative yield, but the nitrating agent is inconvenient and carbon tetrachloride is needed as solvent. Toluene has also been successfully nitrated with copper nitrate supported on montmorillonite clay<sup>3</sup>. Moreover the method affords high *para* selectivity only under conditions of high dilution and a long reaction periods (120 h). Unfortunately, therefore, none of the methods which exhibit *para* regioselectivity are attractive for large-scale application. However, with the progress in surface science and the improved understanding of heterogeneous catalysis, the availability of modified solids now still provided opportunities for clean nitration<sup>4-9</sup>. It is suggested that the clay should be a promising catalyst which could meet desirable 'enviro-economics'. This account describes our efforts involving the use of ion-exchanged bentonite in the field of clean nitration of toluene.

All of the starting materials were chemical purity grade or above. The analyses of toluene and its nitro isomers were carried out by gas-liquid chromatography with a Shimadzu GC-2014C gas chromatography equipped with a hydrogen flame ionization detector and with a 30 m × 0.25 mm *i.d.* OV-101 glass capillary column with nitrogen as a carrier gas using *n*-dodecane as internal standard.

The metal ion-exchanged bentonite catalysts used for nitration of toluene were prepared. To 100 mL of a stirred aqueous solution (1.0 mol/L) of corresponding metal salts in deionized water, 10 g of Na-based commercial bentonite were added. Stirring was maintained under reflux temperature for 8 h. The clay suspension was centrifugated and the supernatant solution was discarded and the washing cycles with deionized water were repeated until disappearance of anion ions from metal salt. The collected metal ion exchanged bentonite, after drying overnight in an oven at 130 °C, was finely ground to pass a 100 mesh screen in a mortar. The powdery clay was calcined for 8 h at 300 °C prior to use.

Followed by nitration of toluene from the following procedure, *i.e.*, a mixture of toluene (10.0 mL), acetic anhydride (8.0 mL), carbon tetrachloride (40 mL) and clay catalysts (2.5 g) was magnetically stirred. Nitric acid (10.0 mL, *d* = 1.4) was added to carbon tetrachloride (20 mL) solvent existing in Dean-Stark trap. The mixture was heated at reflux for 24 h. After cooling, the resulting mixture was filtered and the filtrate was then washed with 5 % sodium bicarbonate solution. The organic layer was adjusted to pH 6-7 with deionized water, subsequently concentrated and analyzed by gas-liquid chromatography.

We chose the mononitration of toluene (**Scheme-I**) using nitric acid as nitrating agent during development of the method. The reaction was initiated by acetic anhydride-carbon tetrachloride extraction of the nitrating species from the aqueous phase in a Dean-Stark trap<sup>5</sup>. Metal ion-exchanged bentonites were easily prepared from commercial sodium based bentonite



M: Al, Pb, Bi, Cr, Mn, Fe, Co, Ni, Cu, Ag, Zn, Cd, Hg, La, Ce, Na

**Scheme-I:** The regioselectivity for nitration of toluene with nitric acid in the presence of metal ion-exchanged bentonites

(Bent) by cation ion-exchange techniques using aqueous solutions of corresponding salts (Table-1). The catalytic selectivity and activity of metal ion-exchanged bentonites were evaluated in the nitration reaction of toluene (Table-2). All metal ion-exchanged bentonites enhanced *para* selectivity of toluene nitration reaction. Of the range of tested Metal-supported bentonites, Ag-Bent appeared a good catalytic character in the regioselective nitration. The ratio of *ortho/para* nitro isomers was below 0.64 in an acceptable yield of 45 %. When no catalyst existed in the reaction, the reaction was hardly selective like sulfonitric process.

TABLE-1  
METAL ION-EXCHANGED BENTONITES USED FOR SELECTIVE NITRATION CATALYSTS

Corresponding salt	M-Bent	Corresponding salt salts	M-Bent
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·18H <sub>2</sub> O	Al-Bent	PbCl <sub>2</sub>	Pb-Bent
BiCl <sub>3</sub>	Bi-Bent	CrCl <sub>3</sub> ·6H <sub>2</sub> O	Cr-Bent
MnSO <sub>4</sub> ·H <sub>2</sub> O	Mn-Bent	FeCl <sub>3</sub> ·6H <sub>2</sub> O	Fe-Bent
Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	Co-Bent	NiSO <sub>4</sub> ·6H <sub>2</sub> O	Ni-Bent
CuSO <sub>4</sub> ·5H <sub>2</sub> O	Cu-Bent	AgNO <sub>3</sub>	Ag-Bent
ZnSO <sub>4</sub> ·7H <sub>2</sub> O	Zn-Bent	CdCl <sub>2</sub> ·2.5H <sub>2</sub> O	Cd-Bent
HgCl <sub>2</sub>	Hg-Bent	LaCl <sub>3</sub> ·H <sub>2</sub> O	La-Bent
Ce(SO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	Ce-Bent	–	–

TABLE-2  
COMPOSITION OF ISOMERS PROVIDED VIA NITRATION OF TOLUENE WITH NITRIC ACID ON METAL ION-EXCHANGED BENTONITES

Catalyst	Nitrotoluene (%)			<i>Ortho/para</i>	Yield (%)
	<i>Ortho</i>	<i>Meta</i>	<i>Para</i>		
Al-Bent	41	2	57	0.72	31
Pb-Bent	39	3	58	0.68	24
Bi-Bent	42	3	55	0.76	43
Cr-Bent	41	4	55	0.74	37
Mn-Bent	40	4	56	0.71	22
Fe-Bent	41	3	56	0.73	40
Co-Bent	39	4	57	0.68	32
Ni-Bent	42	4	54	0.78	28
Cu-Bent	43	3	54	0.80	28
Ag-Bent	38	3	59	0.64	45
Zn-Bent	43	3	54	0.79	7
Cd-Bent	39	4	57	0.68	35
Hg-Bent	39	4	57	0.68	32
La-Bent	40	2	58	0.69	49
Ce-Bent	40	4	56	0.71	36
Na-Bent	41	3	56	0.73	17
–	58	5	37	1.57	8

We have also examined regeneration of the bentonite catalyst (Na-Bent). When recovered bentonite was refluxed for 2 h in carbon tetrachloride and then calcined 8 h at 300 °C prior to use, the same sample could be re-utilized up to five consecutive times with no loss in activity (Table-3). It should be noted that the regioselectivity and yield of even the 5th use of the catalyst were almost as much as those of the first use.

TABLE-3  
EFFICACY OF RECOVERED NA-SUPPORTED BENTONITE ON REGIOSELECTIVITY IN TOLUENE NITRATION

Entry	Catalyst	Nitrotoluene (%)			<i>Ortho/para</i>	Yield (%)
		<i>Ortho</i>	<i>Meta</i>	<i>Para</i>		
1	1 <sup>st</sup> use	41	3	56	0.73	15
2	2 <sup>nd</sup> use	41	3	56	0.73	16
3	3 <sup>rd</sup> use	41	2	57	0.72	15
4	4 <sup>th</sup> use	42	3	55	0.76	18
5	5 <sup>th</sup> use	41	3	56	0.73	17

To sum up, a highly *para* regioselective nitration can be achieved by employing nitric acid as nitrating agents over various metal ions exchanged bentonites catalysts and recycle of the solvents can be easily conducted in industrial preparation process.

## REFERENCES

- H. Zhang, X. Peng and L. Yuan, *Asian J. Chem.*, **24**, 3927 (2012).
- K. Smith and K. Fry, *Tetrahedron Lett.*, **30**, 5333 (1989).
- P. Laszlo and J. Vandormael, *Chem. Lett.*, **11**, 1843 (1988).
- A. Cornelis, A. Gerstmans and P. Laszlo, *Chem. Lett.*, **11**, 1839 (1988).
- T.J. Kwok, K. Jayasuriya, R. Damavarapu and B.W. Brodman, *J. Org. Chem.*, **59**, 4939 (1994).
- N. Wen, X. Peng and W. Xu, *Asian J. Chem.*, **24**, 4458 (2012).
- A.R. Hajipour and A.E. Ruoho, *Tetrahedron Lett.*, **46**, 8307 (2005).
- D. Koley, O.C. Colón and S.N. Savinov, *Org. Lett.*, **11**, 4172 (2009).
- R. Duddu, P.R. Dave, R. Damavarapu, N. Gelber and D. Parrish, *Tetrahedron Lett.*, **51**, 399 (2010).