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Regioselective nitration of *o*-xylene by using a novel clay-based shape-selective acid catalyst

Ganapati D. Yadav [*], Priyal M. Bisht, Sharad V. Lande

Department of Chemical Engineering, University Institute of Chemical Technology, University of Mumbai, Matunga, Mumbai 400019, India

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ABSTRACT

In this work, a new catalyst was prepared by employing carbon molecular sieve (CMS) with natural kaolinite clay and is named UDCaT-8. The catalyst was fully characterized by XRD, DTA–TGA, FTIR, SEM and BET surface area and pore size analysis. *o*-Xylene nitration was conducted under solventless and room temperature condition using UDCaT-8 to get high regioselectivity. The process is eco-friendly, less expensive and leads to high selectivity to 4-nitro-*o*-xylene which is an important intermediate for synthetic vitamin B_2 as well as a raw material for dyes and other chemicals.

1. Introduction

Nitration of aromatic compounds is one of the most widely studied and notoriously non-selective of reactions. Nitro compounds find use in many industrial applications and the selectivity to *para*-isomer is most sought for because of its commercial importance. Industrial nitrations are carried, employing mixed acid (mixture of nitric acid and sulphuric acid), which predominantly gives *ortho*- and *para*-substituted products [1,2]. A lot of research has been focused on dispensing the use of sulphuric acid for the nitration of aromatic compounds and selective synthesis of the desired isomer, in the case of substituted benzenes. This is in accordance with the principles of green chemistry as it reduces pollution caused by the spent acid; also the separation issues of the undesired isomers can be avoided leading to substantial cost savings in the process. A significant amount of research has been directed to address the issue of recovering the spent acid from the conventional mixed acid process in the nitration of benzene and toluene [3–10]. However, there are various limitations, namely, low space time yields, high dilution, use of acetic anhydride-nitric acid or expensive acyl or alkyl nitrate, which are not environmentally benign processes. The nitration reactions have been carried out employing ionic liquids [11] at very low temperatures but the *p*-isomer selectivity is poor. High *p*-selectivity for the nitration of the monosubstituted aromatic compounds employing β-zeolite as catalyst can be achieved [12]. However, β-zeolite is an expensive catalyst. In our laboratory extensive work has been carried out on the nitration reactions and we had reported an efficient methodology with high *p*-selectivity for the nitration of monosubstituted aromatic compounds, viz. chlorobenzene and toluene employing novel eclectically engineered sulphated zirconia and carbon molecular sieve as catalysts with nitric acid as nitrating agent [13,14].

The mononitrated compounds of *o*-xylene are used as intermediates for the production of vitamins, fragrances, agrochemicals, dyes, etc. The 4- and 3-nitro-*o*-xylenes are useful intermediates in the production of riboflavin (vitamin B2) and mefenamic acid (agrochemical), respectively. The selectivity issue gains much more significance as 4-nitro-*o*-xylene is required in large quantities. The β-zeolites catalyzed vapor phase nitration of *o*-xylene using N_2O_4 as a nitrating agent and liquid phase using acetic anhydride and nitric acid mixture offers lower yields of 4-nitro-*o*-xylene with simultaneous production of large amounts of oxygenates [15,16]. Various attempts have been made in the past for nitration of xylene isomers employing expensive or hazardous starting materials [17–19]. The current work focuses on the nitration of *o*-xylene to yield 4-nitro isomer using carbon molecular sieve (CMS) coated natural kaolinite clay as a catalyst in an effort to evolve an eco-friendly, atom economical and economically viable process. Here we report highly efficient process for the nitration of *o*-xylene leading to very high

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[*] Corresponding author. Tel.: +91 22 24102121; fax: +91 22 24145614.
E-mail addresses: gdyadav@yahoo.com, gdyadav@udct.org (G.D. Yadav).

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para-isomer yields by using a novel shape-selective catalyst synergistically produced from kaolinite clay and carbon molecular sieve (CMS). Natural clay, the earliest known solid acid, have been extensively used in various organic transformations because of the ease of handling and work up, low corrosivity. and low cost [18]. One of the major drawbacks of the clay catalyst is that it is not a shape-selective catalyst. Hence it cannot be employed in reactions where selectivity is of paramount importance. However, kaolinite [$Al_2Si_2O_5(OH)_4$] when combined with other materials can produce the desired shape-selective catalyst. In this respect carbon molecular sieve (CMS) can be used in combination with kaolinite to get a composite shape-selective catalyst. The selectivity engineering aspects of catalysts are embodied in this CMS–clay composite media where one acts as a siever and the inside core as the true catalyst. The synergistic combination of CMS and sulphated zirconia is reported to work eleganlty in achieving the desired selectivity [20].

2. Experimental

2.1. Materials

Polyvinylalcohol, NaCl, HCl, *o*-xylene, and HNO_3 (70% w/v) were procured from M/s. s.d. Fine Chemicals (India). The kaolinite clay was obtained from Thonnakkal region of Trivandrum district (south Kerala, India) supplied by M/s. English Indian Clays, Trivandrum, India.

2.2. Catalyst preparation

The catalyst was prepared by refluxing 25 g of kaolinite clay with 1 M NaCl for 8 h. One molar NaCl (16.7 ml) was required for 1 g catalyst to achieve complete replacement of cations. It was filtered and the cake was dried for 8 h at 120 °C. The dried catalyst was crushed and refluxed with 1N HCl for 8 h. 16.7 ml of 1N HCl was required for 1 g of the catalyst. The acid amount and catalytic activity of the clay were enhanced by refluxing it with HCl. This slurry was filtered and washed thoroughly with deionized water until free of chloride ions. The absence of chlorine ion was detected by phenolphthalein and $AgNO_3$ tests. A material balance on Cl before and after precipitation and washing shows no retention on the solid. The filtered catalyst was dried in an oven at 120 °C for 8 h and was crushed to 100 mesh size. This was followed by calcination at 300 °C for 3 h.

To 10 g of the above-prepared catalyst, 8.1 ml polyvinyl alcohol (PVA) solution (2 g PVA dissolved in 25 ml distilled water) was added dropwise until it was just wet. It was mixed well to get a uniform coating. It was dried at 120 °C for 3 h and calcined at 300 °C to get active and selective catalyst UDCaT-8.

2.3. Characterization of catalysts

XRD data of catalysts were recorded by using a Philips PW 1729 powder diffractometer with Cu-Kα (1.54 Å) radiation. Samples were step scanned from 1 to 40 in 0.025° (2θ) steps with a step time of 0.5 s. Infrared spectra of the samples pressed in KBr pellets were obtained at a resolution of 2 cm^{-1} between 4000 and 350 cm^{-1}. Spectra were collected with a Shimadzu instrument and in each case the sample was referenced against a blank KBr pellet.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were obtained simultaneously by using a high temperature analyzer Setaram 92, model 16.18 in the presence of static air. Surface area measurements were done by nitrogen adsorption on Micromeritics ASAP 2010 instrument at an adsorption temperature of 77 K, after pretreating the sample under high vacuum at 150 °C for 4 h. Scanning electron micrographs of UDCaT-8 were taken on Cameca SU 30 microscope. The dried samples were mounted on specimen studs and sputter coated with a thin film of gold to prevent charging. The gold-coated surface was then scanned at various magnifications by using scanning electron microscope.

2.4. Reaction procedure and analysis

All experiments were carried in a 100 ml fully baffled glass reactor of 5 cm internal diameter. The reactants were charged to the reactor kept in a constant water bath whose temperature was maintained at 30 °C. In a typical experiment 70% nitric acid (0.1 mol) was added dropwise over a period of 8 h, to *o*-xylene (0.1 mol) containing the desired catalyst (8.33×10^{-2} g cm^{-3}), under constant stirring. Organic samples (0.2 ml) were removed periodically and washed with 20 ml water to remove unreacted nitric acid. The organic layer was treated with sodium sulphate (0.05 g) to remove traces of water, if any subsequently filtered to obtain a mixture of the reactant, *o*-xylene and nitro products. The products were isolated by distillation and confirmed by GC–MS. The catalyst was recovered for further use by washing with *o*-xylene and dried at 150 °C for 2 h. Samples were analysed on a Chemito Gas Chromatograph (8610) equipped with a flame ionization detector. A column packed with chromosorb WHP impregnated with 10% OV-17 (4 m × 0.0032 m) was used for analysis.

3. Results and discussion

3.1. Characterization

3.1.1. X-ray diffraction

XRD patterns of the untreated kaolinite clay (UKC), NaCl-treated kaolinite clay (Na^+-UKC), HCl-treated Kaolinite clay (H^+-UKC) and PVA coated after acid treatment kaolinite clay (UDCaT-8) (Fig. 1). XRD of UKC depicts presence of non-kaolinite impurities such as quartz and gibbsite [21]. The presence of hematite ($d = 3.7$) and anatase ($d = 3.52$) are also evidenced from the XRD patterns of the kaolinite clay. However, XRD of the Na^+-UKC, H^+-UKC and UDCaT-8 exhibit presence of similar type of morphology of the kaolinite. Indeed, it is expected since the creation of a thin layer of carbon coating surrounding the clay particle would not change the XRD of UDCaT-8. Fig. 2 shows the structure of the catalyst.

3.1.2. FTIR

FTIR of the kaolinite exhibit four characteristic band in the range of 3600–3700 cm^{-1} which are characteristic OH stretching band of the kaolinite as shown in Fig. 3. The other band in the range of 918–1115 cm^{-1} shows existence of the apical Si–O, Si–O–Si in plane vibration and, OH bending vibration. Similarly the two bands at 795 and 755 cm^{-1} exhibit presence of the OH translation vibrations of kaolinite [22]. Similar types of bands are also observed in the case of the UDCaT-8 which is indicative of retentation of the kaolinite structure even after treatment with PVA.

3.1.3. DTA–TGA

The DTA–TGA analysis was performed on all catalysts (Fig. 4). Weight loss was observed when kaolinite was heated above 450 °C in nitrogen atmosphere. The weight loss is attributed to removal of water and humic acid from natural kaolinite [13]. It should be recognized that the preparation of this catalyst involves creating a polymer layer around the particle and then carbonizing it to make a porous film which acts as a sieve. Therefore, the studies were conducted on calcined samples. It also suggests that the outer layer

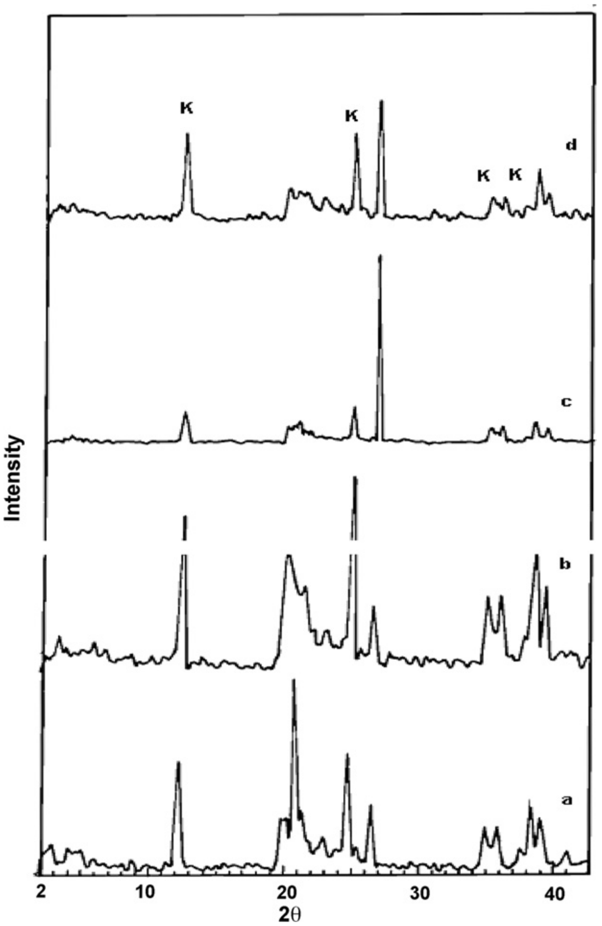


Fig. 1. XRD patterns: (a) UKC, (b) Na^+-UKC, (c) H^+-UKC, and (d) UDCaT-8.

has not resulted into any change in the properties of the catalyst [23].

3.1.4. BET surface area and pore size analysis

The BET surface areas of the catalysts are given in Table 1. These values go on decreasing from UKC through UDCaT-8. When Na^+ ions are replaced by H^+, the area increases marginally. The thin coating of the carbon molecular sieve on the particles results into shape sieving property to UDCaT-8 without loss of activity. With UDCaT-8, once again due to the coating outside, the area decreases. However, the pores volumes of acid-treated clay and UDCaT-8 are

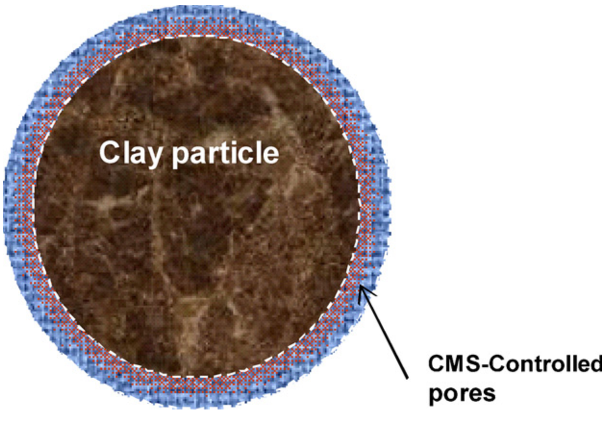


Fig. 2. Conceptual structure of catalyst UDCaT-8.

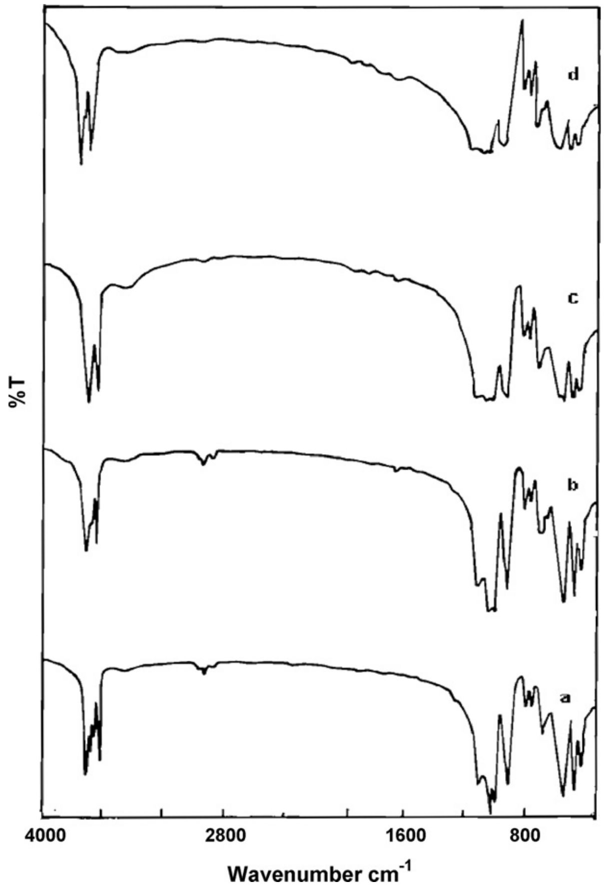


Fig. 3. FTIR patterns: (a) UKC, (b) Na^+-UKC, (c) H^+-UKC, and (d) UDCaT-8.

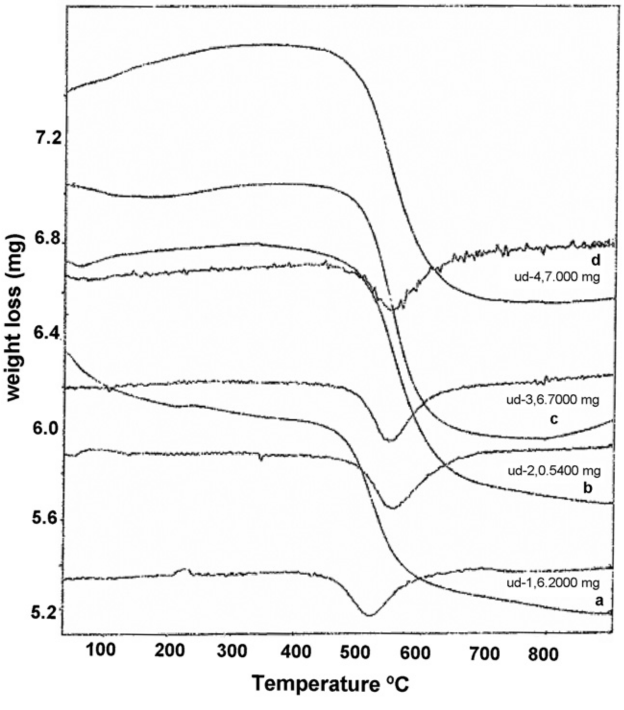


Fig. 4. DTA–TGA patterns: (a) UKC, (b) Na^+-UKC, (c) H^+-UKC, and (d) UDCaT-8.

Table 1
Nitrogen BET surface area and pore volumes of catalyst samples

#	Catalysts	Surface area ($m^2\ g^{-1}$)	Total pore volume ($cm^3\ g^{-1}$)
1	UKC	11	0.03
2	Na^+-UKC	24	0.08
3	H^+-UKC	50	0.09
4	UDCaT-8	43	0.08

not much different since additional porosity is generated in the thin layer. The pore entry diameters at the outer surface of the particles decrease which leads to shape selectivity. Besides, the coating removes the acidity on the outer surface of the particle and hence the selectivity increases [23].

3.1.5. *Scanning electron microscopy (SEM)*

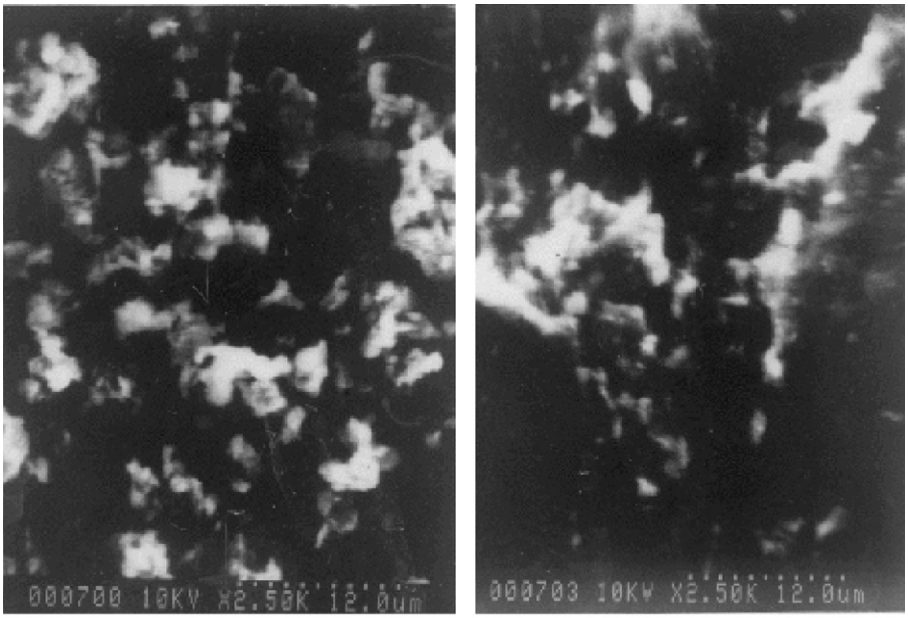
SEM is an optical technique wherein overall contrast is observed due to differential absorption of photons or particles (amplitude contrast) or diffraction phenomena (phase contrast). SEM provides identification of phases and structural morphology of catalyst (Fig. 5). The average particle size of the catalyst was determined from the SEM photograph as 12 μm. The particle size does not increase due to the formation of a very thin layer of PVA coating and carbonization to make CMS.

3.2. *Catalytic activity and stability of catalyst*

3.2.1. *Nitration of o-xylene*

Table 2 lists the results of the experiments conducted under otherwise similar conditions of mole ratio of reactants and catalyst loading; it shows the effect of modified clay catalyst on conversion and selectivity in nitration of *o*-xylene (Scheme 1). The use of the kaolinite clay for the nitration of *o*-xylene gave high selectivity towards the formation of *para*-isomer. No formation of dinitrated by-products was observed in this reaction. When the CMS coating was given to the acid-treated kaolinite clay, there was some loss of activity due to the neutralization of the outer surface acid and hence the conversion was marginally reduced from 18% to 16%. However, there was a substantial increase in 4-nitro-*o*-xylene selectivity to 66% from 53% without any formation of the aldehyde or dinitro product. CMS alone does not give any conversion and hence the synergism term is used. Indeed, separate studies were also done in one of our publications to demonstrate that CMS is indeed produced by calcinations under controlled conditions. This can be attributed to the fact that the CMS around the clay acts as a barrier for the bulkier ortho isomer and, hence, favours the formation of kinetically smaller *para*-isomer.

Alternatively, the continuous process was also developed. *o*-Xylene and nitric acid were taken in 1:1 stoichiometric molar ratio in a fixed bed catalytic reactor over a period of 2 h at 30 °C. Thus 12 ml of *o*-xylene and 6.5 ml of 70% nitric acid were added continuously using a peristaltic pump over a period of 2 h. The organic layer was separated and recycled back to be nitrated with fresh 70% nitric acid for 2 h. The process was again repeated. Thus at the end of 8 h, the conversion was 20% and the product distribution was 4-NO_2-*o*-xyelene 60%, 3-NO_2-*o*-xyelene 34% and 2-methyl benzaldehyde 6%. The results are summarized in Table 3. Thus, from the results obtained it can be concluded that a very high selectivity for the *para* product is obtained in case of *o*-xylene



SEM of UKC

SEM of UDCaT-8

Fig. 5. SEM of UKC and UDCaT-8.

Table 2
Activities of kaolinite clay for *o*-xylene nitration (semi-batch mode)

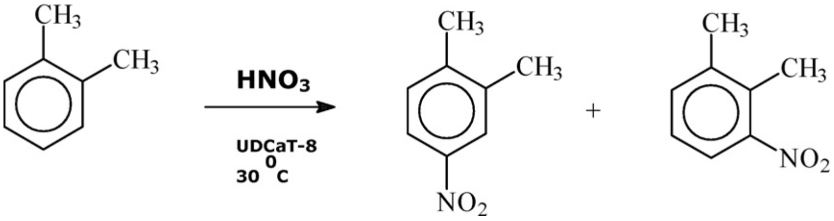
Catalyst	Conversion (%)	Selectivity to 4-nitro-*o*-xylene	Selectivity to 3-nitro-*o*-xylene	Others	
				2-Methyl benzaldehyde	3,4-Dinitro-*o*-xylene
Kaolinite clay (untreated)	6.0	59	37	4	0
Kaolinite clay (acid-treated)	18	53	42	3	2
Kaolinite clay [300] CMS (UDCaT-8)	16.0	66	34	0	0

o-Xylene = 0.1 mol, 70% HNO_3 = 0.1 mol, catalyst loading = 8.33×10^{-2} g cm^{-3}, temperature = 30 °C, speed of agitation = 1000 rpm, time = 8 h.

Table 3
Continuous nitration of *o*-xylene

Pass	Time (h)	Conversion (%)	Selectivity (%)		
			4-Nitro-*o*-xylene	3-Nitro-*o*-xylene	2-Methyl benzaldehyde
1st (fresh)	2	4.6	65.0	35.0	0.0
2nd (1st recycle)	2	11.0	63.0	35.0	2.0
3rd (2nd recycle)	2	16.5	62.0	34.5	3.5
4th (3rd recycle)	2	20.0	60.0	34.0	6.0

o-Xylene = 0.1 mol, 70% HNO_3 = 0.1 mol, catalyst loading = 2.0 g, temperature = 30 °C, total reaction time = 8 h (2 × 4 h).



Scheme 1. Reaction scheme for *o*-xylene nitration using nitric acid over UDCaT-8.

nitration by using CMS-kaolinite (UDCaT-8) as a catalyst at room temperature in the absence of any solvent which are used in many nitration reactions. The pore size distribution of the CMS coating can be fine tuned to impart proper selectivity by using different polymeric materials to prepare the CMS coating around clay. Since no sulphuric acid is used, and high excess of *o*-xylene is used to consume all nitric acid at room temperature, substantial savings in energy consumption can be achieved and also the process becomes safe.

4. Conclusions

A novel shape-selective catalyst, synergistically produced from kaolinite clay and carbon molecular sieve (CMS) is reported and called UDCaT-8. The catalyst is fully characterized. High selectivity for the *para* product in case of *o*-xylene nitration is achieved by using UDCaT-8 as a catalyst. Selective formation of *para* product can be carried out by tailor making the catalyst by using different polymeric materials to prepare the CMS coating around clay. The spent acid problem is completely eliminated since sulphuric acid is avoided. The nitration was carried out under solventless conditions, thus reducing the number of separation stages. The process was carried out at room temperature resulting into energy saving.

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