

## Effect of Ag-promotion on Pd catalysts by XANES

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Pd L<sub>3</sub> near-edge absorption measurements (XANES) were performed on four commercial acetylene hydrogenation catalyst samples, with and without the Ag promoter. The Pd L<sub>3</sub> edge XANES spectra showed that the Ag-promoted catalysts have relatively weaker absorption peaks and they follow the same order as the relative commercial performances of the four catalysts studied in terms of selectivity in ethylene purification, which indicates that there are increases in the Pd d-band electron densities due to the addition of Ag. These results provide a reasonable explanation for the observed improvement in selectivity of the Ag-promoted acetylene hydrogenation catalysts. The Ag L<sub>3</sub> XANES spectra of the supported Pd–Ag catalysts indicate the absence of a white-line feature which seems to suggest that the charge transferred from Ag to Pd may not be the d-type.

**Keywords:** XANES, hydrogenation, catalysts, Ag promoter

### 1. Introduction

Supported palladium catalysts have been widely used in the chemical industry for hydrogenations of hydrocarbons. The activities of palladium catalysts for various selective hydrogenations are usually adjusted through careful control of reaction conditions as well as the fine tuning of catalysts properties by proprietary manufacturing processes to achieve the required selectivity for each specific application.

Ethylene produced from an ethane cracker contains a low concentration (0.1–0.2%) of acetylene, which is a poison to the downstream catalyst in the manufacture of polyolefin. A palladium on alumina catalyst is usually used to purify the ethylene stream by hydrogenating acetylene to a concentration less than 1 ppmv. The catalyst for such an application has to be highly selective to avoid loss of bulk ethylene due to conversions to ethane or green oil. A highly selective catalyst is crucial for an ethylene plant; it can improve the productivity, which directly affects the profitability.

The selection of catalyst for ethylene purification depends on the location of the hydrogenation reactor in the ethylene plant. For front-end ethylene purification, where the ethylene stream is rich in hydrogen (15–25%), the hydrogenation of acetylene must be kinetically controlled to inhibit massive hydrogenation of ethylene to ethane, which could sometimes cause a temperature run-away due to the highly exothermic reaction. Highly selective catalysts such as the G83 type of catalysts developed by United Catalysts Inc. (UCI) are often used for this application. G83C, a Ag-promoted Pd catalyst licensed and manufactured by UCI based on a technology by Phillips Petroleum Company [1], is especially selective.

In the tail-end ethylene purification, hydrogen has been removed from the ethylene stream. There is only limited amount of hydrogen added for the reaction. The potential for ethylene loss due to over-hydrogenation to ethane is therefore limited. However, in the tail-end conditions the catalyst could be deactivated due to formation of polymer, which is sometimes called green oil, on the catalyst surface. A large amount of polymer formation would lead to a short life cycle and the catalyst may need to be regenerated periodically. The G58 series of catalysts are tailored for tail-end ethylene purification.

A great deal of work has been done by United Catalysts Inc. and Phillips Petroleum Company to improve the selectivity of palladium catalysts for ethylene purification [1,2,13]. One of the measures to improve the performance of Pd catalysts in terms of selectivity and life cycle in both front-end and tail-end applications is the addition of Ag as a promoter.

Cordts et al. have studied Ag–Pd solid solutions by X-ray absorption [3]. The effect of increased amount of Ag in Pd–Ag alloys has been investigated by Meitzner and Sinfelt of Exxon Research and Engineering Company [4]. Chae et al. have studied the local density of unoccupied states in ion-beam-mixed Pd–Ag alloys [10]. Coulthard and Sham reported their observations of charge redistribution in Pd–Ag alloys from a local perspective [14]. These authors have observed decreases in unfilled d-states vacancies of Pd due to the presence of Ag.

The present study aims at the investigation of the effect of silver on supported palladium acetylene hydrogenation catalysts by using the high intensity and monochromatic hard X-rays produced at synchrotron radiation facilities. The effect of Ag on the supported palladium selective hydrogenation catalysts is difficult to investigate by conven-

tional characterization methods due to the extremely low Pd loadings (0.01–0.2 wt%) of these hydrogenation catalysts. It is the intent of this investigation to use near-edge X-ray absorption spectroscopy (XANES) to study the electronic effect of Ag on Pd atoms in commercial selective hydrogenation catalysts.

## 2. Experimental

Pd  $L_3$  near-edge absorption spectra of four commercial acetylene hydrogenation catalysts were taken. Since the metal concentrations of these selective hydrogenation catalysts are extremely low, the powder samples from the outer layers of the egg-shell type of catalyst particles in relatively higher concentrations were used for XANES measurements. Although the G58B and G58E catalysts have the same Pd content, and that G83A and G83C catalysts also have the same Pd content, the scraped outer layer powder varies somewhat in Pd concentration. Table 1 contains the approximate analyses of these powder samples after X-ray absorption measurements. The Pd  $L_3$  near-edge absorption intensities of these samples have been normalized for comparison.

The powder samples were reduced at 100 °C with 100%  $H_2$  for 2 h following a typical activation procedure for noble metal catalysts, then purged and kept under high purity  $N_2$  for XAFS measurements.

The Ag and Pd  $L_3$  edge XANES measurements of Pd/ $Al_2O_3$  and Pd–Ag/ $Al_2O_3$  catalysts were performed at the double-crystal monochromator (DCM) beamline with an electron beam energy of 1.5 GeV and a maximum stored current of 200 mA at the Synchrotron Radiation Research Center (SRRC) in Hsinchu, Taiwan. The energy resolution of the monochromator in the energy range of interest, 3170 eV (Ag  $L_3$  edge) and 3350 eV (Pd  $L_3$  edge), was set at  $\sim 1.2$  eV. The absorption spectra were obtained by collecting the soft X-ray fluorescence yield with a high sensitivity seven element germanium detector. The energy scale was calibrated using the spectra of pure Ag and Pd metals. All measurements were performed at room temperature.

The XANES spectra shown in figures 1, 2 and 4 have been divided by the incident intensity  $I_0$  and subjected to subtraction of pre-edge background at  $L_3$  edge. All spectra have been normalized to an edge jump of unity. The normalization procedure was carried out by matching the absorption coefficients from the pre-edge region at  $L_3$  edge to  $\sim 50$  eV above  $L_3$  edges for Ag and Pd, respectively, which

is a commonly practised procedure for the comparison and evaluation of the intensities of resonance absorption spectra of a series of systematically varied compounds [15].

## 3. Results and discussions

Pd  $L_3$  edge XANES of G58B (Pd/ $Al_2O_3$ ) and G58E (Pd–Ag/ $Al_2O_3$ ) tail-end ethylene purification catalysts without and with Ag-promotion are compared in figure 1 along with the spectrum of a Pd foil. The near-edge absorption peak at 3175 eV indicates the excitation of  $2p_{3/2}$  electrons to the vacant 4d-states [4,5]. A stronger absorption peak is expected for catalysts containing Pd atoms with more unfilled 4d-states such that excitations of electrons to these states are highly probable. The spectra in figure 1 show that G58E with Ag promoter has a much weaker white-line absorption peak than the unpromoted G58B catalyst which suggests that there is an increase in the Pd d-band electron density due to the presence of Ag.

There are other factors which may have also contributed to the observed intensities of the absorption peaks of acetylene hydrogenation catalysts. For instance, there is possibly an intra-atomic charge transfer, which increases the d-electron count with increasing cluster size [6]. When the catalyst has very small Pd clusters in high metal dispersion, there are strong metal–support interactions [7]. The interaction of Pd with O of the  $Al_2O_3$  carrier could result in an increase in d-states vacancies due to a charge transfer from palladium to oxygen [8].

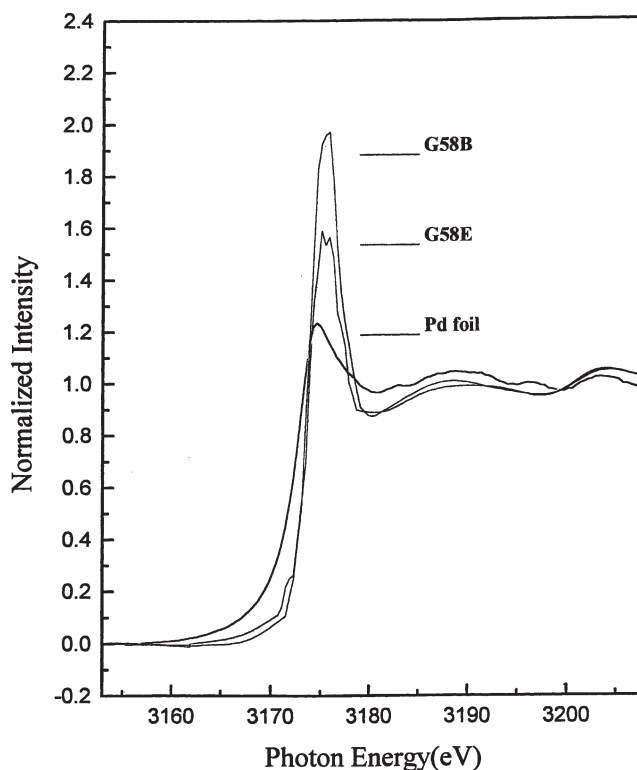


Figure 1. Pd  $L_3$  edge XANES spectra.

Table 1  
Approximate composition of powder sample taken from the surface outer layer of catalyst particles.

Catalyst sample	Pd (wt%)	Ag (wt%)
G58B	0.39	–
G58E	0.30	0.53
G83A	0.051	–
G83C	0.074	0.13

Since the G58E sample for this investigation was prepared by impregnating Ag on the G58B sample, it is likely that the G58B and G58E samples have similar Pd cluster sizes and similar degree of metal-support interactions. Thus, the observed difference in Pd L<sub>3</sub> white-line peak intensities of the two catalysts, as shown in figure 1, could indeed indicate a charge transfer from Ag to the Pd atom in the Ag-promoted catalyst.

These observations of the electronic effect of Ag on Pd agree with the observation of other researchers in studies of Pd-Ag alloys in various compositions. In 1981, Cordts et al. [3] studied Ag-Pd solid solutions by X-ray L absorption edges. They found that the local density of unfilled 4d-states per Pd atom declined upon alloying with silver. Meitzner and Sinfelt [4] studied the electronic structures of Pd-Ag and Pd-Au alloys in 25, 50 and 75% Pd by X-ray absorption. Results of their experiments revealed a relationship of linear decline in unfilled d-states of Pd with the increase of %Ag in the Pd-Ag alloy.

The commercial performances of these catalysts indicate that the G58B catalyst without Ag is more active and G58E with Ag-promotion is slightly less active but of higher selectivity. The Pd L<sub>3</sub> edge XANES results provide a good understanding as to why the Ag-promoted Pd catalyst has a better selectivity for the selective hydrogenation of acetylene. In the case of the unpromoted Pd catalyst with highly dispersed Pd, the Pd atoms have high vacancies in the d-states. It would be more receptive to the chemisorption of unsaturated hydrocarbons which act as electron donors [9] and, therefore, more uncontrolled reactions could take place. Such a catalyst would chemisorb not only the highly unsaturated acetylene but also the bulk ethylene and, therefore, it is likely to have lower selectivity for the hydrogenation of acetylene in the ethylene stream. The addition of Ag to the Pd catalyst increases the d-band electron density of the Pd atom, which would decrease the chemisorption of ethylene and other unsaturated hydrocarbons, yet still selectively chemisorbs acetylene. Therefore, the Ag-promoted catalyst is likely to have a better selectivity for the hydrogenation of acetylene in ethylene. Such catalyst would have a relatively weak absorption peak in the Pd L<sub>3</sub> edge XANES spectra, as observed in our studies.

The Ag L<sub>3</sub> edge XANES of G58E and G83C catalysts containing Ag as well as that of the Ag foil do not have a strong near-edge absorption peak, as shown in figure 2. These Ag L<sub>3</sub> near-edge results seem to indicate that the presence of Pd with Ag in these catalysts has not caused an increase in the unoccupied d-state density of the Ag atom, which suggests that the charge transferred from Ag to Pd may not be the d-type. These results agree with the conclusion of Chae et al. [10] in that the charge transferred away from the Ag site is dominantly of non-d-type.

Theoretical calculations by Lu et al. [11] have shown that the Pd d-band energy level and the Ag sp-orbital energy are sufficiently close that it is possible for Ag atoms to contribute sp electrons to Pd's d-state vacancies. Coulthard and Sham [14] investigated the charge distribution in a se-

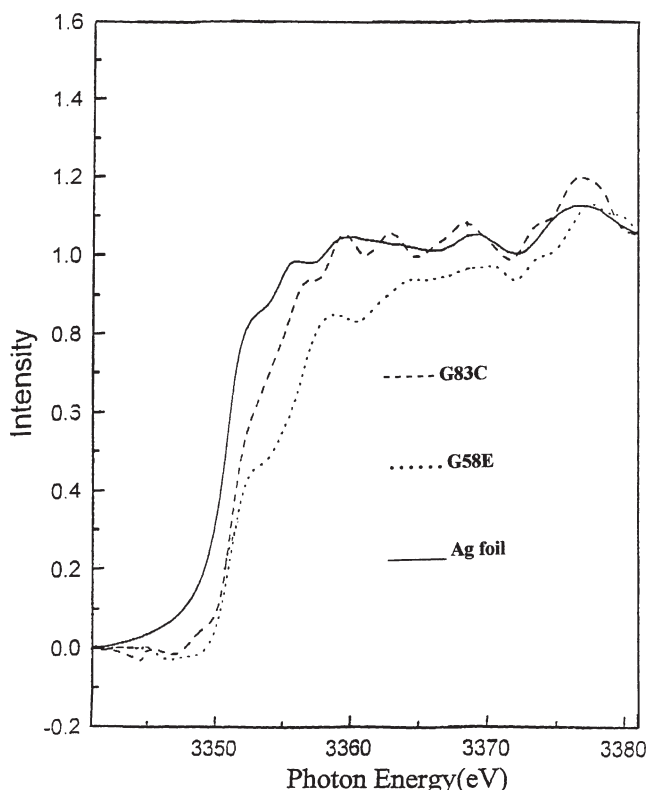


Figure 2. Ag L<sub>3</sub> edge XANES spectra.

ries of Pd-Ag alloys by XANES and X-ray photoemission spectroscopy. They have observed that both Pd and Ag gain in d- and lose in s- and p-charge, however, the less electronegative Ag has an overall charge loss upon alloying with Pd.

The front-end acetylene hydrogenation catalysts G83A (Pd/Al<sub>2</sub>O<sub>3</sub>) and G83C (Pd-Ag/Al<sub>2</sub>O<sub>3</sub>) are designed to be highly selective for the hydrogenation of the hydrogen-rich ethylene stream. These catalysts have very low Pd contents and are supported on a carrier with relatively low surface area [12]. The performance data shown in figure 3 show that, at 540 psig reactor pressure with a feed containing 20% H<sub>2</sub>, the G83C catalyst with Ag cleans up acetylene at a slightly higher temperature of 119 vs. 111 °F of G83A without Ag, yet it has a much wider window of 35 °F for safe operation vs. the 19 °F window of non-promoted G83A before reaching the "light-off" temperature, where major loss in ethylene starts to take place. However, the choice of catalyst for each plant is normally decided based on operating conditions and the specific requirements of each individual plant.

Figure 4 contains the Pd L<sub>3</sub> edge XANES spectra of front-end ethylene hydrogenation catalysts G83A without Ag and G83C with the Ag promoter. The spectra again show that the Ag-promoted catalyst G83C has lower near-edge peak intensity than the non-promoted catalyst G83A. These results and the XANES spectra of G58B and G58E discussed above indicate that the addition of Ag seems to have caused an increase in the d-band electron density or a decrease in the d-states vacancies of Pd in Ag-promoted

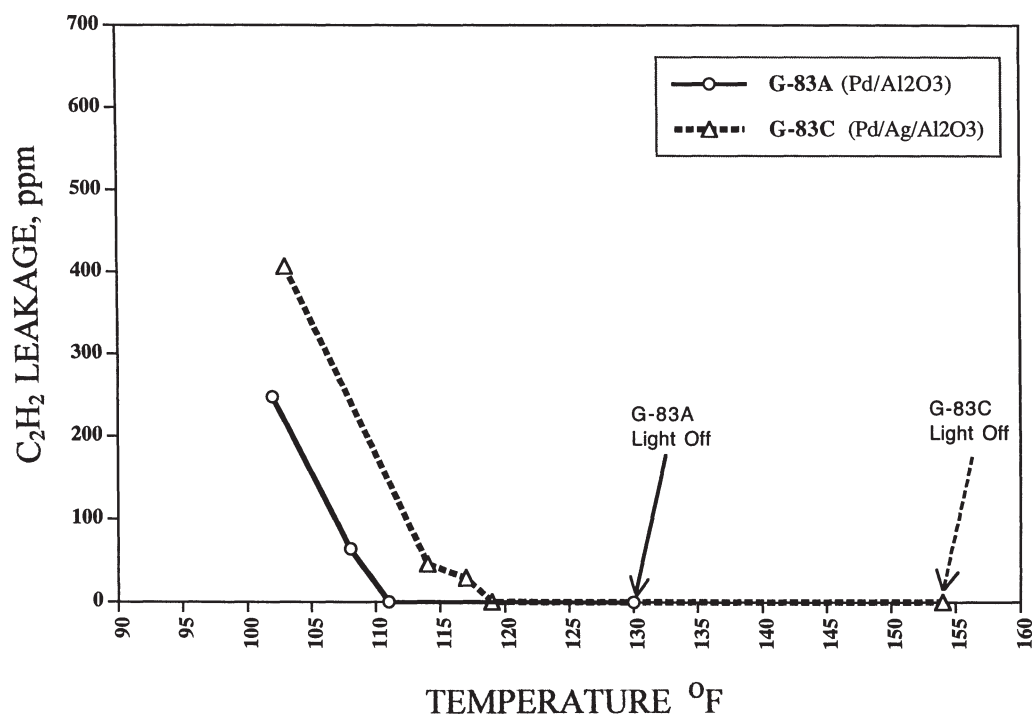


Figure 3. Performance data of front-end acetylene hydrogenation catalysts with and without Ag promoter.

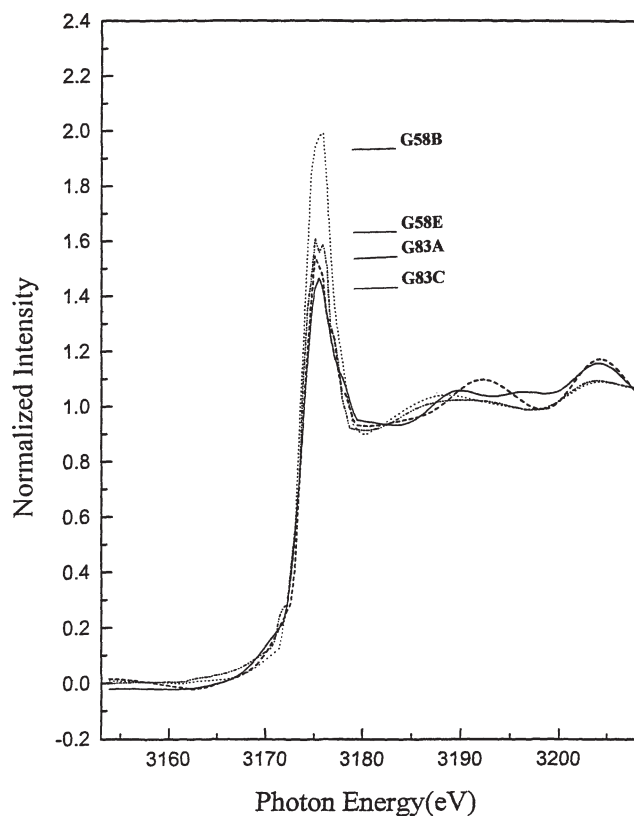


Figure 4. Pd L<sub>3</sub> edge XANES spectra of four commercial catalysts studied.

catalysts. The much lower normalized peak intensities of the more selective G83 catalysts compared to the G58 catalysts further suggest the possibility that the G83 catalysts may have relatively lower dispersions or larger Pd clus-

ters with possibly less metal-support interactions. Further studies of these catalysts by Pd K edge EXAFS measurements would help to confirm the indications drawn from these measurements. It is, however, satisfying to note that the intensities of the Pd L<sub>3</sub> edge XANES absorption peaks of the four hydrogenation catalysts, as shown in figure 4, in fact follow the same order as their commercial performances regarding to selectivity in acetylene hydrogenation in ethylene plants.

#### 4. Conclusions

The apparent differences in intensities of Pd L<sub>3</sub> near-edge absorption peaks of the four acetylene hydrogenation catalysts show that the X-ray absorption measurement is sensitive enough for successful detection of Pd in very low concentrations. The spectra revealed that the catalysts with Ag have weaker white-line absorption peaks than the unpromoted catalysts, which indicates that there are increased Pd d-band electron densities due to the presence of Ag.

These XANES results provide a reasoning and understanding of the effect of Ag-promotion on the Pd catalysts. The observed charge transfer from Ag and Pd or the decrease in unfilled d-states of Pd atoms in the Ag-promoted catalysts would decrease the tendency for the general chemisorption of unsaturated hydrocarbons, which are capable of donating electrons, on the active sites. This would lead to the more selective chemisorption of acetylene with less uncontrolled reactions taking place and, therefore, better selectivity for acetylene hydrogenation.

Indeed, the observed intensities of the Pd L<sub>3</sub> edge XANES absorption peaks of the four catalysts studied fol-

low the same order as their commercial performances regarding to selectivity in ethylene purification.

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