

# Dehydrogenation of *n*-Butane to Butenes and 1,3-Butadiene over PtAg/Al<sub>2</sub>O<sub>3</sub> Catalysts in the Presence of H<sub>2</sub>

Hideki Kurokawa\*, Hayato Namoto, Atsuko Horinouchi, Mitsuhiko Sato, Mitsuki Usui, Hitoshi Ogihara, Hiroshi Miura

Graduate School of Science & Engineering, Saitama University, Saitama, Japan

Email: \*kuro@apc.saitama-u.ac.jp

**How to cite this paper:** Kurokawa, H., Namoto, H., Horinouchi, A., Sato, M., Usui, M., Ogihara, H. and Miura, H. (2018) Dehydrogenation of *n*-Butane to Butenes and 1,3-Butadiene over PtAg/Al<sub>2</sub>O<sub>3</sub> Catalysts in the Presence of H<sub>2</sub>. *Journal of Materials Science and Chemical Engineering*, 6, 16-24.

<https://doi.org/10.4236/msce.2018.67003>

**Received:** March 2, 2018

**Accepted:** July 1, 2018

**Published:** July 4, 2018

---

## Abstract

The Al<sub>2</sub>O<sub>3</sub>-supported PtAg catalysts were prepared and evaluated for the dehydrogenation of *n*-butane at 550°C in the presence of H<sub>2</sub>. The PtAg/Al<sub>2</sub>O<sub>3</sub> catalyst prepared by an impregnation method using the Cl<sup>-</sup> removing Pt/Al<sub>2</sub>O<sub>3</sub> and AgNO<sub>3</sub> showed a higher activity and selectivity to butenes and 1,3-butadiene compared to the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst, but a large amount of coke (about 30 wt% versus the catalyst weight) was formed during the dehydrogenation. The free Ag metal on the prepared catalyst dramatically promoted the coke formation, because the dehydrogenation of 1-butene over the Ag/Al<sub>2</sub>O<sub>3</sub> catalyst produced a large amount of coke. The Cl<sup>-</sup> addition to the Cl<sup>-</sup> free Pt/Al<sub>2</sub>O<sub>3</sub> catalyst decreased the coke formation by the reaction of the free Ag particles and Cl to form AgCl which was inactive for the coke formation. The highest initial conversion (50.3%) was obtained with the selectivity to butenes and 1,3-butadiene (butenes = 80.2% and 1,3-butadiene = 5.9%) when the PtAg/Al<sub>2</sub>O<sub>3</sub> catalyst modified with Cl<sup>-</sup> was used.

## Keywords

PtAg, Simple Dehydrogenation, Coke Formation, 1-Butene, 2-Butene

---

## 1. Introduction

The dehydrogenation of *n*-butane is an attractive route to produce 1,3-butadiene (BD), because *n*-butane is a cheaper raw material [1] [2]. Two possible routes are proposed by researchers in this field; one is the simple dehydrogenation (SDH) of *n*-butane, and another is the oxidative dehydrogenation (ODH) of *n*-butane. Although the SDH has the advantage in both equilibrium and a long catalyst

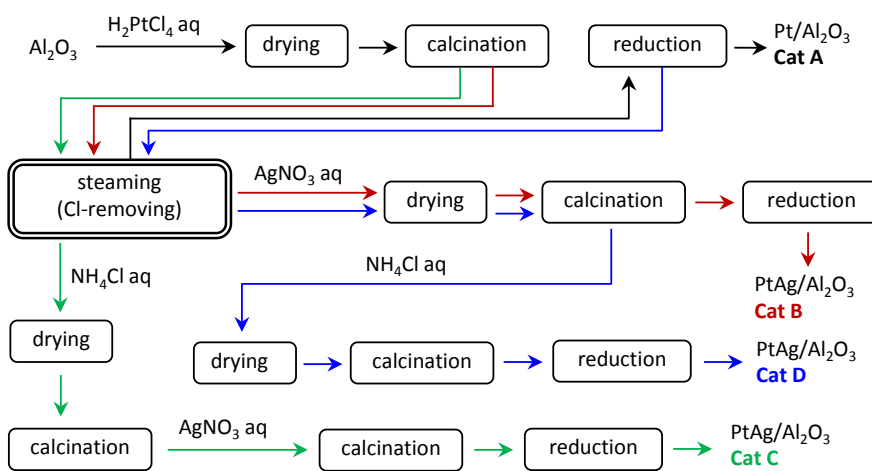
lifetime, the formation of oxygenates as a by-product causes the decreasing selectivity for BD and the increasing separation cost. The SDH process afforded a relatively high selectivity to BD, but a relatively high reaction temperature is necessary to obtain a high BD yield. An alumina-supported Pt catalyst and its bimetallic catalysts modified with a second element, such as Sn, In, Ge, Ga, Cu, Zn, Y, Bi, or alkali metals, were widely investigated for the SDH of *n*-butane to improve the catalytic activity and selectivity to BD [3]-[12]. In this study, we report a new Pt-based bimetallic catalyst for the SDH prepared by modification of the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst with Ag.

## 2. Experimental

### 2.1. Preparation of PtAg/Al<sub>2</sub>O<sub>3</sub> Catalyst

Crushed Al<sub>2</sub>O<sub>3</sub> (Neobead GB, Mizusawa Industrial Chemicals, Ltd., surface area = 190 m<sup>2</sup>·g<sup>-1</sup>) having a 250 - 850 μm size was used for the catalyst preparation. After the sieved Al<sub>2</sub>O<sub>3</sub> and an aqueous solution of H<sub>2</sub>PtCl<sub>4</sub> were added to a 200-ml eggplant flask, they were mixed at 40°C for 30 min. Water was removed from the flask using a rotary evaporator under reduced pressure, then the obtained pale-yellow granules were dried at 130°C overnight and calcined at 550°C for 3 h. Three types (**Cat B-D**) of PtAg/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by the following different methods (**Figure 1**). During the preparation of all the PtAg/Al<sub>2</sub>O<sub>3</sub> catalysts, residual Cl<sup>-</sup> derived from H<sub>2</sub>PtCl<sub>6</sub> was removed by a steam treatment to avoid AgCl formation by the reaction of a Ag compound with Cl<sup>-</sup> before the following steps.

The Cl<sup>-</sup> removing step was performed as follows in **Figure 1**. The granules calcined after the Pt addition were placed in the center of a stainless-steel tubular reactor (internal diameter = 10 mm), then the reactor was placed in a tubular muffle furnace. At 550°C, helium (50 ml/min) and steam (37 ml/min) were introduced into the reactor, and this steam treatment (steaming) was performed for 5 h to remove the Cl<sup>-</sup> for the **Cats B-D** preparation (30 min for the **Cat A** preparation).



**Figure 1.** Outline of catalyst preparation.

**Cat A:** Pt/Al<sub>2</sub>O<sub>3</sub> catalyst as a reference.

The calcined granules were reduced at 550 °C for 3 h to obtain the PtAg/Al<sub>2</sub>O<sub>3</sub> catalyst.

**Cat B:** Cl<sup>-</sup> free catalyst.

The Cl<sup>-</sup> removing granules and an aqueous solution of AgNO<sub>3</sub> were added to a 200-ml eggplant flask, then were mixed at 40 °C for 30 min. Water was removed from the flask using a rotary evaporator under reduced pressure, then the obtained pale-yellow granules were dried overnight at 130 °C, calcined at 550 °C for 3 h, and finally reduced at 550 °C for 3 h to obtain the PtAg/Al<sub>2</sub>O<sub>3</sub> catalyst (**Cat B**).

**Cat C:** Cl-added catalyst.

To the Cl<sup>-</sup> removing granules, an aqueous solution of NH<sub>4</sub>Cl was added to control the residual amount of Cl<sup>-</sup>. After mixing them for 30 min at room temperature, the water was removed, and the obtained granules were calcined at 550 °C. After the Cl<sup>-</sup> addition, the PtAg/Al<sub>2</sub>O<sub>3</sub> catalyst (**Cat C**) was prepared in the same manner as the **Cat B** preparation.

**Cat D:** Cl<sup>-</sup> added catalyst by modified method.

For this preparation, the H<sub>2</sub>PtCl<sub>4</sub>-supported on Al<sub>2</sub>O<sub>3</sub> was calcined and pre-reduced before the steaming (the Cl<sup>-</sup> removal step). The pre-reduction promoted the formation of the Pt catalyst having a high dispersion. The Ag addition was performed by impregnation using the Cl<sup>-</sup> removing granules and an aqueous solution of AgNO<sub>3</sub>. Chloride ions were added to the Ag-added Pt/Al<sub>2</sub>O<sub>3</sub> using an aqueous solution of NH<sub>4</sub>Cl by an impregnation method. The obtained precursor was calcined at 550 °C for 3 h, then reduced at the same temperature for 3 h (**Cat D**).

The prepared catalysts were characterized by a surface area analysis (Microtrac BEL, BELSORP-mini II), X-ray diffraction analysis (XRD, Bruker, D2 phaser), X-ray fluorescent analysis (XRF, PANalytical, PW 2400), thermogravimetry-differential thermal analysis (TG-DTA, Shimadzu, DTG-60), scanning electron microscopy with an energy dispersive X-ray analyzer (SEM-EDX, Hitachi, S-3400), and CO chemisorption (Hemmi Slide Rule, BP-1).

## 2.2. Simple Dehydrogenation of *n*-Butane

Half a gram of the prepared catalyst was placed in the center of the tubular reactor, and the reactor was placed in a tubular muffle furnace. All the catalysts were reduced with a 40 vol% H<sub>2</sub> (He balance) at the reaction temperature for 1 h just before the dehydrogenation. The dehydrogenation was performed at 550 °C for 6 h with hydrogen to suppress the coke formation. The composition of the reactant gas was *n*-butane: He:H<sub>2</sub> = 1:6:1 (molar ratio) with a 99 ml/min total flow rate. The products distribution was quantitatively determined by a gas chromatograph equipped with a thermal conductivity detector (Shimadzu, GC-8A). Two columns, VZ-7 and activated carbon, were used for the analysis.

### 3. Results and Discussion

#### 3.1. Characterization of the PtAg/Al<sub>2</sub>O<sub>3</sub> Catalysts

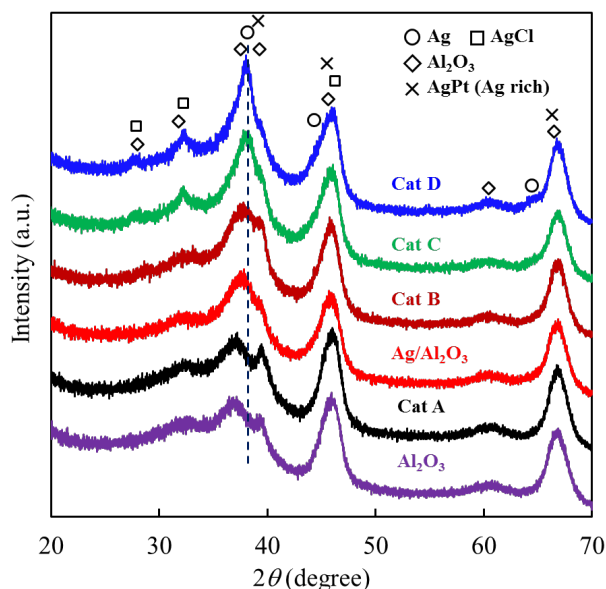
The physicochemical properties of the prepared catalysts are summarized in **Table 1**. The Cl content of the standard Pt/Al<sub>2</sub>O<sub>3</sub> (no washing) catalyst (**Cat A**) was 0.21 wt%. The amount of the CO chemisorption was 33.6  $\mu\text{mol g}^{-1}$  and the Pt dispersion was 54.1%. The PtAg/Al<sub>2</sub>O<sub>3</sub> (**Cat B**) that was prepared by the impregnation method using AgNO<sub>3</sub>aq and the Cl-removed Pt/Al<sub>2</sub>O<sub>3</sub>. In **Cat B**, the Cl content was not more than 0.01 wt%, and the amount of the CO chemisorption decreased two thirds of that observed in **Cat A**. **Cat C** contained 0.19 wt% Cl, which was prepared by the impregnation method using AgNO<sub>3</sub>aq and the Cl<sup>-</sup> added Pt/Al<sub>2</sub>O<sub>3</sub> after the addition of the designated amount of Cl<sup>-</sup> to Cl<sup>-</sup> removed Pt/Al<sub>2</sub>O<sub>3</sub>. **Cat D** was prepared by the addition of the appropriate amount of Cl<sup>-</sup> to the precursor of **Cat B** to convert the Ag metal particles on the catalyst to AgCl that was inactive for the coke formation from the highly-reactive butenes and BD. The chlorine content and the amount of CO chemisorption of **Cat D** were 0.33 wt% and 18.0  $\mu\text{mol g}^{-1}$ , respectively. All the PtAg/Al<sub>2</sub>O<sub>3</sub> catalysts showed lower amounts of CO chemisorption than the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst due to the decrease of the Pt dispersion and/or formation of the PtAg bimetallic phase. During the catalyst preparation of Pt/Al<sub>2</sub>O<sub>3</sub>, many references reported that chlorine on the Al<sub>2</sub>O<sub>3</sub> increased the dispersion of the Pt particles [13]. One certain reason for the decreasing amount of the CO chemisorption was observed for **Cats B** and **C** was due to agglomeration of the Pt particles. Although the lowest amount of the CO chemisorption was observed for **Cat D**, it was considered that the effect of the agglomeration was small for the decreasing amount of the CO chemisorption, because this catalyst was prepared in the same manner as the Pt/Al<sub>2</sub>O<sub>3</sub> (**Cat A**) preparation.

**Figure 2** shows the XRD profiles of the prepared **Cats A-D** with the Ag/Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>. In all the spectra, no peaks assigned to Pt and Pt-based bimetallic compounds were observed due to the low Pt content and the high dispersion of the Pt particles. Meanwhile, the major peak assigned to Ag was clearly observed at  $2\theta = 38.1^\circ$ , and its strong intensity indicated agglomeration of the Ag metal particles. Besides the peaks assigned to Ag, those assigned to AgCl were clearly observed at  $2\theta = 27.9$  and  $32.4^\circ$ , which was produced by the reaction of Ag and HCl during the catalyst preparation.

**Table 1.** Physicochemical properties of the prepared catalysts.

| Catalyst     | Content (wt%) <sup>a</sup> |     |       | Molar ratio of Ag/Pt | CO chemisorption ( $\mu\text{mol/g}$ ) |
|--------------|----------------------------|-----|-------|----------------------|--|
|              | Pt                         | Ag  | Cl    |                      |  |
| <b>Cat A</b> | 1.2                        | -   | 0.21  | -                    | 33.6                                   |
| <b>Cat B</b> | 1.1                        | 3.7 | <0.01 | 6.1                  | 24.2                                   |
| <b>Cat C</b> | 1.1                        | 4.0 | 0.19  | 6.1                  | 21.4                                   |
| <b>Cat D</b> | 1.1                        | 4.0 | 0.33  | 6.1                  | 18.0                                   |

a. These data were the average of values obtained by two measurements.



**Figure 2.** XRD profiles of Al<sub>2</sub>O<sub>3</sub>-supported Pt, Ag, and PtAg catalysts.

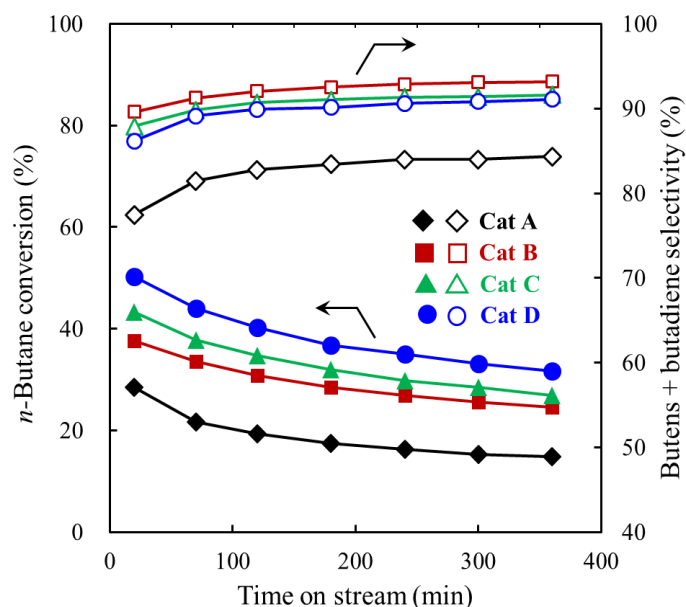
### 3.2. Dehydrogenation of the Catalyst in the Presence of H<sub>2</sub>

The dehydrogenation was performed at 550 °C using **Cats A–D** for 6 h. The conversion of *n*-butane and selectivity of the butenes (1-butene, *cis*- and *trans*-2-butenes) and 1,3-butadiene are shown in **Figure 3**. The selectivity of the by-products, such as CO, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>6</sub>, and isobutane are summarized in **Table 2**.

The Pt/Al<sub>2</sub>O<sub>3</sub> showed the lowest activity among the tested catalysts. The conversion gradually decreased from 28.5% to 14.8%. The selectivity of the butenes and 1,3-butadiene clearly increased with the reaction time (from 77% to 84%). The active sites, which caused a side-reaction, such as cracking, decreased during the initial stage of the reaction by the coke deposition with the decreasing activity. After the reaction, coke (4.0 wt% versus the catalyst weight) was formed on the catalyst.

When Ag was added to the Pt/Al<sub>2</sub>O<sub>3</sub>, the conversion significantly increased from 28.5 to 37.6% with the increasing selectivity of the desired products. As shown in **Table 2**, the addition of Ag suppressed the formation of CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>3</sub>H<sub>6</sub>. Although **Cat B** showed a high activity and selectivity of the butenes and 1,3-butadiene during the *n*-butane dehydrogenation, a large amount (about 30 wt% for the catalyst weight) of coke was formed after the reaction for 6 h. To confirm the reason for such an incredible coke formation, we performed the dehydrogenation using Ag/Al<sub>2</sub>O<sub>3</sub>. The Ag/Al<sub>2</sub>O<sub>3</sub> catalyst showed a low activity for the *n*-butane dehydrogenation, whereas an extremely high activity for the coke formation was observed during the reaction of 1-butene. Therefore, we concluded that the free Ag particles on **Cat B** caused the formation of the large amount of coke.

To decrease the coke formation, we attempted modification of the catalyst with Cl<sup>−</sup> (**Cat C**). The addition of Cl<sup>−</sup> was considered to be able to convert the



**Figure 3.** Dehydrogenation of *n*-butane over **Cat A-D**.

**Table 2.** Distribution of the by-products during the dehydrogenation.

| Catalyst     | Time on stream (min) | Selectivity of by-product (%) |                 |                 |                               |                               |  |
|--------------|----------------------|-------------------------------|-----------------|-----------------|-------------------------------|-------------------------------|--|
|              |                      | CO                            | CO <sub>2</sub> | CH <sub>4</sub> | C <sub>2</sub> H <sub>4</sub> | C <sub>3</sub> H <sub>6</sub> | i-C <sub>4</sub> H <sub>8</sub> <sup>a</sup> |
| <b>Cat A</b> | 20                   | 0.2                           | 0.6             | 9.0             | 6.0                           | 6.2                           | 0.3  |
|              | 360                  | 0                             | 0.2             | 6.2             | 4.4                           | 4.8                           | 0  |
| <b>Cat B</b> | 20                   | 0.4                           | 0.5             | 2.0             | 4.6                           | 2.5                           | 0.3  |
|              | 360                  | 0.2                           | 0.2             | 1.1             | 3.2                           | 2.1                           | 0  |
| <b>Cat C</b> | 20                   | 0.2                           | 0.7             | 2.3             | 5.0                           | 3.1                           | 0.6  |
|              | 360                  | 0.2                           | 0.3             | 1.5             | 3.4                           | 2.9                           | 0.2  |
| <b>Cat D</b> | 20                   | 0.2                           | 0.8             | 2.5             | 5.2                           | 3.3                           | 1.4  |
|              | 360                  | 0.2                           | 0.3             | 1.5             | 3.5                           | 3.0                           | 0.3  |

a. isobutane.

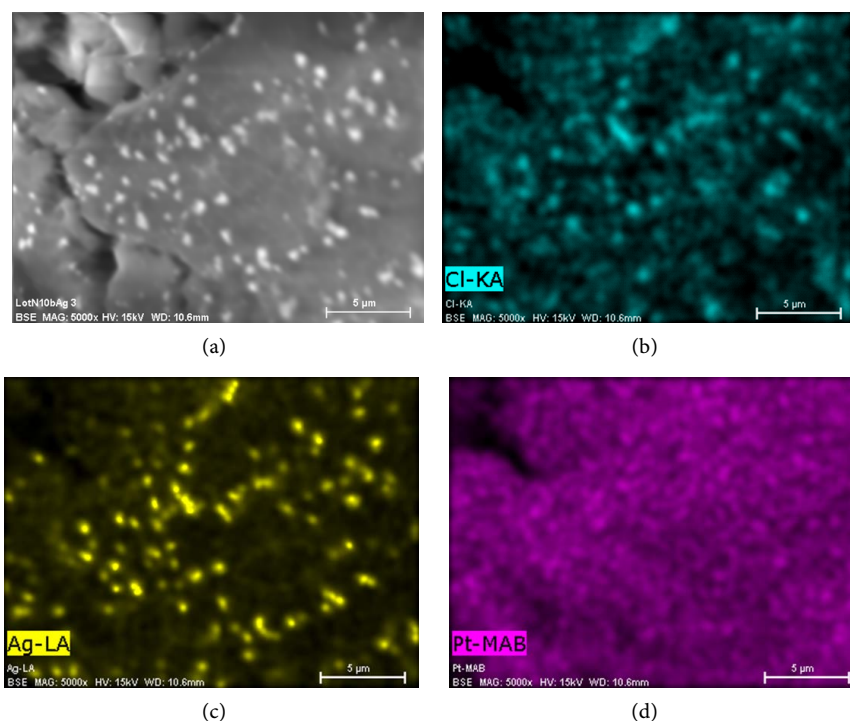
free Ag to AgCl which was inactive for the coke formation. In the XRD profile of **Cat C**, the diffraction peaks corresponding to AgCl were clearly observed. The conversion obtained using **Cat C** was higher than that obtained using **Cat B**. Additionally, the obvious effect of the Cl<sup>-</sup> addition was observed on the amount of coke, which dramatically decreased from about 30 to 4 wt%.

Meanwhile, the selectivity slightly decreased when Cl<sup>-</sup> was added to the Pt/Al<sub>2</sub>O<sub>3</sub>. From the detailed analysis of the products distribution, isobutane, which was an unpredictable by-product, was confirmed. Isobutane is considered to be formed by skeletal isomerization of *n*-butane on the strong acid sites of

$\text{Al}_2\text{O}_3$ . It is well known that the acid sites were induced by  $\text{Cl}^-$  in the  $\text{Al}_2\text{O}_3$ -supported Pt catalysts used for the catalytic reforming of the crude oil.

As a known technology [14], during the re-generation of a Pt/ $\text{Al}_2\text{O}_3$  reforming catalyst, agglomerated Pt metals were re-dispersed in the presence of a Cl-containing compound. We attempted the preparation of a highly-active catalyst based on the above concept. The highest activity was obtained by the dehydrogenation using **Cat D**, which was prepared through the pre-reduction, the dichlorination, the Ag addition, the  $\text{Cl}^-$  addition, and the reduction. The increasing activity was due to the high dispersion of the Pt metals in spite of the lowest amount of CO chemisorption. This low amount of the CO chemisorption might be caused by the formation of PtAg bimetallic compounds.

The SEM photographs of the PtAg/ $\text{Al}_2\text{O}_3$  catalyst (**Cat D**) and the mapping results of Ag and Cl obtained by the SEM-EDX analysis are shown in **Figure 4**. Many spherical particles (0.5 - 2  $\mu\text{m}$ ) were observed in the SEM photograph (A). The EDX mappings (B and C) of Ag and Cl indicated that the most of the particles included Ag, and some of them included Cl. The molar ratio of Ag to Cl was 4.5 in the observed area. This fact meant that these particles consisted of AgCl and metallic Ag particles. It was suggested that the added Cl formed AgCl by reacting with the small Ag particles. The melting point of AgCl (455°C) is lower than the reduction temperature in the catalyst preparation, therefore, the formed AgCl melted and agglomerated during the catalyst preparation. Finally, we concluded that the dramatic decrease in the coke formation was due to the formation of AgCl.



**Figure 4.** SEM-EDX photographs of PtAg/ $\text{Al}_2\text{O}_3$  catalyst **Cat D**. (a) SEM photograph; (b) EDX mapping for Cl; (c) EDX mapping for Ag; and (d) EDX mapping for Pt.

## 4. Conclusion

We prepared PtAg bimetallic catalysts and evaluated these catalysts for the dehydrogenation of *n*-butane in the presence of H<sub>2</sub>. The catalyst prepared by Pt addition, reduction, Cl removal, Ag addition, Cl addition, and finally reduction showed a high activity for the dehydrogenation and produced butenes (1-butene, *cis*- and *trans*-2-butenes) with a high selectivity. The added Ag was used for modification of the Pt particles (bimetallic phase might be formed) to suppress the formation of the cracking products. The addition of Cl to the catalyst decreased the free Ag metal particles which formed a large amount of coke, resulting in the high activity and selectivity for the butenes and butadiene.

## References

- [1] Sattler, J.J.H.B., Martinez, R.J., Jimenez, S.E. and Weckhuysen, B.M. (2014) Catalytic Dehydrogenation of Light Alkanes on Metals and Metal Oxides. *Chem. Rev.*, **114**, 10613-10653. <https://doi.org/10.1021/cr5002436>
- [2] Sanfilippo, D. (2000) Dehydrogenation of Paraffins, Key Technology for Petrochemicals and Fuels. *CATTECH*, **4**, 56-73. <https://doi.org/10.1023/A:1011947328263>
- [3] Linsheng, W., Liwu, L., Tingling, Z. and Hailin, C. (1994) Enhancement of Pt-Sn/Al<sub>2</sub>O<sub>3</sub> Catalyst Stability for Butane Dehydrogenation by Modification with Sm and Li. *React. Kinet. Catal. Lett.*, **52**, 107-111. <https://doi.org/10.1007/BF02129857>
- [4] de Miguel, S.R., Bocanegra, S.A., Vilella, I.M.J., Ruiz, G.A. and Scelza, O.A. (2007) Characterization and Catalytic Performance of PtSn Catalysts Supported on Al<sub>2</sub>O<sub>3</sub> and Na-Doped Al<sub>2</sub>O<sub>3</sub> in *n*-Butane Dehydrogenation. *Catal. Lett.*, **119**, 5-15. <https://doi.org/10.1007/s10562-007-9215-5>
- [5] Bocanegra, S.A., de Miguel, S.R., Borbath, I., Margitfalvi, J.L. and Scelza, O.A. (2009) Behavior of Bimetallic PtSn/Al<sub>2</sub>O<sub>3</sub> Catalysts Prepared by Controlled Surface Reactions in the Selective Dehydrogenation of Butane. *J. Mol. Catal. A: Chem.*, **301**, 52-60. <https://doi.org/10.1016/j.molcata.2008.11.006>
- [6] Bocanegra, S.A., Ballarini, A., Zgolicz, P., Scelza, O.A. and de Miguel, S.R. (2009) Highly Selective and Stable Bimetallic Catalysts Supported on Different Materials for *n*-Butane Dehydrogenation. *Catal. Today*, **143**, 334-340. <https://doi.org/10.1016/j.cattod.2008.10.002>
- [7] Ballarini, A.D., Zgolicz, P., Vilella, I.M.J., de Miguel, S.R., Castro, A.A. and Scelza, O.A. (2010) *n*-Butane Dehydrogenation On Pt, PtSn and PtGe Supported on Al<sub>2</sub>O<sub>3</sub> Deposited on Spheres of □Al<sub>2</sub>O<sub>3</sub> by Washcoating. *Appl. Catal. A: Gen.*, **381**, 83-91. <https://doi.org/10.1016/j.apcata.2010.03.053>
- [8] Veldurthi, S., Shin, C.-H., Joo, O.-S. and Jung, K.-D. (2012) Promotional Effects of Cu on Pt/Al<sub>2</sub>O<sub>3</sub> and Pd/Al<sub>2</sub>O<sub>3</sub> Catalysts during *n*-Butane Dehydrogenation. *Catal. Today*, **185**, 88-93. <https://doi.org/10.1016/j.cattod.2011.11.021>
- [9] Nagaraja, B.M., Shin, C.-H. and Jung, K.-D. (2013) Selective and Stable Bimetallic PtSn/-Al<sub>2</sub>O<sub>3</sub> Catalyst for Dehydrogenation of *n*-Butane to *n*-Butenes. *Appl. Catal. A: Gen.*, **467**, 211-223. <https://doi.org/10.1016/j.apcata.2013.07.022>
- [10] Nagaraja, B.M., Jung, H., Yang, D.R. and Jung, K.-D. (2014) Effect of Potassium Addition on Bimetallic PtSn Supported-Al<sub>2</sub>O<sub>3</sub> Catalyst for *n*-Butane Dehydrogenation to Olefins. *Catal. Today*, **232**, 40-52.



<https://doi.org/10.1016/j.cattod.2013.10.070>

- [11] Lee, M.-H., Nagaraja, B.M., Lee, K.Y. and Jung, K.-D. (2014) Dehydrogenation of Alkane to Light Olefin Over PtSn/-Al<sub>2</sub>O<sub>3</sub> Catalyst: Effects of Sn Loading. *Catal. Today*, **232**, 53-62. <https://doi.org/10.1016/j.cattod.2013.10.011>
- [12] Seo, H., Lee, J.K., Hong, U.G., Park, G., Yoo, Y., Lee, J., Chang, H. and Song, I.K. (2014) Direct Dehydrogenation of *n*-Butane over Pt/Sn/M/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Catalysts: Effect of Third Metal (M) Addition. *Catal. Commun.*, **47**, 22-27. <https://doi.org/10.1016/j.catcom.2014.01.007>
- [13] Baker, R.T.K., Thomas, C. and Thomas, R.B. (1975) Continuous Observation of the Particle Size Behavior of Platinum Alumina. *J. Catal.*, **38**, 510-513. [https://doi.org/10.1016/0021-9517\(75\)90120-7](https://doi.org/10.1016/0021-9517(75)90120-7)
- [14] Foger, K. and Jaeger, H. (1985) The Effect of Chlorine Treatment on the Dispersion of Platinum Metal Particles Supported on Silica and  $\gamma$ -Alumina. *J. Catal.*, **92**, 64-78. [https://doi.org/10.1016/0021-9517\(85\)90237-4](https://doi.org/10.1016/0021-9517(85)90237-4)