

A Durable Catalyst for Vapor Phase Nitration of Benzene with Nitric Acid

Peng ZHOU, Xin Ping WANG, Tian Xi CAI*

State Key Laboratory of Fine Chemicals, School of Chemical Engineering,
Dalian University of Technology, Dalian 116012

Abstract: Experimental results in this work demonstrate that $PW_{12}\text{-H}_2\text{SO}_4/\text{SiO}_2$ catalyst is a good and durable catalyst for vapor phase nitration of benzene to nitrobenzene (NB) using 65% nitric acid at normal pressure. It retains the advantages of using H_2SO_4 as catalyst and the addition of phosphotungstic acid holds back the effusion of sulfuric acid. This new catalyst keeps high activity (the conversion of HNO_3 is more than 92%), high selectivity of NB (more than 97%) and high space time yield (STY 1.5 kg NB/kg cat.h) even after 150 h on stream, under condition of 423 K, $SV=3200$ ml/g h.

Keywords: Nitration, benzene, solid acid, nitric acid, nitrobenzene.

Nitrobenzene is one of the most important chemical intermediates, for preparing drugs, pesticides and explosive *etc.* For more than a century, it has been commercially manufactured by reacting benzene with mixed acid in liquid phase under vigorous agitation. Despite the high efficiency, the mixed-acid process has some drawbacks, among which the huge amount of spent acid and wastewater are by far the most crucial, and this makes an alternative solution desirable.

Nitration of benzene over solid acid in the vapor phase would be the answer to the problem, since it avoided the use of large amount of sulfuric acid. R. Prins *et.al.*¹ firstly reported that nitration of benzene in vapor phase with nitric acid on zeolites would be an interesting alternative to the mixed acid process. They studied modified Y zeolite² and modified mordenite¹. Dealumination mordenite by heat and acid treatments resulted in highly active and stable catalysts for the vapor-phase nitration of benzene with 65% HNO_3 at 443 K and atmospheric pressure. The mordenite catalyst kept total nitrobenzene yield of 0.6 kg NB/kg cat.h, while retaining a stable catalytic activity (up to 80% nitrobenzene yield based on nitric acid) for more than 120 h on stream. ZSM-5 zeolite also had been studied at 413-443 K in vapor phase nitration of benzene, and the activity of the catalyst decreased with reaction time since reagents and products were strongly adsorbed on the zeolite surface and desorbed only at 493-523 K³.

H. Sato *et al.* studied several types of solid acid catalysts such as Al^{3+} -mon-

*E-mail: caitx@chem.dlut.edu.cn

tmorillonite, mixed metal oxides⁴, the oxides treated with sulfuric acid at 500°C ($\text{SO}_4^{2-}/\text{TiO}_2\text{-MoO}_3$ *etc.*), partially neutralized heteropolyacid ($\text{H}_{1.5}\text{Cs}_{1.5}\text{PMo}_{12}\text{O}_{40}$, $\text{H}_{1.5}\text{Tl}_{1.5}\text{PMo}_{12}\text{O}_{40}$)⁵ and sulfuric acid supported on silica⁶. Especially for the $\text{H}_2\text{SO}_4/\text{SiO}_2$, they reported good results such as high yield of NB as 94.6% at 443 K, and high STY of 0.76 kg NB/kg cat h. The same authors found that the effusion of sulfuric acid could not be avoided on any kind of supporters tested, so they tried to compensate the effused sulfuric acid by co-feeding small amount of fresh sulfuric acid (such as 1/1000-1/5000).

The aim of this work is to find a way to prevent the effusion of sulfuric acid, in other words, to develop a more durable catalyst that retains the characteristics of $\text{H}_2\text{SO}_4/\text{SiO}_2$ catalytic system.

Experimental

The catalysts were prepared by impregnation of silica with appropriate active constituent solution. After impregnation for more than 12 h at room temperature, the precursors were dried at 393 K for 4 h then activated at 423 K for 3 h in air.

The catalytic reaction was carried out in a flow reactor with a fixed catalyst bed at atmospheric pressure. Benzene and nitric acid were introduced into the reactor together with nitrogen gas. The nitration products were trapped with ice water, and analyzed by gas chromatograph GC1102 with isopropyl benzene as internal standard. The unreacted nitric acid was extracted and determined by acid-base titration to calculate the conversion of HNO_3 . The yield and selectivity of nitrobenzene were calculated based on the consumed amount of nitric acid.

Results and Discussion

Some additives were selected to examine their effect on the $\text{H}_2\text{SO}_4/\text{SiO}_2$ catalyst. Firstly, their influences on the activity of the catalyst were examined. The results obtained were showed in **Table 1**.

Table 1 Influence of additives on activity and selectivity

| Catalysts | Time-on-stream (h) | Conversion of HNO_3 (%) | Selectivity of NB (%) |
|--|--------------------|----------------------------------|-----------------------|
| 9% H_2SO_4 -10% $\text{H}_3\text{BO}_3/\text{SiO}_2$ | 12 | 93.2 | 97.6 |
| 10% H_2SO_4 -3% $\text{Nb}_2\text{O}_5/\text{SiO}_2$ | 14 | 92.4 | 98.3 |
| 10% $\text{H}_2\text{SO}_4/\text{SiO}_2$ | 11 | 92.8 | 97.3 |
| 10% H_2SO_4 -10% $\text{PW}_{12}/\text{SiO}_2$ | 11 | 92.0 | 97.0 |

Reaction conditions: Benzene/ $\text{HNO}_3/\text{H}_2\text{O}/\text{N}_2=2.2/1/1.8/5.5$ (molar ratio), Temperature: 423 K

All the catalysts tested here showed as high activity and selectivity as those of $\text{H}_2\text{SO}_4/\text{SiO}_2$, with the conversion of HNO_3 higher than 92% and the selectivity of nitrobenzene higher than 97% under conditions of 423 K, $\text{SV}=3200$ ml/g h. This implies that the additives do not affect the activity of the supported sulfuric acid within 11 hours.

Secondly in order to investigate whether the additives can prevent the effusion of sulfuric acid and affect the lifetime of catalyst, we selected niobic acid and heteropolyacid as additives and examined their effect on catalysis stability. We have not examined the stability of $\text{H}_2\text{SO}_4\text{-H}_3\text{BO}_3/\text{SiO}_2$, because boric acid crystal was found at the bottom of the reactor under experimental condition after several hours.

To avoid taking a long time to determine the lifetime of the catalyst under our experimental condition using 10% $\text{H}_2\text{SO}_4/\text{SiO}_2$, the catalysts containing 5% $\text{H}_2\text{SO}_4/\text{SiO}_2$ were selected as standard condition to compare their durability. The results were showed in **Table 2**.

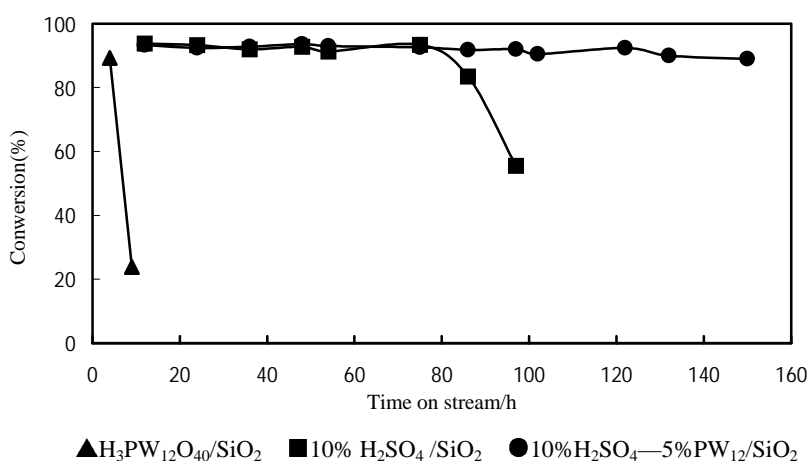
Table 2 Influence of additives on catalyst stability

| Catalysts | Time (h) | Yield (%) |
|--|----------|-----------|
| 5% $\text{H}_2\text{SO}_4/\text{SiO}_2$ | 24 | 43.4 |
| 5% $\text{H}_2\text{SO}_4\text{-}5\% \text{Nb}_2\text{O}_5/\text{SiO}_2$ | 26 | 47.8 |
| 5% $\text{H}_2\text{SO}_4\text{-}5\% \text{SiW}_{12}/\text{SiO}_2$ | 27 | 82.9 |
| 5% $\text{H}_2\text{SO}_4\text{-}5\% \text{PW}_{12}/\text{SiO}_2$ | 24 | 86.0 |

Reaction condition: $T=423 \text{ K}$, $\text{SV}=3200 \text{ ml/g h}$

From **Table 2** we can find that the catalysts of 5% $\text{H}_2\text{SO}_4\text{-}5\% \text{SiW}_{12}/\text{SiO}_2$ and 5% $\text{H}_2\text{SO}_4\text{-}5\% \text{PW}_{12}/\text{SiO}_2$ kept higher activity than that of 5% $\text{H}_2\text{SO}_4/\text{SiO}_2$ after 24 h on stream. It means that $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ and $\text{H}_3\text{PW}_{12}\text{O}_{40}$ may hold back the effusion of sulfuric acid. For clarification, we compared the lifetime of 10% $\text{H}_2\text{SO}_4/\text{SiO}_2$, 10% $\text{H}_2\text{SO}_4\text{-}5\% \text{PW}_{12}/\text{SiO}_2$ and supported phosphotungstic acid catalysts. The result was showed in **Figure 1**.

Figure 1 Influences of additives on the lifetime of the catalyst



From **Figure 1**, it can be seen that the two catalysts with sulfuric acid show rather high stability, and the lifetime of $\text{H}_2\text{SO}_4\text{-PW}_{12}/\text{SiO}_2$ is much longer than that of $\text{H}_2\text{SO}_4/\text{SiO}_2$. Besides, the supported phosphotungstic acid has relatively high initial activity

but it lost activity very quickly (within 10 h), so the longer lifetime of $\text{H}_2\text{SO}_4\text{-PW}_{12}/\text{SiO}_2$ cannot come from $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$ itself. It is clear that the existence of phosphotungstic acid increases the stability of the $\text{H}_2\text{SO}_4/\text{SiO}_2$ catalyst and hold back the effusion of sulfuric acid. It may be that phosphotungstic acid has the character of pseudo-liquid phase and sulfuric acid is a small and polar molecule, so it can enter the inner of phosphotungstic acid freely, just like water and alcohol molecule do⁷. So the effusion of sulfuric acid decreased.

In addition, for the kind of sulfuric acid catalyst, it may exist in liquid form under our preparation conditions, so the surface of catalyst has the character of mobility and the surface active center can be renewed all the time, which makes the catalyst different from the general solid acid catalyst.

Conclusion

To sum up, $\text{H}_2\text{SO}_4\text{-PW}_{12}/\text{SiO}_2$ is a durable catalyst with the characteristic of high activity and high selectivity for vapor phase nitration of benzene by diluted nitric acid at 423 K. It retains the advantages of using sulfuric acid as catalyst. The addition of phosphotungstic acid holds back the effusion of sulfuric acid. By employing this kind of catalyst, it would be possible that the traditional (mixed acid) method of nitration can be replaced by vapor phase nitration, so as to provide a new technology for nitration without environmental problem.

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