Direct Amination of Toluene with Hydroxylamine in the Presence of Vanadium-based Catalysts

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The amination of toluene to toluidines with hydroxylamine hydrochloride was investigated over vanadium-based catalysts supported on different carriers and in different reaction media. Over 50% total yield of toluidines was obtained on the catalysts operated at optimal conditions.

Toluidines are important industrial chemicals of great commercial usefulness and are widely used in various fields of applications such as dye, insecticide ether, sulfur accelerant, mill run etc. Conventional ways for the synthesis of toluidines usually include the following: (1) The nitration of toluene followed by hydrogenation of the nitro group. Although high yield could be obtained in this way, it involves the use of large amounts of sulfuric acid, nitric acid, alkali, and water. In addition thereto, nitrogen oxides are generated during the course of operation to prepare the nitro compounds, and the atomic utilization of the process is low.[1–3] (2) Reaction of halogeno-toluene and cresol with ammonia. Expensive corrosion-resistant equipments should be used for practising the said process. With also low atomic utilization, the reaction is carried out at high temperature and under high pressure, while the desired toluidines are obtained in low yields.[1–3] (3) Direct amination of toluene with ammonia in the gas phase over Ni/NiO cataloreactants[1,2,4,5] or in the presence of Group VIII metal catalysts.[3,4] Both processes are characterized by only very low yields, even at extreme conditions of temperature and pressure. Recently, N. I. Kuznetsova et al.[4] investigated the amination of benzene and toluene with hydroxylamine sulfate, and about 26% yields for toluidines were obtained. This provided a new approach in accordance with the trends towards a sustainable development. In order to broaden this route, different carriers are used to prepare supported-vanadium catalysts and different media are used to realize this reaction in the present work.

Silica, titania, ceria, and γ-alumina were calcined in air ambience at 100 °C (6 h) before use. The catalysts were prepared by impregnation with aqueous solution of NH_4VO_3 for 24 h and dewatered in water bath at 80 °C and then calcined at 400 °C in air for 2.5 h. Each catalyst contained about 13 wt % V_2O_5.

The reactions were carried out separately in open air and in closed system. For the reaction in open air, 0.2 g of catalyst, 15-mL acid solvent composed of water and an acid, 0.1 mol $NH_2OH\cdot HCl$, 0.1 mol toluenes were added in a thermostatted glass flask. The reaction mixture was heated under reflux and stirring in air. After about 4 h, the reaction was stopped, and the reaction mixture was cooled and neutralized by a 30% solution of NaOH. The obtained organic phase and aqueous phase samples were quantitatively analyzed by GC with FID detector. The regioisomers of toluidines obtained were separated and then characterized by ^{1}H NMR (Varian INOVA 400 MHz) using acetone-d_6 as solvent and MS (FINNIGAN-MAT 4510) and IR (PERKIN ELMER 1700) for confirmation. For reaction in closed system, the same amounts of reactants and catalyst were used; and the reaction was carried out in a closed autoclave under atmospheric pressure (≈1.2 atm). The same procedure as mentioned above was used to analyze the products. The main by-product obtained is cresol.

Table 1. The (mol %) yield of toluidines referred to starting toluene and the (mol %) selectivity of toluidines referred to reacted toluene in the presence of different catalysts operated in different media. Open system; Temperature, 90 °C; Reaction time, 4 h; Media, A: V_{H_2O}:V_{CH_3COOH} = 2:1, B: V_{H_2O}:V_{CH_3COOH}:$V_{H_2SO_4}$ = 2:1:1, C: V_{H_2O}:V_{CH_3COOH}:V_{HNO_3} = 2:1:1

Carrier	Selectivity /mol % (media)	Toluidines yield/mol %			
		ortho-	*meta-*	*para-*	Total
SiO_2	79(A)	1.36	1.28	1.38	4.02
	62(B)	15.36	16.40	17.52	49.01
	42(C)	0.81	1.01	1.16	2.98
TiO_2	76(A)	1.56	1.63	1.75	4.94
	60(B)	15.88	20.10	21.30	57.28
	38(C)	1.09	1.18	1.25	3.52
CeO_2	82(A)	14.75	19.52	21.30	55.57
	66(B)	1.43	12.77	9.82	35.08
	47(C)	0.53	0.67	0.81	2.01
γ-Al_2O_3	87(A)	15.97	18.92	21.54	56.43
	69(B[a])	14.32	17.02	17.21	48.55
	49(C[a])	0.34	0.86	1.44	2.64

[a]The catalysts dissolved in the media.

The activity and selectivity for the amination of toluene to toluidines in different reaction media over vanadium-based catalysts supported on different carriers are shown in Table 1. It was reported[4] that this reaction proceeded in media with pK_a of about 3.75 to 6.7. It is indicated in Table 1 that different catalysts need different reaction media to show higher activity and higher selectivity. All the catalysts show little activity and <50% selectivity to toluidines in the media containing nitric acid. For silica and titania-supported catalysts, the reaction medium composed of water, acetic acid and sulfuric acid (V_{H_2O}:V_{CH_3COOH}:$V_{H_2SO_4}$ = 2:1:1) is favorable, the yields obtained are 49 and 57% with a selectivity of 60 and 62%, respectively. Ceria-supported catalyst exhibits higher activity (56%) and selectivity (82%) in the mixture of water and acetic acid V_{H_2O}:V_{CH_3COOH} = 2:1) than in other media. Alumina-supported catalyst shows good activity (56%) and selectivity (87%) in H_2O + HOAc (V_{H_2O}:V_{CH_3COOH} = 2:1) as well as in H_2O + HOAc + H_2SO_4 (V_{H_2O}:V_{CH_3COOH}:$V_{H_2SO_4}$ = 2:1:1) (49 and 69%), however, in the latter medium, the catalyst will dissolve. From the viewpoint of safe operation and economic consideration, ceria and alumina supported catalysts show promise when used in H_2O + HOAc medium; and the yield and selectivity for toluidines are much greater than the previously reported ones.[4] H_2O + HOAc medium is not absolutely safe nor non-corrosive, but it is evidently safer than sulfuric or nitric acids media, because its corrosivity is much lower than them. Although sulfuric assisted medium is also effective for the target reaction, it is rather corrosive and even dissolves the catalyst making its deactivation, then it is not a good alternative medium for the target reaction.

Table 2. The (mol %) yield of toluidines and cresol referred to starting toluene and the (mol %) selectivity of toluidines referred to reacted toluene in the presence of different catalysts operated in the presence or absence of air. Temperature, 90 °C; Reaction time, 4 h; Atmosphere, 1 atm; Media, A: V_{H_2O}:V_{CH_3COOH} = 2:1, B: V_{H_2O}:V_{CH_3COOH}:$V_{H_2SO_4}$ = 2:1:1

System	Carrier/media	Toluidines yield/mol%				Selectivity /mol %	Cresols yield /mol %
		ortho-	*meta-*	*para-*	Total		
Open	SiO_2(B)	15.36	16.40	17.52	49.01	62	5.04
	TiO_2(B)	15.88	20.10	21.30	57.28	60	4.00
	CeO_2(A)	14.75	19.52	21.30	55.57	82	6.03
	γ-Al_2O_3(A)	15.97	18.92	21.54	56.43	87	5.89
Closed	SiO_2(B)	7.95	8.57	8.78	25.30	33	10.36
	TiO_2(B)	8.13	8.51	10.35	26.96	45	8.56
	CeO_2(A)	8.71	9.42	10.08	28.21	37	10.25
	γ-Al_2O_3(A)	5.64	6.42	8.04	20.10	41	8.69

Table 3. The (mol %) yield of toluidine in control experiment to test the dissolution of the catalysts

Toluidines Yields /mol %	Filtrate				Remained catalyst			
	γ-Al_2O_3	CeO_2	TiO_2	SiO_2	γ-Al_2O_3	CeO_2	TiO_2	SiO_2
	2.61	1.77	5.07	5.34	54.34	50.72	51.81	42.05

The vanadium-based catalysts supported on different carrier were studied by means of XRD. It was found that V was highly dispersed over γ-alumina, this may be the origin of the high activities.

The effect of the presence of air on the reaction is studied in the present work by comparatively carrying out the reaction in an open and closed system. The results are shown in Table 2. It is clear from Table 2 that every catalyst shows higher activity and higher selectivity in open system than those in closed one. The yields of toluidines are correspondingly two times greater in open air than those in closed system. It is interesting that the total yields of cresol are correspondingly two times greater in closed system than those in open air. This implies that the selectivity to toluidines is higher in open air (≈87%) than in closed system (≈45%), while that to cresols is higher in closed system than that in open air. N. I. Kuznetsova et al.[4] studied this reaction in closed system, it may be one of the reasons for the higher toluidines yields obtained in the present work. The presence of air may favorite the activation of C–H bond and the open system facilitates the escape of gaseous by-products.

In order to investigate whether the reaction is catalyzed by heterogeneous catalysts or dissolved ions, as well as the stability of the catalysts, two series of control experiments were carried out. The reaction was carried out in the corresponding solvents in the absence of the catalysts, no toluidine was observed to form in H_2O + HOAc and very little (less than 3.5%) toulidine was obtained in H_2O + HOAc + H_2SO_4, indicating the effectiveness of the catalysts.

In another control experiment, the catalysts were first immersed in the corresponding solvents for 4 h (the corresponding reaction time), then filtrated. The remained catalysts and the filtrates were used separately to perform the reaction under the corresponding conditions. The results are shown in Table 3. As indicated in Table 3, very little amount of toluidine was observed when the filtrate were used as the reaction media in the absence of catalysts, while all of the remained catalysts showed activities which were little lower than those over the fresh ones, and the alumina-supported catalyst showed the minimum reduction of toluidine yield.

The stability of the catalysts was tested by separating the used catalysts and reusing it consecutively under the same reaction conditions. As shown in Table 4, the activity decreases slowly when the catalysts are reused, and the alumina-supported catalyst again shows a smaller rate of activity reduction. The above data indicate that the reaction could not proceed in H_2O + HOAc media without the use of catalysts. The ion dissolved from the catalyst is also active for the reaction, however, the amount of dissolution of the metal ion is quite small, and the catalyst could be reused. Alumina-supported catalyst shows higher stability, though further stabilization measure should be taken to develop more effective catalyst.

Table 4. The (mol %) yield of toluidine in control experiments to test the stability. Media, A: V_{H_2O}:V_{CH_3COOH} = 2:1, B: V_{H_2O}:V_{CH_3COOH}:$V_{H_2SO_4}$ = 2:1:1

Carrier/media	Toluidines yield/mol %			
	fresh catalyst	2nd time	3rd time	4th time
γ-Al_2O_3(A)	56.43	55.51	54.32	53.58
TiO_2(B)	57.28	47.35	43.27	43.02
CeO_2(A)	55.57	52.44	51.12	50.35
SiO_2(B)	49.01	41.87	39.25	38.11

The reaction conditions are the same as those in Table 1.

It is seen that toluene could be aminated directly to toluidines with hydroxylamine hydrochloride in the presence of vanadium-based catalysts. 56.4% toluidines yield, which is two times greater than that in literature,[4] and 87% selectivity, could be obtained over γ-alumina supported vanadium catalyst operated in H_2O + HOAc medium. The yield and selectivity for toluidines are higher in open air than those in closed system. The optimized catalyst is rather stable and may be reused. This shows promise for the further development of direct amination catalyst.

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