Regioselective nitration of cumene to 4-nitro cumene using nitric acid over solid acid catalyst

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Abstract

The regioselective nitration of cumene to 4-nitro cumene (4-NC) has been carried out using 70% nitric acid over MoO_3/SiO_2 solid acid catalyst with high conversion (62%) and selectivity (68%) for 4-NC. A series of MoO_3/SiO_2 catalysts with different MoO_3 loadings (1–20 mol%) were prepared by sol–gel technique and characterized using different characterization techniques. XRD analysis revealed the amorphous nature of the catalyst up to 10-mol% MoO_3 loading and formation of α-MoO_3 crystalline phase on amorphous high surface area mesoporous silica support at higher MoO_3 loading. Maximum conversion and selectivity has been obtained with slower addition of nitric acid and simultaneous azeotropic removal of water formed during the reaction.
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Keywords: Nitration; Cumene; Solid acid catalyst; Ring nitration; Side chain nitration

1. Introduction

Nitration of aromatic substrates is a widely studied reaction because of its industrial importance. Catalytic hydrogenation of aromatic nitro compounds is commercially practiced to produce a variety of aromatic amines that have applications as chemical intermediates and specialty chemical products. Many nitro aromatics are extensively used as intermediates for the manufacture of dyes, pharmaceuticals, perfumeries and pesticides. Selective production of 4-nitro cumene is specifically important, as further hydrogenation of 4-nitrocumene (4-NC) to 4-cumidine is an industrially important reaction. The product, 4-cumidine is a versatile chemical intermediate that has applications in dyes, pharmaceuticals, and herbicides [1].

In the traditional nitration process a nitrating mixture of nitric acid and sulfuric acid is used as nitrating agent. This reaction is highly exothermic and is conducted in batch- or continuous reactors. Typically the nitrating agent is a mixture of 56–60% (w/w) H_2SO_4, 27–32% (w/w) HNO_3, and 8–17% (w/w) H_2O at a reaction temperature of 50–90 °C. The reaction mixture forms two phases and the rate of reaction is accordingly dependant on the kinetics and mixing efficiency. Sulfuric acid gets gradually diluted by water generated during the reaction and has to be replaced periodically. Chemical engineering research on nitration processes has yielded many valuable improvements and results shows improved mixing of the reactants, better energy management of modern nitration plants [2]. However the disposal of large quantity of dilute sulphuric acid generated poses environmental problems or it has to be concentrated for recycle which is energy intensive and costly process making nitration of aromatics as one of the most hazardous industrial process.

Nitration of aromatics without any use of sulphuric acid would be an attractive alternative and various types of solid acids have been tried with limited success. Acidic solids have been used for selective nitration reactions, in particular the mononitration of aromatic compounds. The solid acid catalysts can also be designed to give higher

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activity, selectivity, regenerability and longer catalyst life. In the last two decades, substantial progress has been made and several industrial processes that use solid acid catalysts have been introduced successfully.

Cumene is nitrated by the conventional method, using a mixture of nitric acid and sulfuric acid as the nitrating mixture at 5–8 °C, which gives a mixture of 68% 4-NC, 24–28% 2-NC and 1–2% 3-NC along with 1–2% dinitrocumene with almost 99% cumene conversion. Apart from the low selectivity for 4-NC, generation of dilute sulfuric acid waste poses environmental problems. A patent reports cumene nitration using aluminosilicate catalysts with varying Si/Al ratio at 100 °C with 51% cumene conversion and 78% selectivity for 4-NC [3].

In continuation with our earlier efforts on use of solid acid catalysts for nitration of aromatics [4–6], we have investigated liquid phase cumene nitration over silica supported molybdenum oxide catalyst and the results are reported in the present paper.

2. Experimental

2.1. Catalyst preparation

A series of MoO_3/SiO_2 catalysts with varying molybdenum oxide molar concentrations (1, 5, 10, 15 and 20 mol%) were prepared by sol–gel technique. Ammonium heptamolybdate (AHM) and ethyl silicate-40 (CAS registry no. 18945-71-7) were used as molybdenum and silica source, respectively.

In a typical procedure 20 mol% MoO_3/SiO_2 catalyst was synthesized by dissolving 14.11 g ammonium heptamolybdate in 40 ml distilled water at 80 °C. This hot solution was added dropwise to the dry isopropyl alcohol solution of ethyl silicate-40 (48.0 g) with constant stirring. The resultant transparent greenish gel was air dried and calcined at 500 °C in air in a muffle furnace for 12 h. Similarly catalysts with 1, 5, 10 and 15 mol% molybdenum loadings were prepared.

2.2. Catalyst characterization

The X-ray diffraction analysis was carried out using a Rigaku X-ray diffractometer (Model DMAX IIIVC) with Cu-Kα (1.542 Å) radiation. Temperature programmed desorption of ammonia (TPD-NH_3) was carried out using a Micromeritics Autocue 2910. BET surface area was determined using NOVA 1200 Quanta chrome.

The acidity of the samples was determined by pyridine adsorption studies using Shimadzu 8000 series FTIR spectrometer arranged for DRIFT technique. The sample was placed in the DRIFT cell and heated to 400 °C in flow of inert gas (N_2) for 2 h. It was then cooled to 100 °C and pyridine was adsorbed on the sample in N_2 flow. The physisorbed pyridine was removed by flushing the cell with N_2 for 45 min at the same temperature and the spectrum was recorded. Temperature programmed desorption of pyridine was studied at 200, 300 and 400 °C after maintaining the temperature for 45 min. The spectrum of the neat catalyst (before pyridine adsorption) at 100 °C was subtracted from all the spectra.

2.3. Catalytic activity

All liquid phase catalytic nitration reactions were carried out in a batch reactor. In a typical run, 50 ml two neck round bottom flask was charged with 5 g (42 mmol) cumene in 25 ml dichloroethane and 0.50 g (10 wt%, based on cumene) freshly activated catalyst (catalyst heated at 100 °C for 4 h) and the mixture was refluxed at 80 °C. To this hot mixture 4.5 g (50 mmol) nitric acid (70%) was added slowly. Water formed during the reaction was removed using a Dean-Stark apparatus. The temperature of the reaction was maintained by using an oil bath. The samples were withdrawn periodically and neutralized with sodium hydrogen carbonate and analyzed by gas chromatography (Perkin-Elmer Autosystem XL, equipped with capillary column PE-1, 30 m × 0.25 mm ID × 1 μm film thickness and flame ionization detector). Products were confirmed by GC/MS (Shimadzu, DB-I column) and GC/IR (Perkin-Elmer Spectrum 2001, DB-1, 25 m, 0.32 mm ID).

3. Results and discussion

3.1. Catalyst characterization

The X-ray diffraction patterns (Fig. 1) were recorded to ascertain the phase purity of the samples. The XRD pattern of MoO_3/SiO_2 (1 to 20% loading) showed the presence of amorphous silica phase. Catalysts with 15 and 20% Mo loading showed highly crystalline nature with intense peaks at $2\theta = 12.9°$, $23.4°$, $25.8°$ and $27.4°$ corresponding to α-MoO_3 in the orthorhombic phase. No β-MoO_3 phase was observed in the structure because the samples were calcined
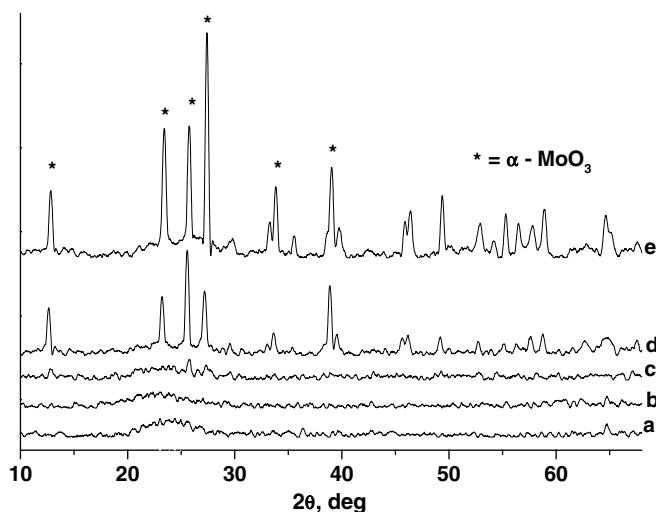

Fig. 1. XRD of MoO_3/SiO_2 with $a = 1$, $b = 5$, $c = 10$, $d = 15$, $e = 20$% Mo loading.

at 500 °C, a temperature at which β- MoO$_3$ phase is not stable [7]. It is interesting to note that even though the MoO$_3$ is in the crystalline form at higher Mo loading, the silica support still retains its amorphous nature leading to the high surface area of the catalysts [8].

The samples prepared by sol–gel technique using ethyl silicate-40 show very high surface area and mesoporous nature of the silica support. The surface area and pore volume of the catalysts is given in Table 1. On increasing the Mo loading the surface area of the catalysts decreased gradually. During the sol–gel synthesis, an aqueous solution of ammonium molybdate is added to ethyl silicate-40, which hydrolyzes ethyl silicate-40. However the control of the rate of hydrolysis is difficult, because of the use of excess water for dissolving ammonium molybdate, which leads to a decrease in the surface area. The basic pH of the solution due to NH$_3$ liberated during hydrolysis of AHM also leads to the formation of the product with lower surface area. It is expected that, as MoO$_3$ loading is increased, the crystalline molybdenum oxide clusters are formed that cover the amorphous silica support, reducing the total surface area of the catalyst. However the catalysts prepared by sol–gel techniques show a very high surface area as compared to the catalysts prepared by impregnation method. For 1% MoO$_3$/SiO$_2$ catalyst prepared by sol–gel technique shows surface area of 583 m^2/gm (surface area of the silica prepared by sol–gel was 606 m^2/g) whereas the catalyst prepared by impregnation method shows a surface area of only 155 m^2/gm where the silica used for impregnation had surface area of 231 m^2/g [9].

Ammonia-TPD experiments were carried out to determine the acid strength of the catalysts. The amount of ammonia desorbed is given in Table 1. The temperature for total desorption of ammonia increases with increase in MoO$_3$ loading indicating increase in acid strength as well as number of acid sites. The catalyst with 20% Mo loading shows maximum number of acid sites (NH$_3$ desorbed: 0.937 mmol/gm) as well as the highest acid strength.
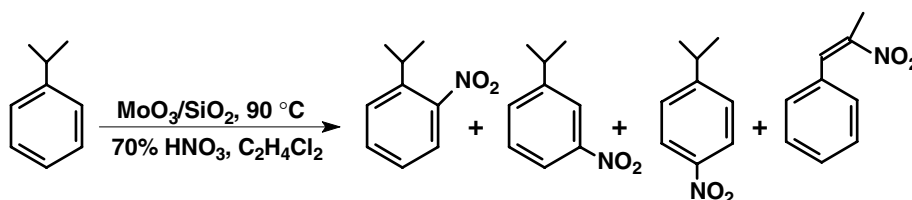
Table 1
Properties of the catalysts

Catalyst	Surface area (m^2/g)	Average pore diameter (Å)	Pore volume (cc/g)	NH$_3$ desorbed (mmol/g)
1% MoO$_3$/SiO$_2$	583	30.7	0.4474	0.1830
5% MoO$_3$/SiO$_2$	432	58.2	0.6297	0.5562
10% MoO$_3$/SiO$_2$	284	79.6	0.5656	0.7056
15% MoO$_3$/SiO$_2$	275	74.2	0.5103	0.863
20% MoO$_3$/SiO$_2$	180	51.6	0.233	0.937

FTIR studies of adsorbed pyridine for determination of nature of acidity reveal that 1% MoO$_3$/SiO$_2$ sample shows presence of predominant Lewis acidity (peak at 1450 cm^{-1}). As the MoO$_3$ loading is further increased, the samples show the presence of both Brønsted (peak at 1540 cm^{-1}) as well as Lewis acid sites. The generation of Brønsted acidity may be correlated to the formation of poly-molybdate Keggin structures [10]. The IR spectra of the catalyst in the framework region shows the presence of peaks at 959 and 914 cm^{-1}, which corresponds to polymolybdate Keggin structures which is reported to exhibit Brønsted acidity. At temperatures of about 500 °C transformation of hexagonal form of molybdenum trioxide into its orthorhombic form takes place. The oxide becomes hydrated and subsequently converted into polymolybdenic trimers [11]. Such structural units are expected to show Brønsted acidity. The MoO$_3$/SiO$_2$ catalysts prepared by impregnation technique are reported to show the presence of only Lewis acid sites without any Brønsted acidity. The NH$_3$ desorption in case of impregnated catalyst takes place at much lower temperature (<250 °C) indicating presence of weak acidity [9].

3.2. Catalytic reaction

The formation of 4-NC is shown in Scheme 1. Cumene nitration was carried out using series of MoO$_3$/SiO$_2$ catalysts at 90 °C in dichloroethane and the catalytic results are given in Table 2.

The results show that among the series of catalysts, 1% MoO$_3$/SiO$_2$ is the best catalyst with maximum cumene conversion of 62% and maximum selectivity (68%) for 4-NC, however there is only marginal decrease in the cumene conversion and 4-NC selectivity in case of other catalysts with higher MoO$_3$ loading. In this reaction along with ring nitration, side chain nitration followed by rearrangement and dehydrogenation to give (2-nitro-1-propenyl) benzene was also observed up to certain extent. Acetophenone was formed as minor oxidation product. In these reactions total selectivity for ring nitration varies between 67% and 91% whereas selectivity for side chain nitration varies between 5% and 27%. Highest activity and selectivity of 1% MoO$_3$/SiO$_2$ can be attributed to very high surface area and small pore diameter as well as low acidity. In the literature there are reports on nitration of aromatics using HNO$_3$ as nitrating agent on solid acid catalysts, which are either Brønsted acids or Lewis acids. Choudary et al. has reported nitration of chlorobenzene using Fe^{+3}

Scheme 1.

Table 2
Results of cumene nitration[a]

Catalyst	Conversion (%)	Selectivity (%)				
		Ortho	Meta	Para	Side chain	Oxidation[b]
1% MoO_3/SiO_2	62	19	3.8	68	4.9	4.3
5% MoO_3/SiO_2	60	11.3	1.7	54	26.0	7
10% MoO_3/SiO_2	58	12.6	2.4	54	27.0	4
15% MoO_3/SiO_2	57	18	3.2	58.6	14.5	5.7
20% MoO_3/SiO_2	55	18.7	3.4	64.6	11.5	1.8

[a] Reaction conditions: Cumene = 42 mmol, 70% HNO_3 = 50 mmol, Catalyst 10 wt%, $C_2H_4Cl_2$ = 25 ml, temperature = 90 °C, time = 10 h.
[b] Acetophenone as oxidation product.

exchanged K-10 montmorillonite as catalyst and HNO_3 as nitrating agent, and the catalytic activity is reported to be due to Lewis acidity of the catalyst [12]. Sato et al. has reported nitration of benzene using nitric acid and montmorillonite exchanged with different multivalent cations as catalysts. The catalyst activity is correlated to the electronegativity of the exchanged cations, which in turn shows variable polarisability of water molecules coordinated to the cations thus exhibiting protonic (Brønsted) acidity [13]. Similarly in the present case polarization of water molecules coordinated to Mo center can give rise to protonic acidity after addition of aqueous HNO_3. However the marginal change in the conversion and selectivity can be attributed to change in the surface area rather than to the change in the acidity.

3.2.1. Influence of solvent and rate of addition of nitric acid

Water formed during the reaction affects adversely the reaction and hence needs to be removed. As the water content of the reaction mixture (water from nitric acid as well as water formed during the reaction) is increased, there is resistance for organic substrate to reach the catalyst surface leading to decrease in the conversion. It is also observed that in presence of excess of water, catalyst forms clusters or lumps which sticks to the surface of the flask and does not gets freely dispersed in the reaction mixture even after increasing the stirring speed. For the effective removal of water by azeotropic distillation, the selection of solvent is an important factor. Different hydrocarbon solvents were tested and low yield of 4-NC was obtained with hydrocarbon solvents. When dicloroethene was used as the solvent for azeotropic distillation, very high conversion and selectivity was obtained. The hydrocarbon solvents used for azeotropic distillation had lower azeotropic boiling point compared to dichloroethane azeotrope and the lower reaction temperature may be the reason for low cumene conversion. The study of influence of rate of nitric acid addition revealed that faster addition rate leads to decrease in the conversion and selectivity. If nitric acid is added at faster rate, nitric acid decomposes to NOx (brown fumes) before it reacts with the substrate, which leads to decrease in the conversion. The maximum selectivity for 4-nitro cumene was obtained when the rate of addition was ~2 ml/hr.

The liquid phase nitration of cumene using 20% MoO_3/SiO_2 was tested in absence of solvent. It was observed that

Table 3
Results of catalyst recycle studies[a]

Recycle	Conversion (%)	4-NC Selectivity (%)
0	62	68
1	62	55
2	60	52
3	58	53
4	57	50
5	55	49

[a] Reaction conditions: Catalyst 0.5 g, temperature = 90 °C, charge added for each cycle: Cumene = 42 mmol, 70% HNO_3 = 50 mmol, $C_2H_4Cl_2$ = 25 ml, time = 10 h.

without solvent, oxidation reaction is more favorable compared to nitration. In case of reaction without solvent, removal of water is not possible which is the reason for low catalytic activity for nitration.

3.2.2. Catalyst recycle study

The catalyst recycle studies were carried out by isolating the catalyst by filtration and recycling it. The filtered catalyst was dried and reused with the fresh charge of cumene and solvent. The results are given in Table 3. The catalyst activity was found to be almost same and there was only marginal decrease in conversion as well as 4-NC selectivity.

4. Conclusion

Regioselective nitration of cumene to 4-nitrocumene was achieved using series of MoO_3/SiO_2 catalysts with high conversion and selectivity. Nitric acid was used as nitrating agent without use of sulphuric acid, which makes this process environmentally benign. The water formed during the reaction affects adversely and hence needs to be removed azeotropically. The catalyst can be recycled up to 5 recycles without considerable loss in the catalytic activity and selectivity.

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