Coking and Ex Situ Catalyst Reactivation Using Supercritical CO₂: A Preliminary Study

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High initial conversions for the cyclododecatriene (CDT) hydrogenation in a slurry reactor at 433 K and 1.2 MPa were obtained from a supercritical (sc) CO₂-cleaned 0.5% Pd/Al₂O₃ catalyst. A recovered intermediate selectivity was achieved by the sc CO₂-cleaned catalyst at the higher CDT conversion values, suggesting an effective cleaning of Pd sites and a possible reconstruction of the residual coke layers onto the surface caused by the solvent nature of sc CO₂. SEM pictures show that the cleanup of the used catalyst with sc CO₂ removes most of the coke and oily materials from the surface. Pd SEM X-ray microanalysis evidenced a decrease of the Pd dispersion on the surface of the used-activated catalyst. Coke was also characterized using elemental analysis and TGA in air, indicating that about 80 wt % of the deactivating materials were efficiently removed from the surface by sc CO₂. The formation of the oligomerized and stabilized residual coke (remaining 20%) should be presumably avoided if the catalytic hydrogenation had taken place at sc (in situ) conditions where oligomerization times are minimized. The SCF conditions are then highly challenging at the catalytic hydrogenation of polyunsaturated hydrocarbons.

Introduction

The use of supercritical fluids (SCF) in heterogeneous catalysis is currently an issue of special interest because of their promising potential to overcome major drawbacks commonly encountered in conventional heterogeneous catalytic processes such as low solubility of the gaseous reagents, limited heat and mass transfer between phases, and rapid catalyst deactivation and/or selectivity losses (Tilscher and Hofmann, 1987; Bochnak and Subramaniam, 1998). A catalytic reaction carried out at SCF conditions might lead to (a) an improvement of the mass transport to the catalyst active sites, (b) the substitution of expensive and toxic organic solvents by dense gas, (c) potential homogeneous distributions of temperature and concentration in the reactor (Hitzler et al., 1998), and (d) the potential supression of poisoning or coke deposition on the surface and/or in the pores of the catalysts.

Regarding the latter point (d) of concern in this preliminary study, indeed, the primary reasons for coke buildup and therefore catalyst deactivation are low volatilities of the “coke” compounds that are formed at low subcritical densities (Savage et al., 1995) as well as the extremely low solubility of coke in most common solvents under subcritical conditions. The loss of catalyst pore diffusivity after coke formation (Asplund, 1996) and the catalyst deactivation by hexene oligomers in the isomerization of 1-hexene (Tilscher and Hofmann, 1987) were reported. Modeling of coke formation (Subramaniam and McCoy, 1994) and studies of supercritical (sc) adsorption–desorption (Ginosar and Subramaniam, 1995) were also studied. The optimum catalyst activity (Baptist-Nguyen and Subramaniam, 1992), the in situ extraction of coke precursors by supercritical fluids (Clark and Subramaniam, 1998) and the deactivation kinetics and modeling of coke removal under sc conditions (Niu and Hofmann, 1997; Niu et al., 1995) were also examined.

Because reactions at supercritical conditions may potentially prevent the deposition of oligomers by promoting the in situ extraction of coke precursors, the aim of this preliminary note (previous to an in situ coke removal) is focused on the study of the structural and catalytic changes undergone by a used commercial Pd/Al₂O₃ catalyst (with coke deposits) when subjected to an ex situ CO₂ supercritical extraction. The batch catalytic hydrogenation of cyclododecatriene (CDT) in the liquid phase at low pressure has been used as the reaction for the catalyst tests.

Experimental Section

Cleanup of the Used Catalyst Pellets by Supercritical Extraction. The extraction setup (Figure 1) has been described in detail elsewhere (Puiggene´ et al., 1997). Ten to fifteen grams of used catalyst were placed in the extraction cell. The extraction was started and the gas rate was set at the desired value and left for a

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certain period of time. The weight of the condensate in the tared U-tube was measured with a digital balance \((0.01 \text{ g})\) after five hours of extraction with a constant flow rate of \(1 \text{ L/min}\). The cleaning process was performed at high pressure \((25 \text{ MPa})\), and different temperatures, using pure \(\text{sc CO}_2\). Table 1 reports the experimental conditions and the catalyst weight lost due to the extraction.

Hydrogenation Runs in a Batch Reactor. The procedure for hydrogenation in slurry as well as in continuous fixed-bed upflow reactors has been described earlier (Stüber et al., 1996). The substrate was 1,5,9-cyclododecatriene (CDT). The initial reactant (CDT) is consecutively hydrogenated to form the corresponding cyclic diene (CDD), the cyclic monoene (CDE), and finally the saturated cyclic alkane (CDA).

To rapidly check the activity and selectivity properties of the catalysts, batch slurry hydrogenations of CDT were carried out in a stirred autoclave (Autoclave Engineers, V \(= 500 \text{ cm}^3\)). At the selected operating conditions \((m_{\text{cat}} = 10 \text{ g}, m_{\text{CDT,0}} = 0.25 \text{ kg}, P_{\text{H2}} = 1.2 \text{ MPa}, T_r = 433 \text{ K}, V_{\text{stirrer}} = 33 \text{ rps})\) external mass-transfer effects were absent. However, Stüber et al. (1995) reported severe intraparticle diffusion effects for catalyst pellets, leading to an internal effectiveness factor of 0.01. Experiments were run with commercially pure CDT and \(\text{H}_2\) and three samples of catalyst: a fresh catalyst (Degussa E263 P/D, 0.5% Pd/Al_2O_3, in powder form), a used catalyst, and a used catalyst cleaned with \(\text{sc CO}_2\). Liquid samples were analyzed by GC equipped with a FID and capillary column (Benaissa et al., 1996).

Scanning Electron Microscopy (SEM). A JEOL, JSM-35C scanning microscope operating at 15–25 kV, work distance of 14 mm, and magnification of 2500–4000 was used. Samples were either gold- or carbon-coated for adequate electron conductivity of the surface on secondary electron and backscattering modes, respectively. X-ray microanalyses of particular points of the surface were also performed.

Thermogravimetric Analysis (TGA). The analyses were carried out on a Perkin-Elmer TGA 7 microbalance (1–100 \(\mu \text{g}\) accuracy), equipped with a 298–1073 K programmable temperature furnace. Ten milligrams of the samples was heated at 5 K/min from 323 to 1073 K in a stream of \(\text{Ar} (2 \text{ mL/s})\) and weight decreases were recorded.

Elemental Analysis. C, H, O, and N were determined on a Carlo Erba EA1108 elemental analyzer.
Results and Discussion

Catalytic Tests. Figure 2 illustrates the time-concentration profiles of the four hydrocarbons (CDT, CDD, CDE, and CDA) obtained for the three catalysts tested. Figure 2 qualitatively indicates that the used catalyst undergoes a certain loss both of activity and, more pronounced, of selectivity with respect to the fresh one. It should be noted that when a criterion of peak appearance of the intermediates CDD and CDE (the latter being the desired reaction product) was applied, we found a typical delay (or activity loss) of 50–60% for the used catalyst. Also, in the case of the used catalyst cleaned-up with supercritical CO2, a clear increase of the maximum CDD and CDE yields with respect to the used catalyst can be seen in Figure 2.

Experimental row data points of the three hydrogenation runs were converted to standard conversion and selectivity. The conversion percentage of CDT, a measure of the catalytic activity, is calculated as follows, where $N_{CDT,0}$ and $N_{CDT}$ are the initial and actual number of moles of CDT in the liquid phase.

$$X_{CDT} = \frac{(N_{CDT,0} - N_{CDT})}{N_{CDT,0}} \times 100\% \quad (1)$$

The selectivity percentage is defined in the classical way as the number of moles of a particular hydrocarbon formed over the total molar sum of products, CDD, CDE, and CDA formed:

$$S_i = \frac{N_i}{(N_{CDD} + N_{CDE} + N_{CDA})} \times 100\%, \quad i = \text{CDD, CDE, CDA} \quad (2)$$

Figures 3 and 4 illustrate the so obtained profiles of CDT conversion versus reaction time and CDD, CDE, and CDA selectivities versus CDT conversion for the three catalyst samples tested and the operating conditions specified earlier.

A result that is worth remarking on is that the catalyst cleaned with supercritical CO2 reaches activity values similar to those of a fresh catalyst during an initial reaction time of about 80 min. Then, it loses its initial activity to reach the values of the used catalyst (see Figure 3).

Concerning the selectivity of CDD, CDE, and CDA, Figure 4 reveals two important features. First, for CDT conversion up to 90%, Figure 4 shows slightly higher CDE selectivities in the case of the used catalyst, whereas for CDT conversion, between 90% and 100%, this tendency is reversed. Maximum selectivities of CDE are found to be only 53% (used catalyst) and 68% (fresh catalyst). This unexpected higher CDE selectivity at lower CDT conversions for a used catalyst has to be relativized as respective selectivities of CDD and CDA are always lower and higher (negative effect) than those of a fresh catalyst (see Figure 4). This means that although the consecutive hydrogenations are globally slowed for the used catalyst, both reactions of intermediates are accelerated for conversions below 90%. Second, the selectivities of CDD, CDE, and CDA for the CO2 deaned catalyst are very close, except for CDA at low CDT conversion, to those of the fresh catalyst (see Figure 4). The second result is very promising as the gain in selectivity is maintained constant throughout the complete hydrogenation run despite the deactivation process observed after an initial period. The results obtained from the catalytic tests are further explained when considering the SEM pictures on the catalysts, the coke characterization by TGA, the elemental analyses, and the X-ray surface microanalyses, discussed below.

SEM/X-ray Microanalyses. Figures 5 and 6 show the SEM micrographs from a fresh catalyst (0.5% Pd/Al2O3) and a used catalyst after sc treatment, respectively. The sc CO2 treatment has enabled a significant cleanup of the surface (formerly a black oily surface) obtaining a brown-black liquid of high molecular weight and cleaned dry pellets with a gray-black dull surface that is shown in Figure 6.

Previous powder XRD studies on these Pd/Al2O3 samples were unable to detect any crystalline phase of palladium or palladium oxide. The dominant Al2O3
pattern and the lack of palladium crystallinity made the determination of metal crystallite sizes impossible. As a result, the surface SEM microanalyses (where a spot amount of amorphous palladium is detected) were carried out.

Figures 7–9 exhibit the surface Pd concentrations on several spots of the surface determined by SEM microanalyses. Figure 7 shows a characteristic Pd peak height monitored on any random point taken from the fresh catalyst surface. The fact that the same peak height is obtained at any point of the surface indicates that Pd is quite well dispersed on the fresh catalyst. Figures 8 and 9 show the characteristic Pd peaks taken from different surface points of the sc CO$_2$ treated catalyst and illustrate the presence of Pd peaks of different heights. It can then be stated that Pd becomes less well dispersed on the used catalyst, giving rise to surface spots with either nil or higher Pd contents than the original fresh catalyst. These results are then in agreement with the proposed surface state given from SEM pictures in Figures 5 and 6.

Even though the used-activated catalyst shows an apparent Pd sintering, the initial catalytic activity, as seen in Figure 3, recovers to reach that of the fresh catalyst and decreases lately, reaching that of the used catalyst, for the non-sc catalytic reaction tested. However, the selectivity of the used-activated catalyst toward CDD, CDE, and CDA remains close to the values of the fresh catalyst (Figure 4), suggesting a reconstruction of the surface structure of the catalyst.

**Coke Characterization.** Table 2 reports the results of the elemental and TG analyses taken from a sample of Pd/Al$_2$O$_3$ after being cleaned with supercritical CO$_2$. The TGA result agrees fairly well with the sum of carbon and hydrogen contents of the sc CO$_2$-cleaned Pd/Al$_2$O$_3$ sample. These analyses indicate a coke H/C atomic ratio lower than 1 (hydrogen value is within the error range of the equipment) and hence coke is still slightly present on the surface of the catalyst pellets after the ex situ sc CO$_2$ treatment. The about 5.1% weight loss after the sample has been fired shows then
Nevertheless, the results obtained suggest that if the catalytic reaction were conducted under SCF (in situ) conditions, the coke oligomerization would not have time to be developed and then a long-life catalyst should be expected. This will be our aim next to this preliminary work.

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Literature Cited


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