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ScienceDirect
Mendeleev Commun., 2009, **19**, 108–109

Mendeleev Communications

Pd/Al$_2$O$_3$ catalyst for selective hydrogenation of benzene in benzene–toluene mixture

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DOI: 10.1016/j.mencom.2009.03.020

Pd/Al$_2$O$_3$ demonstrates (in comparison with Pt/Al$_2$O$_3$ and Ni/Al$_2$O$_3$) higher selectivity toward benzene hydrogenation in competitive hydrogenation of a benzene–toluene mixture, which can be enhanced (up to 76%) by the increase of overall reaction pressure up to 37 atm.

To limit environmental pollution, many countries all over the world are developing and enacting very stiff standards for the acceptable content of harmful substances in the exhaust gases of automotive vehicles. The most stringent restrictions are imposed on benzene due to the carcinogenicity of its combustion materials for humans. The standard EN 228 (Euro-3) accepted in Europe (2000) limits benzene content in motor gasoline at most 1%.[1] In the USA (1998) benzene content in petroleum restricted to 0.8%.[2,3] The standard technique to remove benzene from gasoline is pressure swing adsorption.[4–6] Alternatively, the benzene content can be decreased by selective benzene hydrogenation over a metal catalyst. However, selective hydrogenation of the benzene ring in gasoline is hindered by the preferable adsorption of substituted aromatics contained in the motor fuel on the catalyst surface,[7,8] which results in preferable hydrogenation of the substituted molecules. On the other hand, it was demonstrated that this effect strongly depends on the electronic structure of the metal.[9] The most favourable results were obtained for Pt and Pd catalysts. Therefore, in this study we explore the catalytic properties of Pt/Al$_2$O$_3$, Pd/Al$_2$O$_3$ and Ni/Al$_2$O$_3$ in hydrogenation of a benzene–toluene mixture as a model reaction and the influence of the most important factors, which can affect the selectivity of the process: (1) reaction temperature, (2) overall aromatics conversion and (3) overall reaction pressure. A choice of Ni was dictated by a similarity of its electronic structure to Pd and Pt due to their position in the Periodic Table.

The Pt-, Pd- and Ni-containing catalysts were prepared by incipient-wetness impregnation with a water solutions of [Pt(NH$_3$)$_4$]Cl$_2$, [Pd(NH$_3$)$_4$](NO$_3$)$_2$ and Ni(NO$_3$)$_2$, respectively. Additional experiments revealed that the nature of the precursor (chloride or nitrate) does not notably affect the catalytic data. The resulting material was calcined in flowing air at 500 °C (2 h) and reduced in H$_2$ flow at 350 °C (1 h). Competitive hydrogenation of a benzene–toluene mixture (1:1 molar ratio) was carried out at a total aromatic partial pressure ~60 Torr, and a hydrogen partial pressure of 670 Torr. Catalytic performance of each catalyst was evaluated at two temperatures: 110 and 160 °C by changing LHSV (from 0.25 to 1 h^{-1}) in order to ensure variation of the overall aromatics conversion over a wide range (2–3% to 90–100%).

Overall aromatics conversion [A_{conv} (%)] was calculated by the following expression:

$$A_{\mathrm{conv}} = (m_{\mathrm{benzene}} conv_{\mathrm{benzene}} + m_{\mathrm{toluene}} conv_{\mathrm{toluene}}) \times 100,$$

where m_{benzene} and m_{toluene} are the molar ratios of benzene and toluene in aromatics mixture, respectively; $conv_{\mathrm{benzene}}$ and $conv_{\mathrm{toluene}}$ are the benzene and toluene conversions, respectively.

Selectivity toward benzene hydrogenation [S_{benzene} (%)] was calculated by the following equation:

$$S_{\mathrm{benzene}} = \frac{m_{\mathrm{benzene}} conv_{\mathrm{benzene}}}{A_{\mathrm{conv}}} \times 100.$$

The dependences of the selectivity in benzene hydrogenation on the overall aromatics conversion for 0.9% Pt/Al$_2$O$_3$, 1.6% Pd/Al$_2$O$_3$, and 3.1% Ni/Al$_2$O$_3$ are shown in Figure 1. We used different metal concentrations to equalize the catalytic activity of these samples and to compare catalytic performance in the same temperature range. It should be noted that all catalysts demonstrated very similar activities in hydrogenation of the model mixture. Comparing the data obtained for Ni/Al$_2$O$_3$ and Pt/Al$_2$O$_3$ catalysts in terms of selectivity for benzene hydrogenation, we can conclude that the performance of Ni/Al$_2$O$_3$ is very similar to that of the Pt/Al$_2$O$_3$ catalyst. At low aromatics conversion, toluene hydrogenation definitely prevails over benzene hydrogenation. Thus, selectivity towards benzene hydrogenation at low conversion is ~30–35%. With increasing aromatics conversion, selectivity for benzene hydrogenation increases gradually. However, over the whole range of aromatics conver-

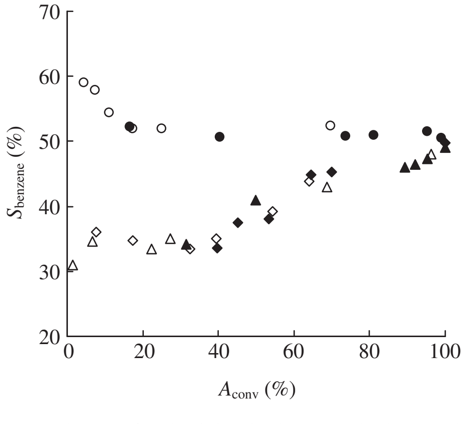

Figure 1 Dependence of selectivity in benzene hydrogenation on the overall aromatics conversion for Pd/Al$_2$O$_3$ (○, ●), Pt/Al$_2$O$_3$ (◇, ◆) and Ni/Al$_2$O$_3$ (△, ▲) catalysts in the hydrogenation of benzene–toluene mixture (1:1 molar ratio). Open symbols, reaction at 110 °C; solid symbols, reaction at 160 °C.

sion, $S_{benzene}$ remains lower than 50%. This implies that toluene hydrogenation prevails.

The performance of Pd/Al_2O_3 differs significantly from the performance of Ni- and Pt-containing catalysts. The selectivity of Pd/Al_2O_3 for benzene hydrogenation is greater than 50% over the entire range of aromatics conversion (Figure 1). This implies that Pd catalyst shows a tendency to preferably hydrogenate benzene. This tendency is particularly pronounced at low conversion (Figure 1). With increasing overall aromatics conversion, selectivity for benzene hydrogenation diminishes. However, it remains above 50% over the whole conversion range. Only cyclohexane and methylcyclohexane were identified as products. Neither isomerisation nor cracking was observed.

The data obtained can be explained by the difference in the adsorption coefficients of benzene and substituted aromatics.[9] The ratio $K_{T/B}$ of the adsorption coefficients of toluene and benzene determined from a kinetic analysis of the competitive hydrogenation of these hydrocarbons differs for the Pt and Pd catalysts.[9] For the Pd-containing catalyst $K_{T/B} = 1$, which means that benzene is as strongly adsorbed as toluene, whereas $K_{T/B} = 8$ for the Pt-containing catalyst corresponding to a prevailing toluene adsorption on the vacant Pt sites. The $K_{T/B}$ ratios follow in the range Pd < Pt < Rh < Ir << Os < Ru.[9] In spite of the fact that $K_{T/B}$ ratio was not calculated for Ni-containing catalyst, our data indicate that its value is close to that of Pt. Analyzing the effect of the reaction temperature on the selectivity of benzene hydrogenation for the Ni/Al_2O_3, Pt/Al_2O_3 and Pd/Al_2O_3 catalysts (Figure 1), we can conclude that $S_{benzene}$ is not dependent on the reaction temperature (at least in the investigated temperature range).[8] The selectivity for benzene hydrogenation is governed by the overall aromatics conversion, and the reaction temperature does not influence on the dependence of $S_{benzene}$ on A_{conv}. Presumably, the observed selectivity independence of temperature is due to a constancy of $K_{T/B}$ ratio within temperature range studied.

According to the experimental data obtained, Pd appears to be the most promising metal in terms of selectivity in benzene hydrogenation. These data are in a good agreement with the literature.[8] However, Poondi and Vannice analyzed the kinetic parameters for this reaction under atmospheric pressure and at low aromatics conversion (below 15%).[8] Therefore, for Pd/Al_2O_3 sample we examined the influence of elevated pressure (1–37 atm) on the catalyst selectivity in terms of benzene hydrogenation. The basic idea behind this experiment was the following. As it was discussed above, the main reason of the low selectivity in the presence of substituted aromatics lies in the stronger adsorption of substituted aromatics on the metal surface. Thus, substituted aromatics block the metal, making the surface inaccessible for benzene. By increasing the overall reaction pressure, it is possible to replace a part of aromatics with adsorbed hydrogen. Thus, there is a chance to liberate a part of the metal surface from substituted aromatics and make it accessible for benzene adsorption.

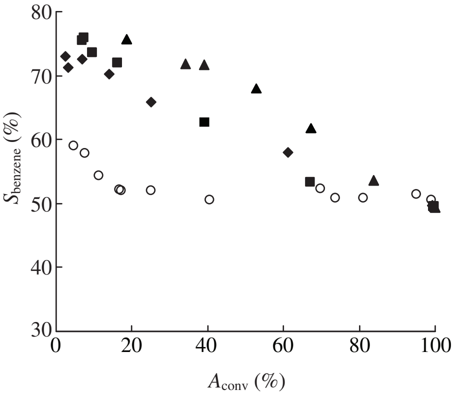

Figure 2 Effect of the overall reaction pressure on the performance of Pd/Al_2O_3 catalyst in the hydrogenation of benzene–toluene mixture (1:1 molar ratio): (○) 1 atm, (◆) 11 atm, (■) 23 atm and (▲) 37 atm.

The data on the competitive hydrogenation of the benzene–toluene mixture at elevated pressure (Figure 2) indicate the steady increase in the reaction selectivity toward benzene hydrogenation with the increase in the overall reaction pressure. The most encouraging results were obtained in the experiments carried out at 37 atm. As can be seen in Figure 2, even when overall aromatics conversion reaches 40%, selectivity for benzene hydrogenation exceeds 70%.

Clearly, the selectivity of benzene hydrogenation can be effectively improved by increasing overall reaction pressure. This fact can be explained by the increase of the surface concentration of the adsorbed hydrogen on the metal surface with an increase in the overall reaction pressure. This leads to a liberating of the metal surface from strongly adsorbed substituted aromatics and makes the metal surface more accessible for adsorption of benzene molecules.[10]

Analysis of reaction thermodynamics showed that toluene hydrogenation is favorable compared to benzene. However, the reaction is not affected by thermodynamics since the reaction temperature is significantly lower as compared to temperature when thermodynamics limitations become significant (> 200 °C at $P = 1$ atm, > 350 °C at $P = 37$ atm).

We are grateful to UOP LLC for the profound interest and support of this research.

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Received: 8th September 2008; Com. 08/3213