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Research Note

Deactivation behavior of a TiO_2-added Pd catalyst in acetylene hydrogenation

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Abstract

The deactivation behavior of a TiO_2-added Pd catalyst, reduced at 773 K, for the selective hydrogenation of acetylene showed that the added TiO_2 suppressed the formation of green oil and, consequently, improved the lifetime of the catalyst. The average number of carbon atoms per green oil molecule was smaller for the TiO_2-added catalyst than for the Pd-only catalyst because multiply coordinated Pd sites were suppressed on the TiO_2-added catalyst. The added TiO_2 also retarded the sintering of Pd particles during catalyst regeneration, presumably due to the anchoring effect of TiO_2, and suppressed green oil formation, even after the regeneration step.

Keywords: Acetylene hydrogenation; Pd; TiO_2; Deactivation; Green oil; Sintering

1. Introduction

Acetylene contained in the ethylene stream from a naphtha cracker unit is commonly removed by selective hydrogenation using Pd-based catalysts [1]. In our previous paper [2], we reported that TiO_2, when added to a Pd catalyst, significantly improves catalytic performance from the standpoints of both ethylene selectivity and catalyst lifetime, particularly when the catalysts were reduced at high temperatures, e.g., 773 K. Our study confirmed that added TiO_2 interacted strongly with the Pd surface, similar to the case of TiO_2-supported Pd catalysts, which show strong metal–support interactions (SMSI), after reduction at high temperatures.

This Note reports on the results of our continued work on the deactivation of TiO_2-added Pd catalysts, particularly on the nature of the green oil that accumulates on the catalyst surface, the sintering of Pd particles during catalyst regeneration, and the performance of the regenerated catalyst. The deactivation behavior of TiO_2-added Pd catalysts is compared with those of catalysts containing other promoters.

2. Experimental

Pd/SiO_2, containing 1.0 wt% of Pd, and TiO_2-added Pd/SiO_2, containing TiO_2 at a Ti/Pd atomic ratio of 1.0, were prepared by the same procedure as described in our previous paper [2]. Ag-added Pd/SiO_2, containing Ag at an Ag/Pd atomic ratio of 1.0, was prepared by an incipient wetness impregnation method using $AgNO_3$ as the Ag precursor. The catalyst samples were calcined in air at 573 K for 3 h and then reduced in H_2 at either 573 or 773 K for 1 h prior to use. The accelerated deactivation of the catalysts was made under the same condition as in our previous study [3]. The green oil deposited on the catalysts was analyzed by thermogravimetry (TA Instruments, TGA2050) in an air flow at 40 cm^3/min, while the temperature was raised from 303 to 1123 K at a rate of 10 K/min. Infrared (IR) spectra of the green oil and CO adsorbed on the catalysts were obtained by using an IR spectrometer (MIDAC, Model M2000) equipped with a DTGS detector. A diffractometer (Mac Science), equipped with a graphite monochromator using Cu-K_α (50 kV, 100 mA) as the radiation source, was used in the X-ray diffraction (XRD) study of the catalysts. Hydrogen chemisorption was made by using ASAP2010 (Micromeritics).

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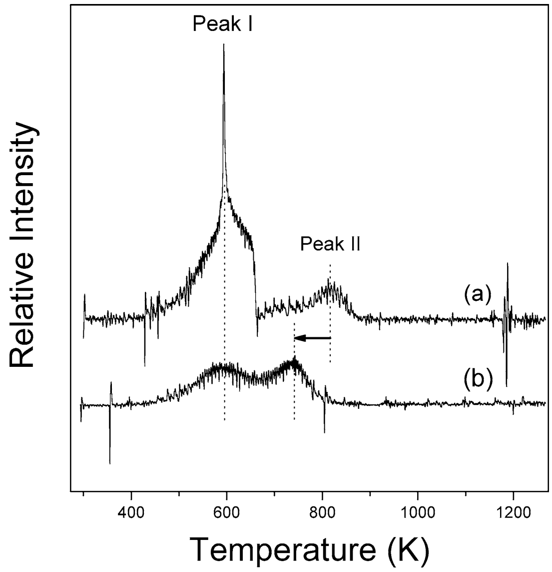

Fig. 1. Differential thermogravimetric analysis of used catalysts in air: (a) Pd/SiO_2/573, (b) Pd–Ti/SiO_2/773.

3. Results and discussion

3.1. Deactivation by green oil accumulation

The TGA results obtained for the two catalysts, which had been used for converting the same accumulated amounts of acetylene, showed significant weight losses at temperatures between 473 and 873 K, due to the burn off of green oil deposited on the catalyst surfaces. The weight loss was larger for the Pd-only catalyst reduced at 573 K, Pd/SiO_2/573, (59.2%) than for Pd–Ti/SiO_2/773 (35.1%). Fig. 1 shows the results of a differential thermogravimetric analysis (DTGA), obtained from the TGA curves, which can be deconvoluted into two major peaks: Peak I at 573–643 K, representing coke produced on and in the vicinity of the Pd, and Peak II at 673–873 K, representing graphite-like coke present on the support [4]. Two changes occur when the Pd catalyst is modified with TiO_2. The area of Peak I is significantly decreased, indicating that the formation of green oil on and in the vicinity of Pd is suppressed, and the location of Peak II is shifted to lower temperatures, indicating that green oil produced on the support can be removed at relatively low temperatures.

The average carbon number per green oil molecule was estimated from the IR spectrum (not shown here), which consisted of four major peaks appearing at 2960, 2930, 2880, and 2860 cm^{-1}, respectively [5]. We calculated the CH_2/CH_3 ratio of green oil based on the relative intensity of the asymmetric C–H stretching peaks, at 2960 cm^{-1} for CH_3 groups and at 2930 cm^{-1} for CH_2 groups. The CH_2/CH_3 ratio was smaller for Pd–Ti/SiO_2/773, 2.9, than for Pd/SiO_2/573, 4.2, indicating that the green oil deposited on the former has a shorter chain length than that on the latter. Since the extinction coefficient of a CH_3 group is three times larger than that of a CH_2 group, the average carbon number per molecule of green oil for the two catalysts was estimated from three times the CH_2/CH_3 intensity ratios. The estimated carbon numbers, 19 for Pd–Ti/SiO_2/773 and 27 for Pd/SiO_2/573, fall in the same range as those reported for green oil obtained in industrial processes [6] and indicate that the added TiO_2 decreases the chain length of the green oil.

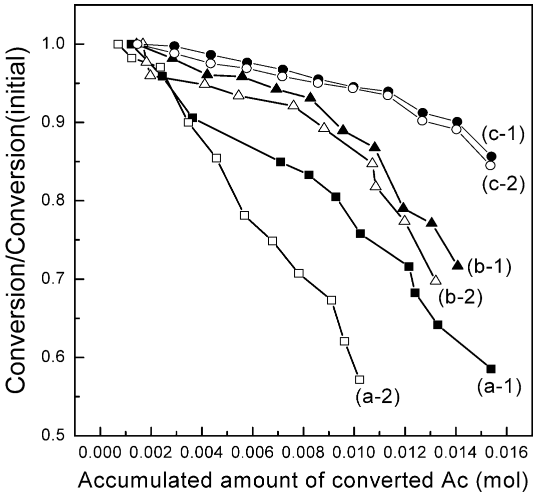

Fig. 2. Deactivation of catalysts, before and after regeneration, with accumulated amounts of converted acetylene; regenerating conditions: $O_2 = 20\ cm^3/min$, temperature $= 873$ K for 2 h. (a) Pd/SiO_2/573, (b) Pd–Ti/SiO_2/773, (c) Pd–Ag/SiO_2/573; (1) fresh, (2) after regeneration.

3.2. Deactivation by sintering

Fig. 2 shows that the deactivation rates of Pd–Ti/SiO_2/773, either fresh or regenerated after being used for extended periods, are slower than those of Pd/SiO_2/573. Catalyst deactivation was not caused by pore blockage because the pore volumes and average pore diameters of the catalysts were changed to smaller extents than the activity decrease made during the reaction period. An estimated Weisz–Prater number also assured the absence of pore-diffusion limitations in the reaction system. Catalysts used for converting the same amounts of acetylene were regenerated in air at 873 K, before being reduced and used again for the deactivation tests. In the case of Pd/SiO_2/573, the activity decreased at a faster rate after the regeneration, which is obviously due to the sintering of Pd crystallites during the regeneration process. On the other hand, the deactivation of regenerated Pd–Ti/SiO_2/773 proceeded nearly at the same rates as were observed before the regeneration, indicating that added TiO_2 suppresses the sintering of Pd crystallites. The behavior of Ag-added catalysts will be discussed in Section 3.3.

The average sizes of the Pd particles in Pd/SiO_2/573 and Pd–Ti/SiO_2/773, before and after regeneration, were estimated by XRD. After regeneration, the size was increased from 45 to 120 Å for Pd/SiO_2/573, whereas it was only slightly increased, from 48 to 61 Å, for Pd–Ti/SiO_2/773. The Pd particle sizes were also estimated by H_2 chemisorption,

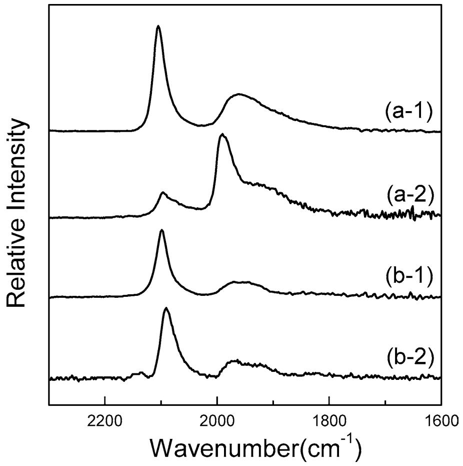

Fig. 3. Infrared spectra of CO adsorbed on the catalysts before and after catalyst regeneration: (a) Pd/SiO_2/573, (b) Pd–Ti/SiO_2/773; (1) fresh, (2) after regeneration.

which indicated the same trend as observed by XRD. That is, the H/Pd ratio for Pd/SiO_2/573 was decreased from 0.44 to 0.21, corresponding to a particle size from 21 to 44 Å, after the regeneration. On the other hand, the ratio for Pd–Ti/SiO_2/773, which was smaller than for Pd/SiO_2/573 due to the surface coverage of Pd by TiO_2, was decreased to a smaller extent, from 0.20 to 0.14, corresponding to a size change from 45 to 66 Å.

Fig. 3 shows IR spectra of CO adsorbed on the catalysts before and after regeneration. The spectra consist of four peaks assigned to different CO adsorption modes [7]. We calculated the area ratios of multiply bound (1995–1870 cm^{-1}) to linearly bound CO (2200–2100 cm^{-1}), A_m/A_l, for the different catalysts based on the IR spectra. After regeneration, the A_m/A_l ratio was increased from 2.6 to 4.9 in the case of Pd/SiO_2/573, due to the sintering of Pd crystallites, but the ratio was increased only slightly from 1.6 to 1.9 in the case of Pd–Ti/SiO_2/773, indicating that the sintering of Pd crystallites is suppressed by the added TiO_2.

3.3. The role of Ti oxide in the catalyst deactivation

Acetylene is not only hydrogenated to produce ethylene, but also is hydro-oligomerized with adjacent acetylene molecules to produce 1,3-butadiene and green oil with higher numbers of carbon atoms [8]. These hydro-oligomerization reactions proceed preferentially on multiply coordinated sites [9]. When TiO_2 is added to a Pd catalyst, green oil formation on the Pd surface is substantially suppressed because the added TiO_2 dilutes the Pd surface, thus reducing the number of multiply coordinated Pd sites (Fig. 3). Furthermore, due to dilution by TiO_2, further hydro-oligomerization of green oil to a higher carbon number is also suppressed and, as a result, it can be removed at relatively low temperatures compared to the case of Pd/SiO_2 (Fig. 1). All of the above trends, originating from the dilution effect of TiO_2 species, reduce the extent of catalyst deactivation by green oil accumulation.

The retarded Pd sintering on Pd–Ti/SiO_2 is also related to characteristic interactions of the added TiO_2 with Pd. When a catalyst is oxidized in air for regeneration, TiO_2 species, which are present on the Pd surface, migrate back close to the support, which is intrinsic to the SMSI phenomenon [10], so that they are located at the interface between the Pd particles and the support. Accordingly, it would be expected that, during catalyst regeneration, Pd particles would be surrounded by TiO_2 species such that the former are protected from sintering. A fraction of the TiO_2 species, which may remain on the Pd surface during the oxidation process, could still retard the sintering of the Pd particles by lowering the mobility of the latter.

The turnover frequencies, calculated based on the H_2 chemisorption data, changed after the regeneration: from 0.20 to 0.41 s^{-1} on Pd/SiO_2/573 and from 0.49 to 0.56 s^{-1} on Pd–Ti/SiO_2/773. The regeneration also changed the relative rates of acetylene oligomerization versus hydrogenation, i.e., from 0.43/0.57 to 0.58/0.42 on the former catalyst and from 0.17/0.83 to 0.22/0.78 on the latter. Accordingly, the increase in turnover frequency after regeneration is due to an increase in the relative rates of oligomerization and the rates remain smaller than those of hydrogenation on Pd–Ti/SiO_2/773.

We compared the performance of TiO_2-added catalysts with that of other promoted catalysts, containing either SiO_2 or Ag. The former is a typical geometric modifier of Pd, as reported by this group [3], and the latter modifies Pd largely by electronic interactions, although a geometric effect is also claimed to contribute [11]. TiO_2 modifies Pd by both electronic and geometric effects but the latter seems to be the major factor, as described above and in our previous paper [2]. The deactivation results, shown in Fig. 2 and in our previous report [3], indicate that the catalyst lifetime is improved in the order Pd–Ag/SiO_2 > Pd–Ti/SiO_2 = Pd–Si/SiO_2. The behavior after the regeneration also follows the same order. The catalysts show more distinct differences in their selectivity (Fig. 4), which is improved in the order Pd–Ag/SiO_2 > Pd–Ti/SiO_2 > Pd–Si/SiO_2. Accordingly, it can be temporarily concluded that Pd–Ag/SiO_2/573 exhibits the best performance among three catalysts in both lifetime and selectivity, which may suggest that electronic promotion is more important than geometric. However, it is noteworthy in Fig. 4 that the conversions obtained on Pd–Ag/SiO_2/573 are consistently lower than those obtained on the other catalysts. The turnover frequencies of Pd–Ag/SiO_2, which changed from 0.86 to 0.90 s^{-1} after the regeneration, were consistently higher than those of Pd–Ti/SiO_2. However, the Pd surface area estimated by H_2 chemisorption was significantly lower for Pd–Ag/SiO_2, $H/Pd = 0.08$, than for Pd–Ti/SiO_2, $H/Pd = 0.20$, and consequently the conversions were lower for the former than for the latter. A systematic study to compare the performance of catalysts containing the optimum amounts of individual promoters will clarify this issue.

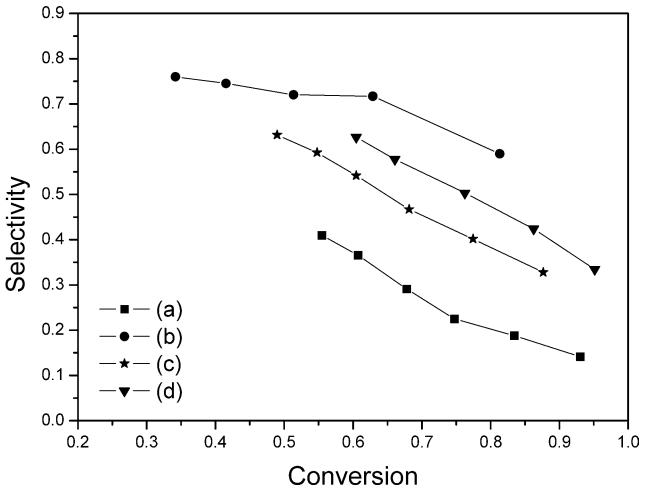

Fig. 4. Changes in ethylene selectivity with conversion in acetylene hydrogenation on various catalysts (temperature = 333 K, H_2/acetylene = 2); (a) Pd/SiO_2/573, (b) $Pd–Ag/SiO_2$/573, (c) $Pd–Ti/SiO_2$/773, (d) Pd–Si/SiO_2/573.

4. Conclusions

TiO_2, when added to a Pd catalyst, reduces the amount of green oil deposited on and in the vicinity of Pd sites and maintains the average carbon number of green oil molecules relatively low by diluting the multiply coordinated Pd sites. TiO_2 also suppresses Pd sintering in the regeneration step by reducing the mobility of Pd crystallites. Accordingly, the TiO_2-added Pd catalyst becomes deactivated at slower rates than the Pd-only catalyst, and the deactivation of the former catalyst is nearly unaffected by the regeneration.

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