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Vapor-phase Nitration of Benzene to Nitrobenzene over Supported Sulfuric Acid Catalyst

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Abstract: Vapor-phase nitration of benzene over solid acid catalyst is expected to be a clean process with no sulfuric acid waste. We investigated this process over solid acidic catalysts utilizing diluted nitric acid (60-70%) as nitrating agent, and found that supported sulfuric acid catalyst exhibited a very high catalytic activity. Under the conditions of reaction temperature 160-170℃, space velocity (SV) 1200 h^{-1}, the yield and the space-time yield (STY) of nitrobenzene (NB) based on HNO_3 were more than 98% and 0.75 $kg \cdot kgcat^{-1} \cdot h^{-1}$ over 10% H_2SO_4/SiO_2 (by weight) catalyst respectively.

Keywords: Nitration (vapor-phase), sulfuric acid (supported catalyst), nitrobenzene

Nitrobenzene is an important chemical intermediate for producing dyestuffs. It is also used as a solvent. The industrial synthesis of nitrobenzene has been carried out in liquid phase with a mixture of nitric acid and concentrated sulfuric acid. This conventional nitration process still has some unsolved problems such as treatment of waste sulfuric acid and disposal of wastewater.

The vapor-phase nitration of benzene to prepare nitrobenzene over the solid acidic catalysts in diluted nitric acid has been investigated for several years. It is expected to be a clean process without large amount of diluted sulfuric acid waste[1]. Besides diluted nitric acid (60-70%, by weight) is more economical compared with concentrated nitric acid.

H. Sato *et al*. have reported several types of efficient catalysts for this purpose, such as modified Y-zeolite[2], modified mordenite[3], montmorillonite ion-exchanged with a multivalent metal ion (*e.g.*, Al^{3+}-montmorillonite)[4], mixed metal oxides (*e.g.*, TiO_2-MoO_3)[4], oxides treated with sulfuric acid at 500°C (*e.g.*, SO_4^{2-}/TiO_2-MoO_3)[5]. Among them, $SO_4^{2-}/TiO_2(4)$-$MoO_3(1)$ kept a fairly high yield of nitrobenzene (87-91%) at a fairly high space-time yield (STY) of nitrobenzene (0.72 $kg \cdot kgcat^{-1} \cdot h^{-1}$)[5].

Our study showed that the catalyst supported sulfuric acid on SiO_2 is very effective for the vapor phase nitration of benzene. The catalyst supported sulfuric acid will be described in detail in the following section.

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Experimental

Shaped silica support (Sphere, 20-40 mesh, product of Qing Dao Ocean Chemical Plant) were first dried for 8 h at 200°C and then cooled in a dry box. A certain amount of shaped silica support was impregnated with a slight excess of various concentrations of sulfuric acid. After 12-15 h, the sulfuric acid supported on the shaped silica was first dried at 100°C, and then treated for 8 h at given treatment temperature and subsequently stored in a dry box.

The vapor phase nitration was carried out in a flow reactor made up of quartz with a fixed catalyst bed and a thermocouple at atmospheric pressure. Diluted nitric acid and benzene were introduced into the flow reactor by two measuring pumps respectively. At the some time, nitrogen carried gas was also introduced into the flow reactor. The nitration products were trapped in ice-water, and then analyzed by gas chromatography. The yield of nitrobenzene (NB) was calculated based on nitric acid.

Results and Discussion

Comparison of nitration activities among several solid acidic catalysts

Table 1 Nitration activities of several solid acidic catalysts

Catalyst	Pretreatment temp. t /(°C)	Yield of NB %	STY of NB kg·kg-cat.$^{-1}$·h^{-1}
SO_4^{2-}/TiO_2	170	24.4	0.19
$SO_4^{2-}/TiO_2(9)$-$ZrO_2(1)$	170	46.3	0.36
$SO_4^{2-}/TiO_2(4)$-$MoO_3(1)$	170	77.0	0.59
15% $H_3PW_{12}O_{40}/SiO_2$	180	83.4	0.64
15%H_2SO_4/SiO_2	185	93.5	0.71

SV=1200h^{-1}, Benzene/HNO_3=2/1(molar ratio). NB; nitrobenzene, STY; space-time yield

In **Table 1**, nitration activities of different solid acidic catalysts on vapor phase nitration of benzene were investigated. 15% H_2SO_4/SiO_2 (by weight) and 15% $H_3PW_{12}O_{40}/SiO_2$ (by weight) catalysts had fairly good catalytic activity, but the activities of SO_4^{2-}/TiO_2, $SO_4^{2-}/TiO_2(9)$-$ZrO_2(1)$ and $SO_4^{2-}/TiO_2(4)$-$MoO_3(1)$ are relatively poor, 15% H_2SO_4/SiO_2 catalyst showed highest activity: 93.5% yield of nitrobenzene based on HNO_3 (STY = 0.71 kg·kg-cat.$^{-1}$·h^{-1}). It caused to consider that the nitration involves electrophilic attack on the aromatic ring by the nitronium NO_2^+. The Brönsted acidic site are responsible for the generation of NO_2^+ ion from nitric acid [4, 6] rather than from Lewis acid site. More Brönsted acidic site are on the surface of 15% H_2SO_4/SiO_2 catalyst, but the Lewis acidic site is more on SO_4^{2-}/TiO_2, $SO_4^{2-}/TiO_2(9)$-$ZrO_2(1)$ and $SO_4^{2-}/TiO_2(4)$-$MoO_3(1)$ catalysts.

Effect of the amount of H_2SO_4 supported on SiO_2 on the nitrobenzene yield

The effect of the amount of H_2SO_4 supported on SiO_2 on the nitrobenzene yield is shown in **Table 2**. With H_2SO_4 loading (by weight) supported on SiO_2 from 1% to 20%, the

yield of nitrobenzene increased from 79.3% to 92.8%.

Table 2 Effect of the amount of H_2SO_4 supported on SiO_2 on the yield of nitrobenzene

Catalyst	Reaction Temperature *t* /(°C)	Yield of NB %	STY of NB kg·kg-cat.$^{-1}$·h^{-1}
1%H_2SO_4/SiO_2	185	79.3	0.61
5%H_2SO_4/SiO_2	185	86.5	0.67
10%H_2SO_4/SiO_2	185	92.0	0.71
15%H_2SO_4/SiO_2	185	93.5	0.72
20%H_2SO_4/SiO_2	185	92.8	0.71

SV=1200h^{-1},Benzene/HNO_3=2/1(molar ratio). NB; nitrobenzene, STY; space-time yield

With more than 1% loading, the catalytic activity increased obviously, so that the yield of nitrobenzene achieved 92.0% as 10% loading. Above 10% loading, the yield of nitrobenzene was no increased further. Therefore, the 10% load of H_2SO_4 supported on SiO_2 was selected.

Effect of the pretreatment temperature of catalysts on the nitrobenzene yield

Table 3 Effect of the pretreatment temperature on the yield of nitrobenzene

Catalyst	Reaction Temperature *t* /(°C)	Yield of NB %	STY of NB kg·kg-cat.$^{-1}$·h^{-1}
10%H_2SO_4/SiO_2	120	98.2	0.75
10%H_2SO_4/SiO_2	200	94.2	0.72
10%H_2SO_4/SiO_2	300	88.7	0.68
10%H_2SO_4/SiO_2	400	80.6	0.62

Reaction temperature *t*=170℃, SV=1200h^{-1}, Benzene/HNO_3=2/1(molar ratio).
NB; nitrobenzene,STY; space-time yield.

From the results shown in **Table 3**, with an increase of the treatment temperature of supported sulfuric acid catalyst from 120°C to 400°C, the yield of nitrobenzene decreased from 98.2% to 80.6%, and the space-time yield of nitrobenzene decreased from 0.75 to 0.62 kg·kg-cat.$^{-1}$·h^{-1}. Therefore, 120°C was the optimum treatment temperature.

Effect of reaction temperature on the nitrobenzene yield

The effect of the reaction temperature on the nitrobenzene yield, as shown in **Table 4.** When the reaction temperature increased from 145°C to 195°C, the yield of nitrobenzene increased and then decreased. At the range of the reaction temperature of 160-170°C, the maximum of the yield and the space-time yield of nitrobenzene were obtained. Therefore, 160-170°C was the optimum range of reaction temperature for the vapor phase nitration of benzene to nitrobenzene over solid acidic catalysts.

Table 4 Effect of reaction temperature on the yield of nitrobenzene

Catalyst	Reaction Temperature t/°C	Yield of NB %	STY of NB / kg·kg-cat.$^{-1}$· h^{-1}
10%H_2SO_4/SiO_2	145	92.4	0.71
10%H_2SO_4/SiO_2	158	98.9	0.76
10%H_2SO_4/SiO_2	171	98.2	0.75
10%H_2SO_4/SiO_2	180	94.2	0.72
10%H_2SO_4/SiO_2	195	90.4	0.69

10%H_2SO_4/SiO_2 catalyst was treated at 120°C, SV=1200h^{-1}, Benzene/HNO_3=2/1(molar ratio). NB; nitrobenzene, STY; space-time yield

Conclusion

Among various solid acidic catalysts tested by us for the vapor phase nitration of benzene to nitrobenzene with diluted nitric acid (60-70%, by weight), supported sulfuric acid catalyst was believed to be most effective one. Using 10% H_2SO_4/SiO_2 as the catalyst at the reaction temperature of 160-170°C, space velocity 1200 h^{-1}, the yield and the space-time yield of nitrobenzene (NB) based on HNO_3 were more than 98% ,0.75 kg·kg-cat.$^{-1}$·h^{-1} respectively.

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