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Superior Silver Sorbents for Removing 2-Vinyl Thiophene from Styrene by π-Complexation

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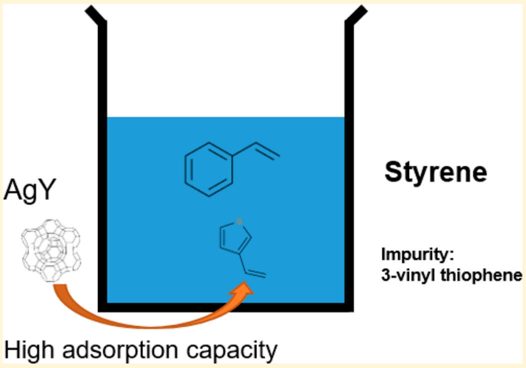
ABSTRACT: Styrene made from raw pyrolysis gasoline contains sulfur impurities such as 2-vinyl thiophene. We prepared three sorbents, namely, AgY, $AgNO_3/\gamma\text{-}Al_2O_3$, and $AgNO_3/SiO_2$, to remove 2-vinyl thiophene from styrene. All three sorbents showed good desulfurization performance while AgY had the highest sulfur capacity. This was due to π-complexation, where the silver cations in AgY can bond 2-vinyl thiophene more strongly than styrene. The desulfurization capacity of $AgNO_3/\gamma\text{-}Al_2O_3$ was better than that of $AgNO_3/SiO_2$ when taking its lower silver loading and surface area into consideration. Moreover, prewetting the sorbents was critical for desulfurization but can cause polymerization. Comparison between desulfurization of gasoline and styrene, using AgY, shows its superior sulfur adsorption capacity for desulfurization of styrene. A possible mechanism on the preferential adsorption for 2-vinyl thiophene over styrene by Ag^+ is given via the comparison between thiophene and benzene.



1. INTRODUCTION

Styrene, the precursor of polystyrene, is an important chemical used to produce latex, synthetic rubber, and polystyrene resins by polymerization. The resins are raw materials for the manufacture of plastics, which are commonly used in food, safety, and health industries. The purity and stability of the styrene monomer are crucial to meet the desired quality. Impurities may inhibit the polymerization process and thus jeopardize the mechanical properties of the polymer. The color of the polymer may also be affected by the impurities. Furthermore, impurities can negatively influence the stability of styrene monomer during storage because of the reactive styrene vinyl group. It can lead to premature polymerization, causing styrene loss and potential fouling of the system.

Although the catalytic dehydrogenation of ethylbenzene is the major source of styrene production, advances in technologies allow us to separate styrene from the hydrocarbon streams, such as pyrolysis gasoline.[1,2] Despite its high cost, further advances may make it economically feasible in the near future. For example, the styrene can be recovered from the raw pyrolysis gasoline derived from the steam cracking of naphtha, gas oils, and natural gas liquids.[3] However, the styrene obtained by separation is generally inferior to that obtained by the catalytic dehydrogenation of ethylbenzene due to the higher sulfur impurities, especially 2-vinyl thiophene.

Selective adsorption by π-complexation has drawn the attention of researchers. It has been used to separate organic sulfur components from fuels.[4−13] The selectivity of π-complexation adsorption is higher than that of physical adsorption because the π-complexation bonds are stronger than those of van der Waals interactions. Meanwhile, the interactions are still weak enough to be broken by moderate changes in temperature or pressure. Zeolites containing cuprous and silver cations are the superior sorbents for desulfurization by π-complexation. Our research group invented and continuously developed π-complexation sorbents to remove thiophenes from liquid fuels.[14−18] Previous results showed the sulfur content was reduced from 430 to <0.2 ppmw in a commercial diesel fuel.[19] Therefore, these π-complexation sorbents may be potentially useful in the adsorption of 2-vinyl thiophene from styrene. Note that the application of π-complexation sorbents in removing 2-vinyl thiophene from styrene will require prewetting treatment, which is absent in the conventional desulfurization of thiophenes from liquid fuels. The sorbents may also have side effects such as premature polymerization. Therefore, it is worth investigating the sorbents for removing 2-vinyl thiophene from styrene.

In this work, we prepared silver-based sorbents for removing 2-vinyl thiophene from styrene. The polymerization effect of the sorbents has been evaluated as well.

2. EXPERIMENTAL SECTION

2.1. Preparation of Sorbents. Three types of silver sorbents were prepared, namely, AgY, $AgNO_3/\gamma\text{-}Al_2O_3$, and $AgNO_3/SiO_2$.

AgY was prepared by the ion-exchange procedure. NaY (5 g) (Zeolyst International, SiO_2/Al_2O_3 = 5.1, surface area = 900

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m^2/g) was added to 150 mL of 0.2 M $AgNO_3$ solution under constant stirring. After ion-exchange for 48 h at room temperature, the product was filtered, washed with deionized water, and dried at 100 °C overnight. The silver content was approximately 15 wt % according to Shimizu et al., as the procedure used in this work was identical to the one used in that work.[20]

Both $AgNO_3/\gamma\text{-}Al_2O_3$ and $AgNO_3/SiO_2$ were prepared using impregnation. $\gamma\text{-}Al_2O_3$ (Alfa Products) and SiO_2 (Strem Chemicals) had a surface area of 77 and 695 m^2/g, respectively.

Our previously used procedure, by Padin and Yang, was used in this work.[21] The surface area of substrates was very important to achieve the monolayer dispersion of silver nitrate. Based on the calculation from our report,[21] the monolayer dispersion of $AgNO_3$ on the substrate required an $AgNO_3$ content of 4.77×10^{-4} g/m^2. Therefore, $AgNO_3$ loadings on $\gamma\text{-}Al_2O_3$ and SiO_2 were supposed to be 37 and 332 mg/g. In practice, the calculated amount of $AgNO_3$ was dissolved in 15 mL of deionized water, followed by adding 5 g of $\gamma\text{-}Al_2O_3$ or $AgNO_3/SiO_2$. The samples had been stored at room temperature for 3 h before they were dried at 100 °C overnight.

For sorbents, one of the most important characteristics is the BET surface area. AgY was prepared using ion-exchange so that its surface area was not likely to change. $AgNO_3/SiO_2$ and $AgNO_3/Al_2O_3$ were prepared using impregnation to achieve a monolayer dispersion of silver species. According to literature data,[22] the monolayer dispersion did not lead to drastic decreases in surface area. Therefore, the surface areas of the three sorbents were similar to the corresponding substrates.

2.2. Adsorption Experiments. Two sets of static adsorption experiments were carried out in a batch reactor. Prior to the experiments, the sorbents can be prewetted with toluene. For the first type, 1 g of sorbents (dry basis), with or without prewetting, were placed into a flask containing 10 mL of solution containing 300 ppm of 2-vinyl thiophene in styrene (2-vinyl thiophene and styrene were provided by GTC Technology). It was used to examine the effects of prewetting on desulfurization and polymerization. For the second type, 1 g of sorbents (dry basis) was put into a flask containing 10 mL of solution containing 60 or 120 ppm of 2-vinyl thiophene in styrene. This was for obtaining the adsorption equilibrium data. All samples were stored at room temperature for 4 h to reach adsorption equilibrium.

The concentrations of 2-vinyl thiophene were analyzed by GC with a sulfur detector. The polystyrene was analyzed on the basis of the standard of ASTM D2121.

A modified Henry's Law was used to fit the adsorption isotherms.

$$K_H \times C = \text{ads}$$

where K_H is the Henry's Law constant, C (ppm) the concentration of 2-vinyl thiophene in the styrene, and ads (mg S/g) the adsorption amount of 2-vinyl thiophene in the sorbents. This isotherm is also the approximation of the Langmuir isotherm in the low-concentration range.

3. RESULTS AND DISCUSSION

The first adsorption experiment was carried out to determine the effects of prewetting on desulfurization and polymerization.

Experiments were performed by placing 1 g of sorbents (dry basis) with or without prewetting into a flask containing 10 mL of solution containing 300 ppm of 2-vinyl thiophene in styrene for 4 h. The purpose of prewetting the sorbents was to eliminate the heat release when in contact with the styrene, which may cause premature polymerization. The results are shown in Table 1. It can be seen that prewetting played a crucial role in desulfurization. The sorbents without prewetting did not adsorb sulfur. The desulfurization capacity of prewetted AgY was the best among all sorbents, while that of the prewetted $AgNO_3/\gamma\text{-}Al_2O_3$ and $AgNO_3/SiO_2$ was quite similar. Surprisingly, polymer content in the styrene treated by the prewetted sorbents was even higher than that in the styrene treated by sorbents without prewetting. Generally, the polymerization in the AgY- and $AgNO_3/\gamma\text{-}Al_2O_3$-treated styrene was much lower than that in the $AgNO_3/SiO_2$-treated one.

Table 1. Desulfurization Performance and Polymerization of Different Sorbents

sample	pretreatment	sulfur removal (%)	polymer (%)
AgY	not prewetted	0	0.4
	prewetted	12.9	1.7
$AgNO_3/\gamma\text{-}Al_2O_3$	not prewetted	0	0
	prewetted	7.1	0.3
$AgNO_3/SiO_2$	not prewetted	0	5.5
	prewetted	5.4	11.9

Prewetting is a common approach to pretreating sorbents. It can eliminate heat released when sorbents are in contact with the liquid. It also allows better interaction between the solid and liquid phases. According to a previous work, the sorbents were prewetted by hydrocarbons before they were used for desulfurization of diesel fuels.[23] In our experiments, the prewetting treatment did not necessarily inhibit the polymerization. Rather, it facilitated the process. We might conclude that the heat released by the sorbents without prewetting was not the main cause for polymerization. Instead, the prewetted samples served as "catalysts" for polymerization. Moreover, $AgNO_3/SiO_2$ was the most effective "catalyst" among all tested.

Although prewetting can lead to unwanted polymerization, it is crucial for desulfurization. As we can see, sorbents without prewetting did not absorb the 2-vinyl thiophene at all. In contrast, the prewetted sorbents did remove the sulfur from styrene. AgY was the best sorbent due to π-complexation. Our previous studies showed that π-complexation bonds between Cu^+ or Ag^+ in ion-exchanged zeolites and thiophene are stronger than the bonds between cations and benzene. Here, benzene was a model compound for aromatics, whereas thiophene represented the basic compound for sulfur.[19] In this work, the system was quite similar, in that 2-vinyl thiophene represented the sulfur compound while styrene was aromatic. It justified the excellent desulfurization performance of AgY. In comparison, there is no distinctive difference in the sulfur removal capacities of $AgNO_3/\gamma\text{-}Al_2O_3$ (7.1%) and $AgNO_3/SiO_2$ (5.4%). However, it should be noted that the silver loading of $AgNO_3/\gamma\text{-}Al_2O_3$ was much lower than that of $AgNO_3/SiO_2$ owing to the lower surface area. In this case, we can conclude that the desulfurization performance per unit of Ag loading (or per unit of surface area) of $AgNO_3/\gamma\text{-}Al_2O_3$ was better than that of $AgNO_3/SiO_2$. This result may be related to that of Sarda et al., who evaluated the desulfurization performance of Ni/Al_2O_3 and Ni/ZSM-5. It was found that the alumina support enables both the chemical and physical adsorption pathways toward removing the organic sulfur component.[24] Therefore, the removal of 2-vinyl thiophene from styrene may be partially attributed to these mechanisms.

As discussed, prewetting is important to desulfurization. In the second experiment, we used only the prewetted sorbents. In practice, 1 g of prewetted sorbents (dry basis) was put into the flask containing 10 mL of solution containing 60 or 120 ppm of 2-vinyl thiophene in styrene. The adsorption equilibrium data are shown in Figure 1. The points in Figure 1 were fitted linearly. The slopes of the fitted lines in Figure 1 were interpreted as Henry's Law constants, which are listed in Table 2.

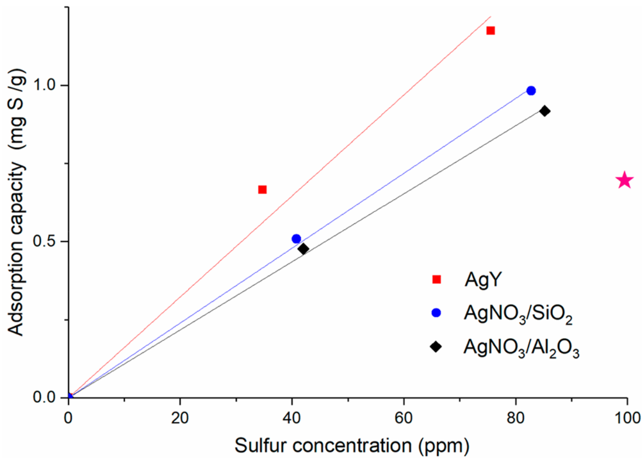

Figure 1. Desulfurization performance of sorbents at different sulfur concentrations (as ppmw of 2-vinyl thiophene in styrene). The added symbol (star) shows the capacity of AgY for selective adsorption of thiophene (at 100 ppmw) from a model gasoline.[28]

Table 2. Henry's Law Constants of Different Sorbents for Desulfurization of Styrene

sample	K_H	R^2
AgY	1.62×10^{-2}	0.989
AgNO$_3$/γ-Al$_2$O$_3$	1.09×10^{-2}	0.999
AgNO$_3$/SiO$_2$	1.20×10^{-2}	0.999

As we can see, AgY was the best adsorbent at lower sulfur concentration, which was in accordance with the data in Table 1. Meanwhile, AgNO$_3$/γ-Al$_2$O$_3$ and AgNO$_3$/SiO$_2$ showed a similar performance, though AgNO$_3$/SiO$_2$ had a slightly better value in adsorbed amount, which was in conflict with the data in Table 1. This might be due to errors in the sulfur analysis. The R^2 values for the three fitting lines were all above 0.989, suggesting that the calculated Henry's Law constants were reasonable. The K_H values for AgY, AgNO$_3$/γ-Al$_2$O$_3$, and AgNO$_3$/SiO$_2$ were 1.62×10^{-2}, 1.09×10^{-2}, and 1.20×10^{-2}, respectively, where we can conclude that the AgY has the best adsorption capacity of 2-vinyl thiophene from styrene.

One may suggest adding the adsorption capacity of other sorbents from references in order to make the results more comparable. Although that is reasonable, it is not realistic because there is no report on the desulfurization of 2-vinyl thiophene elsewhere to our best knowledge. The closest comparison would be to provide the desulfurization of thiophene and its derivatives over numerous sorbents given in a review[25] on that subject. However, that may be misleading because the sorbents, sorbate, systems, and sulfur concentrations in the literature are different from the ones in our experiment. So, no direct comparison can be made to determine which sorbent is better. This would be a good response to any argument that the adsorption capacity in our experiment was lower than those reported in the previous studies.[26,27]

It is interesting to compare the desulfurization capacities of AgY for gasoline and that for styrene (i.e., this work). Using a fixed-bed flow system, Michlmayr of Chevron[28] studied the selective adsorption of thiophene of AgY from a hydrofined C_5-C_6 cut to which was added 20 vol % C_5-C_6 olefins and 100 ppmw of thiophene. A sulfur-free gasoline was obtained, and the saturated capacity for thiophene was 0.023 mmol/g (at 100 ppmw thiophene feed concentration, at 22 °C). Michlmayr's results showed that AgY is a highly sulfur-selective sorbent and has a high capacity. Compared to the results shown in Figure 1, it can be seen that AgY is also a high-capacity sorbent for desulfurization of styrene. This comparison shows that the Ag sorbents studied in this work are superior for the desulfurization of styrene. Further work is needed to study sorbent regeneration and cyclic adsorption–desorption performance.

Finally, a note on the possible mechanism of the preferential adsorption for 2-vinyl thiophene over styrene by Ag^+ is given. The mechanism of π-complexation is best understood through molecular-orbital-theory calculations. Detailed molecular-orbital comparison of adsorption or binding for thiophene versus benzene on Ag–Y has been performed in our laboratory.[19,29] Our results showed that the binding involved two steps (using thiophene as an example): (a) σ-donation of π-electrons of thiophene to the 5s orbital of Ag, and (b) d–π^* back-donation of electrons from the 4d orbitals of Ag to π^* orbitals of thiophene. More importantly, the π-complexation bond between Ag^+ and thiophene (20.0 kcal/mol) was stronger than that with benzene (19.1 kcal/mol), which was verified by experimental measurements of heat of adsorption.[19] The pair of compounds considered in this work (2-vinyl thiophene versus styrene) is, respectively, thiophene and benzene with a vinyl group ($-CH{=}CH_2$) attached. The vinyl group will make a small (smaller than the aromatic rings) and equal or nearly equal (comparing the two adsorbates) contribution to the binding to Ag via the double bond of the vinyl group. Thus, it is reasonable to expect that the binding for 2-vinyl thiophene is stronger than that for styrene by Ag^+. Further studies, such as molecular-orbital calculations and experimental heat of adsorption comparisons, are needed.

4. CONCLUSION

We prepared three sorbents, namely, AgY, AgNO$_3$/γ-Al$_2$O$_3$, and AgNO$_3$/SiO$_2$, for removing 2-vinyl thiophene from styrene. AgY was the best sorbent with regards to the best desulfurization capacity and limited polymerization effects. The superior performance of AgY was owed to π-complexation, where the AgY would bond 2-vinyl thiophene more strongly than styrene. Also, the desulfurization performance of AgNO$_3$/γ-Al$_2$O$_3$ was better than that of AgNO$_3$/SiO$_2$ when taking its lower silver loading and surface area into consideration. Furthermore, prewetting was critical for desulfurization but can cause polymerization. Comparison between desulfurization of gasoline and styrene, using AgY, shows its superior sulfur adsorption capacity for desulfurization of styrene.

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Notes

The authors declare no competing financial interest.

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