

Solvent-Free Nitration of Toluene in the Presence of Nb₂O₅/SiO₂ Catalyst

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ABSTRACT: A series of Nb₂O₅/SiO₂ catalysts with varying Nb₂O₅ loadings (5–25 wt%) were prepared using the sol-gel technique. The catalytic activity of the materials was evaluated by nitration of toluene. Nb₂O₅/SiO₂ catalyst showed good catalytic activity, selectivity, and reusability for the nitration of toluene. Under the optimal conditions, conversion of toluene by 86% to mono-nitrotoluene was achieved with 100% selectivity. Experiments were designed by Minitab software, and the effect of reaction conditions was examined on the amount of meta isomer. The optimal reaction condition was also achieved for the lowest amount of meta isomer using this software. The reusability of the catalyst also was studied in this work at the same operating conditions, and the catalyst was stable for four runs without losing catalytic activity.

KEYWORDS: Nitration; Solid acid; Nb₂O₅/SiO₂ Catalyst; Mono-nitrotoluene; HNO₃.

INTRODUCTION

Aromatic nitro compounds are important inorganic chemistry due to their easy availability and conversion into various functional groups [1]. They are frequently used to synthesize drugs, pharmaceuticals, dyestuffs, perfumes, plastics, and explosives [2]. So, the nitration of aromatic substrates is one of the most important and widely studied chemical reactions [1-4]. As important intermediates in the chemical industry, nitrotoluenes are industrially produced by the liquid phase nitration of toluene using a mixture of nitric and sulfuric acid as a nitrating agent [5]. However, these mixed nitric-sulfuric acid systems have many disadvantages. A large quantity of dilute sulfuric acid is generated as waste in the conventional process, and its disposal or recycling processes are costly. Other associated problems are over-nitration, oxidation byproducts, and poor selectivity [6-8]. Therefore, many efforts have been directed

towards developing eco-friendly and reusable alternatives in recent years. In the aromatic nitration reactions, some solid acid catalysts exhibited good catalytic performance, which mainly included AlCl₃/SiO₂ [3], MCM-41[4], H₃PW₁₂O₄₀/MCM-41 [9], beta zeolite [10,11], NaZSM-5 [12], H₃PO₄/MoO₃/SiO₂ [13], sulfated SnO₂ [14], Cs_{2.5}H_{0.5}PMoO₄₀/SiO₂ [15], MoO₃/SiO₂ [16], H₃PO₄/ZSM₅ [17], WO₃/ZrO₂, NaHSO₄/SiO₂ [18], CuFe_{0.8}Al_{1.2}O₄ [19], and H₄SiW₁₂O₄₀/ZrO₂ [20], WO₃/SiO₂ [21], FeCl₃-SiO₂ [22]. Despite these researches, industries still largely rely upon early methods, and these researchers have not been able to meet their needs and persuade them to use the modern methods [3]. Therefore, in this regard, research is ongoing, and it should be possible to achieve a nitration process with good efficiency, desirability, and acceptability in industries using a specific catalyst with mild and favorable conditions.

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Niobium oxides and their compounds are important in catalytic reactions with various functions, such as promoter, support, redox materials, and acid catalysts [23-24]. The materials containing niobium have been pointed out as effective catalysts in many processes, such as dehydration of alcohols, hydrolysis, oxidation, esterification, alkylation, isomerization, and photocatalysis [24-28]. Different surface species and catalytic activity produced depend on the support materials, niobium precursors, amount of niobium loading, and the experimental conditions. Jehng and Wachs [29] claimed that the molecular structure of the surface niobium species on SiO_2 depends on the preparation method. It has been reported that for supported niobium oxide on silica, both Brønsted and Lewis acid sites remain bound to the support surface even in the presence of water and act as an effective catalyst for acid-catalyzed reactions [30].

This study aims to investigate the effect of a niobium-based silica catalyst on the nitration of toluene as a new catalyst to develop a mild, easy-to-handle, and efficient catalytic protocol without involving sulfuric acid. For this purpose, different conditions of nitration of toluene with varying Nb_2O_5 loadings (5–25 wt%) are investigated. Catalysts are prepared through the sol-gel method, and their catalytic activities are evaluated in a 100 ml three-necked flask in a batch.

EXPERIMENTAL SECTION

Materials and methods

All solutions were prepared from reagent-grade chemicals. Toluene and 2-propanol (99.9%) were purchased from Merck Chemical Company. Ammonium Niobate (V) Oxalate Hydrate (ANBO, 99.99%), Tetraethyl Orthosilicate (TEOS, 98%), Nitric acid (70%), and other chemicals used in this study were purchased from Sigma-Aldrich chemical company.

All experiments were carried out on a laboratory scale. Gas Chromatography (GC) analysis was used for all experiments. GC analysis was performed in an Agilent 6890 N model system equipped with an HP-5 column (5% phenyl methyl siloxane), column capillary (30.0 m \times 320 μm \times 0.25 μm nominal), and Electron Capture Detector (ECD).

Powder X-Ray Diffraction (XRD) analysis was performed with a Philips PW1730 using a Cu radiation source (40 kV and 30 mA). Specific surface area and

porosity were evaluated using N_2 gas-adsorption technique (Quanta-Chrome/NOVA 1200e), Brunauer-Emmett-Teller (BET), and Barrett-Joyner-Halenda (BJH) analyses, respectively. The BET surface area of the sample (ca. 0.13 g) was measured at 77 K. The catalyst was thermally characterized (TGA/DSC) in Universal V4.5A TA Q600 Instrument, and Fourier Transform InfraRed (FT-IR) (Perkin Elmer BX) was used to determine its structural behavior.

Design of experiments

Response surface methodology (RSM) is an important method for designing experiments and studying effective interactions between experiment parameters to achieve optimum response [31]. In the present work, Central Composite Design (CCD) was utilized to design experiments and optimize the nitration conditions. There are four independent factors effective on nitration of toluene process: niobium loading percent (5-25%), reaction temperature (25-85°C), nitric acid/toluene (A/T) molar ratio, and toluene/catalyst (T/C) molar ratio. Here, the obtained percentage of methanitrotoluene was a response, a dependent variable that is optimized to the minimum amount possible and modeled using a multivariate linear regression technique.

Sol-gel catalyst preparation

The $\text{Nb}_2\text{O}_5/\text{SiO}_2$ catalysts were prepared with 5, 10, 15, 20, and 25 wt% of Nb_2O_5 by sol-gel method using ammonium niobium oxalate on silica [32,33]. In a typical preparation, TEOS was dissolved in 2-propanol followed by adding ammonium hydroxide aqueous solution (pH = 8.0–10.5) under mechanical stirring at 25°C for 30 min. Next, 20 ml of ANBO/ $(\text{NH}_4[\text{NbO}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2] \cdot x\text{H}_2\text{O})$ aqueous solution was added to the above synthesis solution. The resulting gel was aged at room temperature for 3 days, dried at 110°C for 24 h, and finally calcined at 550 °C for 5 h.

Toluene nitration

The catalytic nitration of toluene with HNO_3 was carried out in a 100-mL three-neck flask equipped with a magnetic stirrer and a dropping funnel. Firstly, the selected catalyst and 70% HNO_3 were added into the flask, and then toluene was added dropwise in the flask *via* a dropping funnel for 15 minutes. The reactions were performed

for 2.5 h. The organic phase was separated and washed with 5 wt% NaHCO_3 solution and deionized water. Then, the products were quantitatively analyzed by GC with an Electron Capture Detector (ECD) using an HP-5 column. This experiment was repeated 31 times with different conditions.

RESULTS AND DISCUSSION

Catalyst characterization

The behavior of the $\text{Nb}_2\text{O}_5/\text{SiO}_2$ catalyst as a function of the temperature helps understand the subsequent phenomena of the niobium pentoxide formation inside the silica matrix [34]. The TGA/DSC curve of the calcined catalyst (Fig. 1) showed a weight loss of $\sim 7\%$ until 180°C due to the removal of adsorbed and structural waters. The results are in line with those reported by other authors. At temperatures above 180°C , the TGA/DSC curves give no high weight loss.

As shown in Fig. 2, the FT-IR spectra of the sample exhibit the absorption bands at 463 , 803 , and $1000\text{--}1300\text{ cm}^{-1}$ for bending modes, symmetric stretching, and asymmetric stretching of bulk Si-O-Si, respectively [32-35].

These spectra show that the absence of the carboxylic groups' bands at 1700 cm^{-1} ($\text{C}=\text{O}$ stretching) in the treated sample can be attributed to Nb_2O_5 formation and ANBO decomposition. The large bands at 800 and 1100 cm^{-1} can be attributed to Nb-O stretching and out-of-plane distortions [28, 32].

The XRD pattern of fresh catalyst calcined at 550°C (Fig. 3) showed that the crystalline structure collapses due to the heating process with loss of the carboxylic groups. Indeed, the XRD pattern of this sample exhibits a diffuse maximum at about $2\theta = 24^\circ$ typical amorphous silica [36]. Based on Fig. 1, the diffraction peaks can be indexed to the simultaneous presence of orthorhombic phase of Nb_2O_5 (T- Nb_2O_5 ICDD No. 27-1003) and monoclinic phase (H- Nb_2O_5 ICDD No. 37-1468) [37,38]. Reflections of two main phases structurally corresponding to T- Nb_2O_5 and H- Nb_2O_5 are visible in the pattern. The presence of these two phases indicates the phase transition at this temperature.

Characterization of the fresh 15% Nb_2O_5 catalyst was also performed using BET measurements. The results show that the surface area of this sample was $446\text{ m}^2/\text{g}$. The textural characteristics obtained by BET and BJH theories are listed in Table 1.

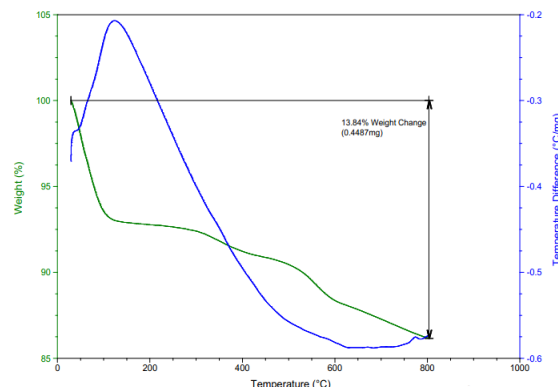


Fig. 1: The TGA/DSC curves of fresh 20% $\text{Nb}_2\text{O}_5/\text{SiO}_2$ catalyst recorded at 10 K min^{-1} .

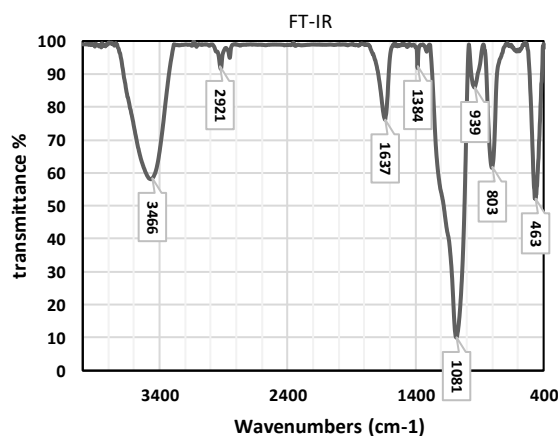


Fig. 2: The FT-IR spectra of fresh 20% Nb catalyst calcined at 550°C .

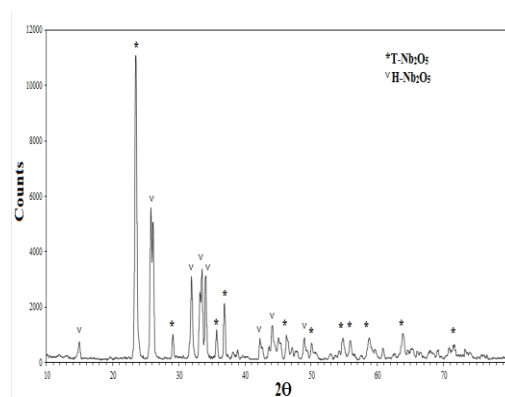


Fig. 3: The XRD pattern of fresh 10% Nb catalyst calcined at 550°C .

Table 1: Textural properties of fresh 15% Nb₂O₅ catalyst calcined at a temperature of 550 °C.

Sample	SSA (m ² /g)	C	Average pore diameter (nm)	Total pore volume (cm ³ /g) (p/p ₀ =0.99)
Fresh catalyst	446	197	2.57	0.28

Gas chromatography analysis

Injector and detector temperatures were 225 °C and 300 °C, respectively. The injected volume was 2 µL with a split ratio of 1:6 was used for the column inlet. Nitrogen was used as carrier gas at a 2 mL/min constant flow rate, with ECD as a detector. Temperature conditions used for the separation of components were as follows: the initial temperature was 100 °C (hold 2 min), the first temperature ramp (100 °C/min to 200 °C), and the second temperature ramp (20 °C/min to 280 °C), and finally hold 5.5 min at 280 °C.

The results from the nitration of the toluene-HNO₃ reaction under different experimental conditions designed by Minitab were presented in Table 2. The nitration products involve ortho-nitrotoluene (ONT), para-nitrotoluene (PNT), and meta-nitrotoluene (MNT). All catalysts showed 100% selectivity towards mononitrotoluene. Among all catalysts, 15% Nb₂O₅ catalyst showed the highest conversion (86%) to mononitrotoluene at 55 °C. The amount of all product (o+m+p), ortho/para (o/p) ratio, and meta/product (m/(o+m+p)) ratio was also presented in this table. In the following, data analysis and modeling are performed with the Minitab software.

Modeling of nitration process

In the liquid phase nitration of toluene, controlling the content of meta-nitrotoluene is very important in obtaining trinitrotoluene, toluene diisocyanate, etc. The amount of meta-nitrotoluene in these reactions should be minimal [39]. Therefore, the effect of reaction conditions was examined on the amount of meta isomer by Minitab software.

For obtaining the nitration model, analysis of variance (ANOVA) was performed for statistical analysis and data evaluation. The results from ANOVA were given in Table 3, including the sum of squares for errors and F-statistic and p-value. In multivariate linear regression analysis, the effect of linear terms, squared terms, and interaction factors of MNT products was investigated to achieve optimum response (Table 4). In the validation of the MNT response model, R-squared value 91.04% and adjusted R-squared value (adj) 83.21% were obtained. The

p-value should be p<0.05, and F-statistic should be greater. A p-value >0.05 is not acceptable for the model.

In Fig. 4, two-dimensional contour plots are represented. Response contour plots show two-variable interaction variations while the remaining variables remain constant.

According to these plots, the amount of MNT increases by increasing the temperature from 25 to 85°C, supported by experimental data. Table 5 shows the average products only in terms of reaction temperature.

Optimization of response

Response optimization was carried out using a verified model obtained for MNT isomer and optimization to reach the minimum MNT. The minimum MNT was obtained using Minitab following these conditions a temperature of 55 °C, 15% catalyst loading, acid/toluene molar ratio of 3%, toluene/catalyst molar ratio of 2.12%.

Catalyst reusability

The reusability of catalysts has been studied in this work at the same operating condition. The spent catalyst was re-used under the same reaction conditions for the next run. Each run was performed after washing and drying the catalyst. So, the catalyst was stable for four runs without losing its catalytic activity. Table 6 presents the data for catalyst reusability. Decreased catalyst activity in the fifth run was due to reduced catalyst weight and lost active surface species.

CONCLUSIONS

The Nb₂O₅/SiO₂ catalysts were prepared in the range of 5-25wt% of Nb₂O₅ by the sol-gel technique using ammonium niobium oxalate hydrate and calcined at 550 °C. Activity and selectivity of catalysts were evaluated by nitration of toluene reaction with HNO₃. The nitration reaction experiments were designed by Minitab software under different operating and optimal conditions. Among all experimental data, 15% Nb₂O₅ catalyst showed the highest conversion (86%) and lowest MNT isomer

Table 2: Design experiment and results for nitration of toluene.

Order no.	%Nb ₂ O ₅ loading	Temp	A/T	T/C	ortho	metha	para	o+m+p	o/p	%m/(o+m+p)
1	10	40	3.25	1.38	53.66	11.16	28.14	92.96	1.91	12
2	10	40	1.75	2.13	39.5	4.51	24.67	68.68	1.6	6.57
3	10	40	3.25	2.13	36.57	3.53	21.07	61.18	1.74	5.78
4	10	40	3.25	2.13	32.17	4.1	19.84	56.11	1.62	7.31
5	10	40	1.75	1.38	22.33	8.55	14.43	45.31	1.55	18.87
6	10	70	3.25	1.38	78.41	18.3	41.63	138.33	1.88	13.23
7	10	70	1.75	1.38	20.17	11.74	13.57	45.48	1.49	25.81
8	15	25	2.5	1.75	36.23	3.61	17.27	57.11	2.1	6.32
9	15	40	3.25	2.12	36.6	3.51	21.07	61.18	1.74	5.74
10	15	55	2.5	1	90.54	21.57	57.28	169.4	1.58	12.73
11	15	55	1	1.75	72.85	25.83	47.19	145.87	1.54	17.71
12	15	55	2.5	1.75	44.39	6.43	33.12	83.94	1.34	7.66
13	15	55	2.5	1.75	47.1	7.58	28.5	83.18	1.65	9.11
14	15	55	2.5	1.75	45.51	6.12	30.45	82.08	1.49	7.46
15	15	55	2.5	1.75	45.73	7.11	29.2	82.04	1.57	8.67
16	15	55	2.5	1.75	46.6	7.3	27.9	81.8	1.67	8.92
17	15	55	2.5	1.75	40.32	5.98	26.82	73.12	1.5	8.18
18	15	55	4	1.75	28.81	3.61	16.44	48.86	1.75	7.39
19	15	70	1.75	2.12	45.53	21.2	34.35	101.08	1.33	20.97
20	15	85	2.5	1.75	52.25	43.44	26.08	121.77	2	35.68
21	20	40	1.75	2.13	96.66	17.92	53.96	168.55	1.79	10.63
22	20	40	3.25	2.13	61.46	6.21	36.16	103.82	1.7	5.98
23	20	40	1.75	1.38	33.22	4.43	19.71	57.35	1.69	7.73
24	20	40	3.25	2.13	11.7	2.08	7.13	20.91	1.64	9.95
25	20	40	1.75	1.38	8.6	1.05	4.15	13.8	2.07	7.62
26	20	55	2.5	1.75	45.51	6.12	30.45	82.08	1.49	7.46
27	20	55	2.5	1.75	43.37	6.4	31.21	80.98	1.39	7.9
28	20	70	1.75	2.13	45.53	55.43	34.35	135.3	1.33	40.97
29	20	70	3.25	2.13	64.03	14.31	33.31	111.66	1.92	12.82
30	20	70	3.25	1.38	56.85	17.34	34.22	108.41	1.66	16
31	25	55	2.5	1.75	80.38	23.47	43.55	147.39	1.85	15.92

Table 3: ANOVA for MNT modeling.

Source	DF	Adj SS	Adj MS	F-statistic	P-value
Model	14	17.96	1.28	2.72	0.032
Linear	4	12.06	3.01	6.4	0.003
Cat	1	6.00	6.00	12.75	0.003
temp	1	4.81	4.81	10.21	0.006
A/T Ratio	1	0.55	0.55	1.19	0.293
T/C ratio	1	0.68	0.68	1.46	0.245
Square	4	1.03	0.25	0.55	0.702
Cat*Cat	1	0.01	0.01	0.02	0.886
temp*temp	1	0.91	0.91	1.93	0.185
A/T *A/T	1	0.00	0.00	0.02	0.896
T/C*T/C	1	0.06	0.06	0.13	0.725
2-Way Interaction	6	6.16	1.02	2.18	0.104
Cat*temp	1	0.99	0.99	2.12	0.166
Cat*A/T	1	1.18	1.18	2.52	0.133
Cat*T/C	1	2.47	2.47	5.26	0.037
temp*A/T	1	1.37	1.37	2.92	0.108
temp*T/C	1	0.11	0.11	0.23	0.635
A/T *T/C	1	0.01	0.01	0.03	0.873
Error	15	7.06	0.47		
Lack-of-Fit	9	6.93	0.77	35.3	0
Pure Error	6	0.13	0.02		
Total	29	25.03			

Table 4: Interaction and coefficient of factors of MNT.

Term	Effect	Coef	SE Coef*	T-value	P-value
Constant	-	1.52	0.255	5.96	0.000
Cat	2.346	1.173	0.329	3.57	0.003
Temp	2.1	1.05	0.329	3.2	0.006
A/T	-0.716	-0.358	0.329	-1.09	0.293
T/C	-0.694	-0.347	0.287	-1.21	0.245
Cat*Cat	-0.152	-0.076	0.521	-0.15	0.886
Temp*Temp	1.449	0.725	0.521	1.39	0.185
A/T*A/T	0.138	0.069	0.521	0.13	0.896
T/C*T/C	0.273	0.137	0.382	0.36	0.725
Cat*Temp	1.999	0.999	0.686	1.46	0.166
Cat*A/T	-2.18	-1.09	0.686	-1.59	0.013
Cat*T/C	-2.361	-1.18	0.515	-2.29	0.037
Temp*A/T	-2.346	-1.173	0.686	-1.71	0.108
Temp*T/C	-0.499	-0.249	0.515	-0.48	0.635
A/T*T/C	-0.167	-0.084	0.515	-0.16	0.873

* The "SE Coef" stands for the standard error of the coefficient.

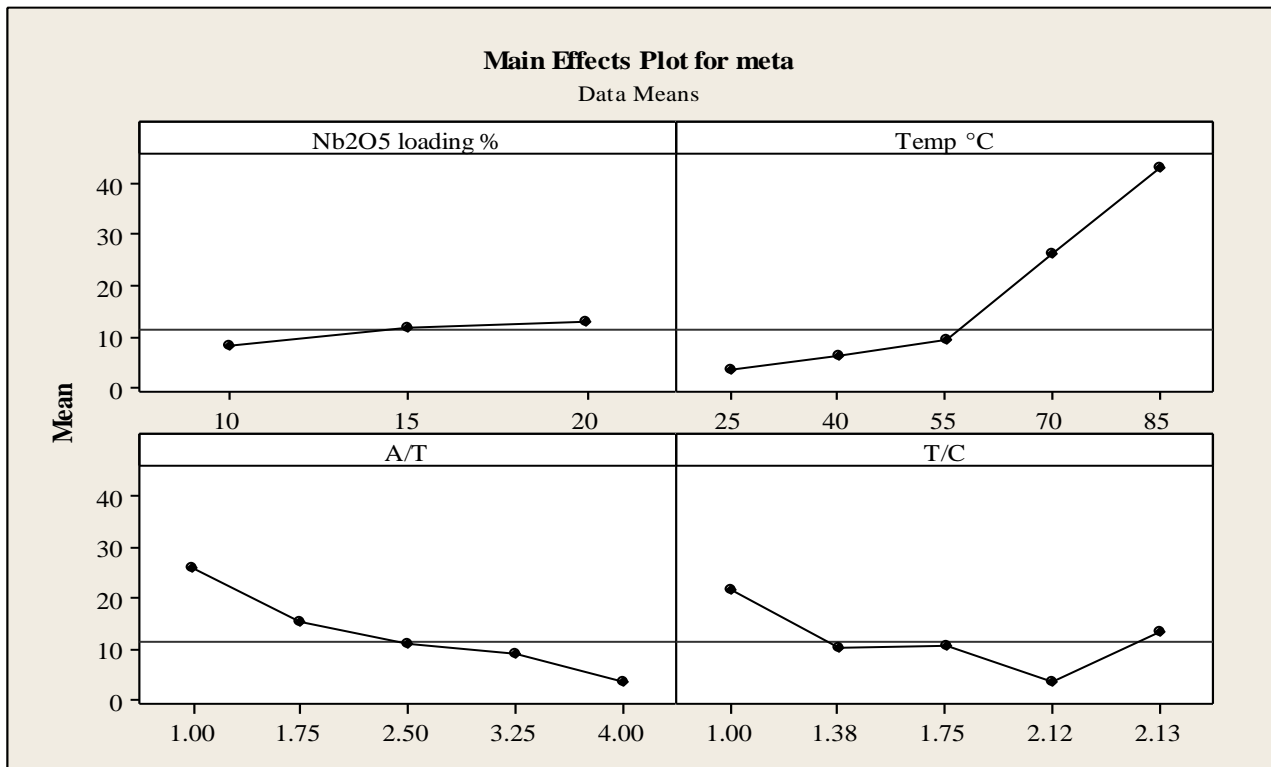
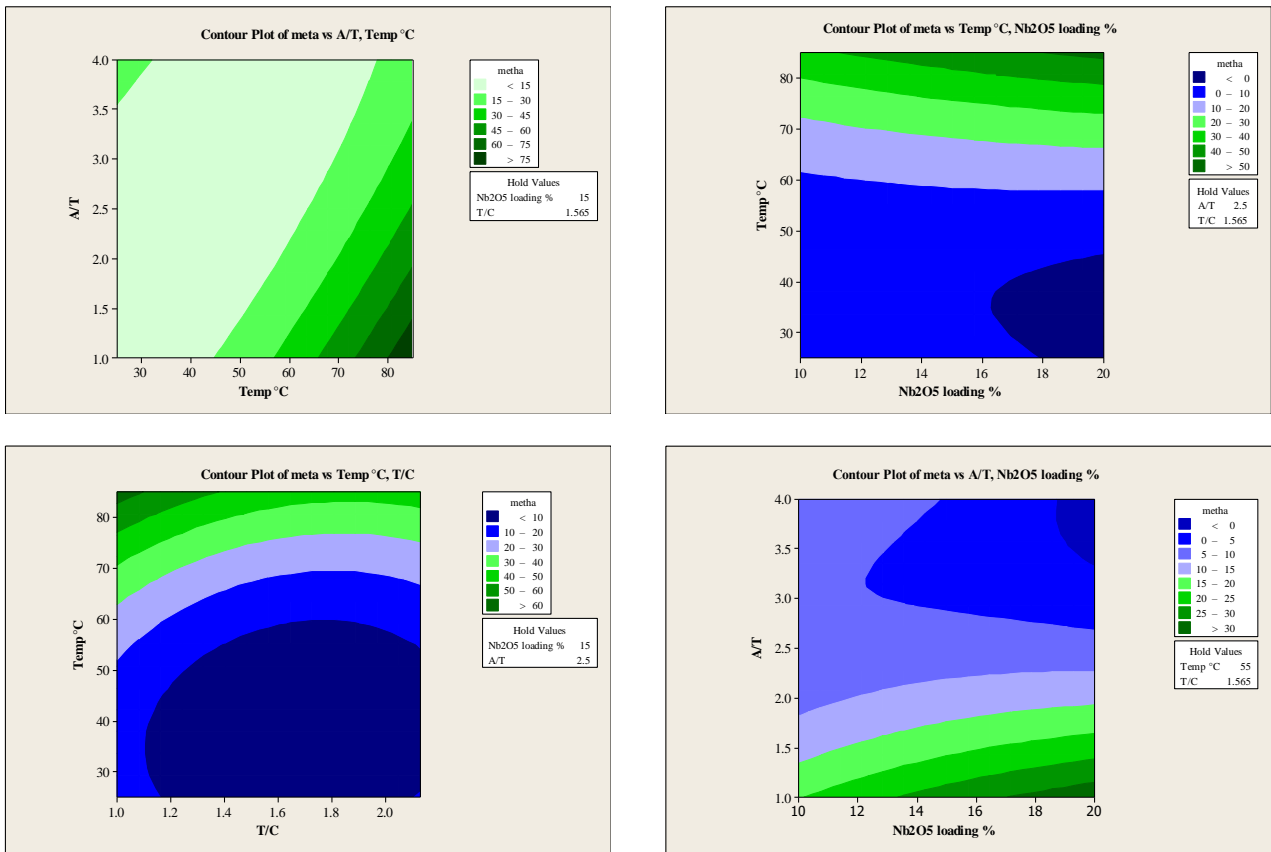


Fig. 4: DOE plots of MNT.

Table 5: The effect of reaction temperature on number of products and meta/product ratio.

Temperature	Total average product	%(m/o+m+p)
25	57	6
40	82	8
55	103	11
70	121	26
85	122	36

Table 6: Testing catalyst reusability at the same conditions.

Order no.	%Nb loading	Temp	A/T	T/C	Spent order	Ortho	Meta	Para	Total
1	15	55	2.5	1.75	1	48.47	8.72	33.06	90.26
2	15	55	2.5	1.75	2	45.51	6.12	30.45	82.08
3	15	55	2.5	1.75	3	47.10	7.58	28.50	83.18
4	15	55	2.5	1.75	4	45.70	7.10	29.20	82.00
5	15	55	2.5	1.75	5	34.34	17.46	23.45	75.25

conversion. All catalysts showed 100% selectivity towards mononitrotoluene. The effect of reaction conditions on the amount of meta isomer was analyzed through experimental data and Minitab software. Increasing the temperature from 25 to 85°C increases the number of products, MNT, and MNT/product ratio, confirmed by the experimental data. Temperature changes and toluene/catalyst molar ratio had the greatest and least effect on the amount of MNT, respectively. The optimum condition for MNT minimum amount was obtained using Minitab at these conditions, including a temperature of 55 °C, catalyst loading of 15%, acid/toluene molar ratio of 3%, and toluene/catalyst molar ratio of 2.12%. The reusability of the catalyst was also studied at the same operating conditions. The catalyst was stable for four runs without losing its catalytic activity.

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