MODIFICATION OF SELECTIVITY AND CARBON DEPOSITION DURING THE INITIAL STAGES OF THE n-BUTANE DEHYDROGENATION OVER MONO AND BIMETALLIC CATALYSTS

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Abstract— The initial carbon deposition and the generation of dehydrogenating selectivity during the initial steps of the reaction are investigated for Pt and PtSn catalysts supported on pure and Na-doped alumina by using a pulse technique (injection of n-butane pulses). Results demonstrate that Pt supported on pure alumina is not a proper dehydrogenation catalyst. It shows a high hydrogenolytic and cracking behavior and an important carbon formation that deactivates the catalyst. However the combined presence of tin and sodium inhibits not only the carbon deposition reactions but also the C-C breaking reactions, increasing in an important way the dehydrogenating selectivity to the different butenes to a value about 80%.

Keywords — butane dehydrogenation, bimetallic catalysts, carbon deposition, generation of selectivity.

I. INTRODUCTION

The production of light molecular weight olefins, such as butenes (1-butene, cis- and trans-2-butene, and butadiene) from n-butane, is a process with high industrial interest (Haatch and Matar, 1981; Bhasin et al., 2001). This process is carried out at atmospheric pressure and at high temperatures due to the endothermy of the reaction. In these conditions, this process is complex with a series of competing reactions (like hydrogenolysis, cracking, isomerization) occurring simultaneously including significant carbon formation that is deposited on the surface of the metallic particles and on the support with the consequent catalyst deactivation. The catalysts used in this process must give high yields to butenes, with a minimum deactivation by coke. For this reason, catalysts based on Pt with a promoter (Sn, Ge, In) and supported on non acid materials are used (Ballarini et al., 2010; Serrano-Ruiz et al., 2007; Sun et al., 2011).

In this paper, the phenomena occurring when n-butane pulses are injected over different Pt and PtSn catalysts supported on pure and Na-doped alumina are studied. By using a pulse technique, we can investigate the initial carbon deposition and the generation of dehydrogenating selectivity during the initial steps of the reaction. This technique is adequate to determine quickly the best promoter of the active metal for a determined dehydrogenation process.

II. EXPERIMENTAL

A commercial γ-Al2O3 (CK-300 from Cyanamid Ketjen, S\textsubscript{BET} = 180 m\textsuperscript{2}g\textsuperscript{-1}) previously calcined in flowing air at 650°C during 3 h was used as the support. The alumina doped with Na (0.5 wt%) was obtained by impregnating the support with an aqueous solution of NaOH, using a volume of solution/weight of support ratio of 1.4 mL g\textsuperscript{-1} and a NaOH concentration such as to obtain the desired Na loading on the support. Then, Pt and Sn were incorporated to the doped support by successive impregnation. First Pt was deposited from an aqueous solution of H\textsubscript{2}PtCl\textsubscript{6} (0.011 M) to obtain a Pt loading of 0.3 wt%, and dried at 120°C for 12 h. Then the samples were impregnated with a hydrochloric solution of SnCl\textsubscript{2} to obtain a Sn loading of 0.5 wt%. The impregnation volume/support weight ratio was 1.4 mL g\textsuperscript{-1} in all cases. After the impregnation, samples were dried at 120°C. Besides, the monometallic Pt (0.3 wt%)/Al\textsubscript{2}O\textsubscript{3} catalyst was prepared by alumina impregnation with an aqueous solution of H\textsubscript{2}PtCl\textsubscript{6}. The PtSn/Al\textsubscript{2}O\textsubscript{3} sample was prepared by successive impregnation, first Pt (0.3 wt%), dried and finally Sn (0.5 wt%) was deposited from SnCl\textsubscript{2}. Then, samples were dried at 120°C and finally calcined at 500°C in flowing air for 3 h.

The acid properties of pure and Na-doped alumina samples were determined by isopropanol (IP) dehydration reaction at 250°C and atmospheric pressure in a flow reactor, using a H\textsubscript{2}/IP molar ratio of 18 and a space velocity of 32 h\textsuperscript{-1}.

The pulse experiments were performed by injecting pulses of pure n-butane (0.5 mL STP) into the catalytic bed (0.1 g of sample) at 530°C. The catalytic bed was kept under flowing He (30 mL min\textsuperscript{-1}) between the injections of two successive pulses. Prior to the experiments, all samples were reduced “in situ” under flowing H\textsubscript{2} at 530°C for 3 h. The composition of each pulse after the reaction was determined by using a GC-FID equipment with a packed column (Porapack Q). The temperature of the chromatographic column was 30°C. In these experiments the n-butane conversion was calculated as the difference between the chromatographic area of n-butane fed to the reactor (previously determined in a blank experiment) and the chromatographic area of non-reacted n-butane at the outlet of the reactor (loaded with catalyst), and this difference was referred to the chromatographic area of n-butane fed to the reactor. The selectivity to the different reaction products (i) was defined as the ratio: mol of product i/Σ mol of all products (except H\textsubscript{2}). The carbon amount retained by the catalyst after the injection of each pulse was calculated through a mass balance between the total carbon amount fed to the reactor and the total carbon amount detected by the chromatographic analysis at outlet of the reactor. The accumulative carbon retention was calculated as the sum of the carbon amount retained after each pulse.
Table 1: Values of n-butane conversion as a function of the pulse number for different catalysts.

<table>
<thead>
<tr>
<th>Pulses Number</th>
<th>Catalyst</th>
<th>(n\text{-butane conversion} (%)</th>
<th>Selectivity to butenes</th>
<th>Relative carbon retention (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pt/Al(_2)O(_3)</td>
<td>100</td>
<td>80</td>
<td>85</td>
</tr>
<tr>
<td>2</td>
<td>Pt/Al(_2)O(_3)-Na</td>
<td>93</td>
<td>61</td>
<td>78</td>
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<tr>
<td>3</td>
<td>Pt/Al(_2)O(_3)-Na</td>
<td>85</td>
<td>59</td>
<td>72</td>
</tr>
<tr>
<td>4</td>
<td>Pt/Al(_2)O(_3)-Na</td>
<td>82</td>
<td>52</td>
<td>68</td>
</tr>
<tr>
<td>5</td>
<td>PtSn/Al(_2)O(_3)</td>
<td>76</td>
<td>52</td>
<td>65</td>
</tr>
<tr>
<td>6</td>
<td>PtSn/Al(_2)O(_3)-Na</td>
<td>70</td>
<td>50</td>
<td>62</td>
</tr>
<tr>
<td>7</td>
<td>PtSn/Al(_2)O(_3)-Na</td>
<td>67</td>
<td>49</td>
<td>60</td>
</tr>
<tr>
<td>8</td>
<td>PtSn/Al(_2)O(_3)-Na</td>
<td>64</td>
<td>47</td>
<td>59</td>
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<tr>
<td>9</td>
<td>PtSn/Al(_2)O(_3)-Na</td>
<td>62</td>
<td>43</td>
<td>58</td>
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<tr>
<td>10</td>
<td>PtSn/Al(_2)O(_3)-Na</td>
<td>60</td>
<td>41</td>
<td>58</td>
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</table>

Test reactions of the metallic phase were performed in a differential flow reactor at atmospheric pressure. Cyclo-hexane (CH) dehydrogenation was carried out at 300ºC, by using a \(H_2/CH\) molar ratio of 29 and a CH flow rate of 6 mL h\(^{-1}\). The activation energy in CH dehydrogenation for different catalysts was obtained by measuring the initial reaction rate at 270, 285 and 300ºC. Cyclopentane (CP) hydrogenolysis was done at \(T = 300ºC\), \(H_2/CP\) molar ratio = 25 and a volumetric flow of CP = 6 mL h\(^{-1}\). Previous to test reactions, catalysts were reduced under \(H_2\) flow at 500 ºC. The sample weight used in these experiments was the appropriate to obtain a CH or CP conversion lower than 7% in order to obtain a differential behavior of the reactor. The reaction products were benzene and \(n\)-pentane for the first and second reaction, respectively. In both cases, the reaction products were analyzed by using a gas chromatographic system (packed column with Chromosorb and FID as detector).

III. RESULTS AND DISCUSSION

Results obtained in a pulse system are shown in Table 1 and in Figures 1 and 2, that displays the \(n\)-butane conversion, the selectivity to butenes and the relative carbon retention in the catalyst, respectively, as a function of the number of pulses, for different catalysts: Pt/Al\(_2\)O\(_3\), Pt/Al\(_2\)O\(_3\)-Na (0.5 wt%), PtSn/Al\(_2\)O\(_3\) and PtSn/Al\(_2\)O\(_3\)-Na (0.5 wt%).

It can be observed that the \(n\)-butane conversion (Table 1) was very high for the first pulses of butane injected to the monometallic Pt/Al\(_2\)O\(_3\) catalyst. In fact, the conversion for the first butane pulse is 100%, and it decreases as the number of pulses increases.

The selectivity to butenes (Fig. 1a) is negligible for the first pulse since there is a complete selectivity to methane (100%). For the successive pulses, the selectivity to olefins begins to increase up to a 13% for the 20\(^{th}\) pulse for Pt/Al\(_2\)O\(_3\) catalyst. The relative carbon retention (Fig. 2) increases quickly in the first pulses and then this increase becomes slower. Similar results were obtained during the initial stages of propane dehydrogenation using a similar monometallic catalyst (Jackson et al., 1997, McNamara et al., 2003). In order to understand the catalytic behavior of the monometallic catalyst during the injection of \(n\)-butane pulses, a discussion of these results is presented next.

Results presented in Table 1 and Figures 1a and 2 indicate that at the beginning of the reaction (first pulse) for Pt/Al\(_2\)O\(_3\) catalyst, the C-C bonds breaking reactions and the carbon formation are the main reaction routes. The carbon formation would produce a selective block-
ing of the most active sites, thus decreasing the selectivity to methane and increasing the selectivity to the different butenes. Taking into account previous results, the main reaction in the first pulse would be: \( \text{C}_8\text{H}_{18} \rightarrow 2\text{CH}_4 + 2\text{C} + \text{H}_2 \). After the injection of several pulses, the C-C bond breaking activity decreases while the selectivity to butenes begins to increase. In this sense, C formation would be playing a poisoning role of the high activity sites of the catalyst. Another point to be considered in the analysis is the acidity of the commercial gamma-alumina used as a support, since it can catalyze undesirable reactions of cracking and mainly the coke deposition due to the existence of acid tetrahedral Lewis Al\(^{13+}\) sites. The presence of acid tetrahedral Lewis Al\(^{13+}\) sites on the commercial \( \gamma \)-alumina was determined by FTIR of adsorbed CO in a previous paper (de Miguel et al., 1994).

The monometallic catalyst supported on Na (0.5 wt \%)-doped alumina displays a lower activity than Pt/Al\(_2\)O\(_3\) catalyst, which goes from 80 to 40% from the first to the 10\(^{th}\) pulse (Table 1). The selectivity to butenes is slightly higher, thus reaching values of 20% in the last pulse for Pt/Al\(_2\)O\(_3\)-Na catalyst (Fig. 1b). Besides, a pronounced diminution of the carbon retention values along the pulses is observed in Fig. 2 (about 40% of the carbon retained by the monometallic catalyst without Na). Hence the formation of carbon deposits on the catalyst in the n-butenes reaction at 530°C, with the con-sequent catalyst deactivation, is produced both by acid and metallic sites. The poisoning effect of the alkali metals like Na on the acid properties of the alumina was studied by means of the isopropanol dehydration to propylene and di-isopropylether. It was found that the isopropanol conversion at 250°C of the undoped gamma-alumina (about 60%) sharply decreases as the amount of Na increases, thus reaching a complete inhibition of the dehydration capacity (conversion < 1%) for a Na addition of 0.5 wt\%. In the case of coke formation by the metallic function, the reaction behaves as a demanding one and it is carried out on similar sites as the hydrogenolysis. This means that it requires determined ensembles of Pt atoms. In order to determine the influence of Na addition to Pt/Al\(_2\)O\(_3\) catalyst on the character of the metallic phase, test reactions were carried out. Table 2 shows the initial reaction values for cyclopentene hydrogenolysis at 300°C, and it can be observed an important decrease of the hydrogenolytic activity of the Pt/Al\(_2\)O\(_3\) catalyst as the Na addition to the active metal increases. Taking into account the sensitive-structure character of this reaction (Borgna et al., 1997), it can be inferred that the Na addition would cause a geometric modification of the metallic phase (besides the poisoning of the acid centers of the support) thus producing blocking and dilution effects. To determine if any electronic modification of Pt particles is produced due to Na addition, additional experiments of cyclohexene hydrogenolysis were carried out on Pt/Al\(_2\)O\(_3\) and Pt/Al\(_2\)O\(_3\)-Na catalysts and the results are shown in Table 2. CH dehydrogenation is a structure-insensitive reaction (Rodriguez-Ramos and Guerrero-Ruiz, 1992) which is carried out on a single site. The small decrease of the initial activity and the constancy of the activation energy values for this insensitive reaction clearly indicate the absence of electronic effects between Pt and Na.

From the above mentioned results, it is shown that the Na addition to Pt/Al\(_2\)O\(_3\) catalysts not only poisons the acid sites of the alumina with the consequent inhibition of cracking reactions but it also produces a geometric modification of Pt sites as well, thus decreasing the concentration of the hydrogenolytic ensembles. These important modifications in the catalyst structure by the Na addition would cause the increase of the hydrogenolysis selectivity, the decrease of the C-C bond breaking reactions and the pronounced diminution of the deactivation by the carbon deposition during the successive pulses.

On the other hand, Sn addition to Pt/Al\(_2\)O\(_3\) catalyst mainly increases in an important way the selectivity to all butenes. This selectivity increases with the addition of successive pulses (see Fig. 1c), reaching values of about 50% for the 20\(^{th}\) pulse. The promoter effect of Sn on Pt is much higher than that achieved by Na addition. Besides PtSn/Al\(_2\)O\(_3\) catalyst displays lower n-butenes conversions (Table 1) and carbon retention (Fig. 2) than Pt/Al\(_2\)O\(_3\). In the first pulse, the initial conversion decreases from 100% in the monometallic sample to about 85% in the bimetallic catalyst. In consequence, these results indicate that the Sn addition to Pt produces a decrease of the hydrogenolytic capacity of the active metal and hence it also decreases the coke deposition. The increase of the selectivity to all butenes in the

Table 2: Influence of Na and Sn addition to Pt/Al\(_2\)O\(_3\) on the cyclohexene dehydrogenation and cyclopentene hydrogenolysis activities (RCH and RCP) and activation energy (ECH) of CH hydrogenolysis.

<table>
<thead>
<tr>
<th>CATALYST</th>
<th>RCH (mol/h g)</th>
<th>ECH (Kcal/mol)</th>
<th>RCP (mol/h g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/Al(_2)O(_3)</td>
<td>108</td>
<td>23</td>
<td>2.4</td>
</tr>
<tr>
<td>Pt/Al(_2)O(_3)-Na</td>
<td>82</td>
<td>23</td>
<td>1.2</td>
</tr>
<tr>
<td>PtSn/Al(_2)O(_3)</td>
<td>29</td>
<td>33</td>
<td>negligible</td>
</tr>
<tr>
<td>PtSn/Al(_2)O(_3)-Na</td>
<td>28</td>
<td>28</td>
<td>negligible</td>
</tr>
</tbody>
</table>
PtSn/Al₂O₃ catalyst would be associated to the presence of a modified metallic phase. In order to understand the effects produced by Sn addition to Pt, results of CH dehydrogenation indicate that bimetallic PtSn/Al₂O₃ catalyst show a decrease of the activity and an important increase of the activation energy \( (E_{act}) \) with respect to the supported monometallic catalyst (Table 2). These behaviors can be related to a certain electronic interaction between Pt and Sn, with probable alloy formation. In the case of the CP hydrogenolysis, a negligible activity is observed for the different bimetallic catalysts supported on alumina (Table 2). This means that Sn also produces a geometric modification of the metallic phase and therefore the concentration of the metallic ensembles necessary for the CP hydrogenolysis reaction is drastically diminished. Even though Na addition only modifies geometrically the Pt, Sn modifies not only geometrically but also electronically the active metal. This fact produces a benefit in the catalytic behavior, mainly in the increase of the selectivity to butenes and the decrease of carbon retention. With respect to the acid sites of the alumina, Sn has a much lower poisoning effect on these sites like Na does. These remaining acidic sites can catalyze undesirable reactions of cracking and coking.

Taking into account not only the poisoning effect of Na on the acidic sites of the alumina but the dilution and blocking effects of the alkali metal on Pt particles, and the development of geometric and electronic effects of Sn on Pt sites as well, it is worth studying the associated influence of both elements (Na and Sn) on the catalytic performance of Pt/Al₂O₃ catalysts during the initial stages of the n-butane dehydrogenation. In this way, Figure 1d shows the influence of the injected butane pulses on the selectivity to butenes for PtSn/Al₂O₃-Na catalysts. Both monometallic catalysts (Figs. 1a and 1b) maintain a very low dehydrogenating selectivity to butenes (lower than 20%) and the bimetallic PtSn/Al₂O₃ catalyst shows a value of 50% for the last pulse. However the bimetallic sample supported on Na-doped alumina reaches the highest selectivity that goes from 60% (first pulses) up to 77% for the 20th pulse. This means that in the initial stages of the reaction, the beneficial effects of the tin addition to Pt/Al₂O₃-Na (0.5 wt%) catalyst are observed, thus inhibiting the hydrolytic and cracking reactions and hence increasing the dehydrogenating reactions towards the different butenes. With respect to the carbon retention during the initial stages of the reaction, the bimetallic catalyst supported on Na-doped alumina shows very low carbon retention along the different injected butane pulses (Fig. 2). This means that during the initial stages of the reaction, the combined presence of tin and sodium inhibits not only the coke deposition reactions but also the C-C breaking ones, increasing in an important way the dehydrogenating selectivity to the different butenes. With respect to the butane conversion (Table 1), the conversion from the 3rd to the 10th pulse reaches values about 35%, near to the equilibrium conversion for pure dehydrogenation.

In this PtSn/Al₂O₃-Na catalyst, the main reaction is the dehydrogenation of n-butane to butenes, while the hydrogenolysis, cracking and coke formation reactions are practically suppressed due to tin and Na effects on Pt.

The inhibition of hydrogenolysis reactions by the simultaneous presence of Na and Sn is also observed in the case of cyclopentane hydrogenolysis (Table 2), where a negligible activity is found for PtSn/Al₂O₃-Na catalyst. This can be due to important blocking and dilution effects produced by Sn and Na on Pt. Besides, this catalyst shows a decrease of the initial activity for CH dehydrogenation and an important increase of the activation energy with respect to the supported monometallic catalyst (see Table 2), which can be related to electronic modifications of the metallic phase. Moreover in this catalyst, the acid sites of the support are completely poisoned and they cannot promote undesirable reactions of cracking and coking. Hence the beneficial influence of the simultaneous addition of Sn and Na leads to a catalyst with an excellent behavior in selectivity and with a low carbon deposition.

**IV. CONCLUSIONS**

- The pulse technique is an adequate tool to determine quickly the best promoter of the active metal for a determined dehydrogenation process.
- At the beginning of the reaction for Pt/Al₂O₃ catalyst, the C-C bond breaking reactions and the carbon formation are the main reaction routes. The carbon formation would produce a selective blocking of the most active sites, thus decreasing the selectivity to methane and increasing the selectivity to the different butenes.
- Na addition to Pt/Al₂O₃ catalyst not only poisons the acid sites of the alumina with the consequent inhibition of cracking reactions but it also produces a geometric modification of Pt sites, thus decreasing the concentration of the hydrolytic ensembles.
- The promoter role of Sn on Pt strongly decreases the hydrogenolytic capacity of the active metal by geometric and electronic effects, thus leading to an improvement of the selectivity to butenes. Besides, it also decreases the carbon retention.
- The combined presence of tin and sodium inhibits not only the carbon deposition reactions but also the C-C breaking reactions, increasing in an important way the dehydrogenating selectivity to the different butenes up to a value of about 80%.

**REFERENCES**


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