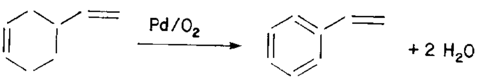
JOURNAL OF CATALYSIS 50, 172–175 (1977)

NOTES

Dual-State Behavior of Palladium/Alumina Catalysts in 4-Vinylcyclohexene-1 Oxidative Dehydrogenation

Supported palladium catalysts are active in 4-vinylcyclohexene-1 (VCE) oxidative dehydrogenation to styrene (STY) (*1*, *2*):



VCE STY

In this process, the selectivity to styrene generally increases after a short initial run of some hours (*2*). This prompted us to study the changes in palladium-on-alumina catalysts during the initial period of VCE oxidative dehydrogenation and, in particular, to see if their behavior was dependent on the preparation method.

Therefore, we considered a number of catalysts prepared by various methods and grouped them into three classes according to the final treatment: Class A catalysts were calcined in a muffle-furnace at high temperature; class B catalysts were reduced with hydrogen in a fluidized bed, at high temperature and then were flushed with nitrogen and stored in air; class C catalysts were reduced at room temperature with an alkaline hydrazine solution, under vigorous stirring, and then were washed and dried for 5 hr at 150°C under vacuum.

Details of catalyst preparation are reported in Table 1.

The above catalysts were tested, according to Ref. (*2*), in a fixed-bed 10-mm-diameter reactor fed with a mixture of VCE, oxygen, and nitrogen. Class A, B, and C catalysts have more or less the same activity for the VCE oxidative dehydrogenation, and, in any case, the small differences cannot be simply correlated with the final treatment conditions. Experiments were performed at VCE conversion values always higher than 90%.

Reaction products were almost exclusively styrene and ethylbenzene (ETB). Experimental conditions and selectivity values measured in the first hour of the test run and then again some hours later are reported in Table 1.

In the first hour only class C catalysts were more selective to STY than to ETB. But the styrene selectivity rapidly increased both in class A and in class C catalysts. On the contrary, no significant selectivity modification was found in class B catalysts which remained much more selective to ETB than to STY. The change in selectivity observed for class A and C catalysts is sometimes accompanied by a very small decrease in activity, VCE conversion still being higher than 90%.

These palladium-on-alumina catalysts were also used for VCE dehydrogenation in the absence of oxygen (*3*): In this reaction, VCE was completely converted to ETB.

Therefore, it seems likely that fresh palladium-on-alumina catalysts, prepared according to methods A, B, or C, have an "intrinsic" selectivity to ethylbenzene, both for oxidative and nonoxidative VCE dehydrogenation; however, in the presence of VCE and oxygen some modification occurs in class A and C catalysts, which

ISSN 0021-9517

TABLE 1

Catalyst	Pd (%)	Preparation method[a]	Final treatment	Reaction conditions[b]		Reaction time	Selectivity (%) to	
				(°C)	($VCE/O_2/N_2$)	(hr)	STY	ETB
A1	0.5	a, e	A: 8 hr at 500°C	157	1/3/29	0.25	16.0	82.9
						2.25	26.5	72.8
A2	1.0	d, e	A: 8 hr at 500°C	175	1/3/29	1.00	35.8	63.0
						3.50	59.9	38.3
A3	0.5	b, e	A: 8 hr at 500°C	210	1/3/29	0.50	13.0	85.5
						3.50	66.1	32.8
B1	1.0	a, f	B: 6 hr at 300°C	175	1/3/29	0.50	7.6	91.9
						3.00	7.8	91.6
				190	1/3/29	1.50	16.0	83.3
						4.50	18.4	81.5
B2	1.0	a, f	B: 12 hr at 300°C	170	1/3/29	1.00	10.2	89.4
						5.00	11.6	87.5
B3	1.0	b, f	B: 6 hr at 300°C	175	1/4/38	0.50	21.4	77.8
						5.00	18.9	79.4
C1	1.0	c, f	C	175	1/4/38	0.50	50.1	47.0
						2.00	69.7	28.7
C2	1.0	b, f	C	150	1/3/29	1.00	56.5	41.7
						3.00	72.0	27.3

[a] Catalysts are prepared by supporting a palladium compound on a commercial alumina (Ketjen, grade E, 49 m^2/g): by impregnation (just wetting the support) with $PdCl_2$, dissolved in water with a slight excess of (a) CH_3COOH, (b) KCl, (c) HCl; by (d) addition of NaOH to a solution of $PdCl_2 + n$ NaCl, with stirring, so as to precipitate $PdO \cdot n\ H_2O$ directly on the support. Catalysts were then dried for 4 hr at 110°C in air (e) or under vacuum (f).

[b] Contact time is always 3 sec.

quickly become more and more selective to styrene.

Furthermore, it was found (*2*) that, when these catalysts turned selective to STY in the VCE oxidative dehydrogenation, they also achieved some activity for the oxidative dehydrogenation of ETB to STY, while fresh catalysts were not at all active for this reaction.

Therefore, it could be inferred that styrene formation in VCE oxidative dehydrogenation goes through ETB dehydrogenation with a consecutive-reaction mechanism:

$$\mathrm{VCE} \rightarrow \mathrm{ETB} \rightarrow \mathrm{STY}.$$

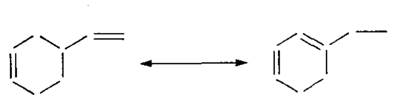
Nevertheless, we could never find ETB conversion values high enough to account for all the styrene formation in the VCE oxidative dehydrogenation. For example, with a class A catalyst (*2*), after a 3-hr test run, STY and ETB formation rates in the VCE oxidative dehydrogenation were, respectively, about 7.4×10^{-7} and 2.8×10^{-7} mole sec^{-1} ml_{cat}^{-1}; when VCE was replaced in the feed with ETB, at the same temperature (240°C), we could not obtain STY formation rates higher than 1.5×10^{-7} mole sec^{-1} ml_{cat}^{-1}. This suggests that, on the contrary, most of the styrene is formed directly through VCE dehydrogenation, according to a parallel-reaction mechanism:

$$\begin{tikzcd}[row sep=small] & ETB \\ VCE \arrow[ur] \arrow[dr] & & . \\ & STY \end{tikzcd}$$

This mechanism would also be in agreement with the fact that, upon changing the contact time during the test run for the A3 catalyst, the STY/ETB ratio did not change.

On the basis of these results only, it is not possible to establish the reaction mechanism; it seems clear, however, that the actual situation of the palladium catalysts during the oxidative dehydrogenation of VCE is a complex one. In particular, it appears likely that, as class A and C catalysts become more selective to styrene during the first few hours of the test run, some kind of surface modification occurs, consisting, for instance, in the formation of new catalytic sites, active for the VCE → STY dehydrogenation (and, to a lesser extent, for the ETB → STY dehydrogenation), which could become competitive with those sites active for the VCE → ETB reaction.

Palladium catalysts are well known to be active for both dehydrogenation and isomerization reactions (*4*). On a purely speculative basis, it is tempting to suggest that the sites giving STY could be dehydrogenation sites, while those giving ETB could be isomerization sites,



ethylcyclohexadiene dehydrogenation to ethylbenzene being a rapid reaction under our conditions (*5*). On this basis, one might think that class A and C samples, when fresh, behave mainly as isomerization catalysts, and that some "*in situ*" modifications, occurring under the VCE oxidative dehydrogenation conditions (due, for example, to an interaction of the dispersed Pd/Al_2O_3 system with oxygen or water), cause the dehydrogenating power to prevail.

As we cannot describe in physical and chemical terms (e.g., palladium surface structure, oxidation state, dispersion, etc.) the actual surface situation of class A and C catalysts during their changes to give higher selectivities to styrene; we cannot even give a definitive explanation of the different behavior of class B catalysts. Nevertheless, this dual-state behavior of our palladium-on-alumina catalysts in the VCE oxidative dehydrogenation could be simply explicable on the basis of some properties of the fresh catalysts. Thus, for example, in the oxidation of methanol over unsupported palladium catalysts, different products were obtained depending on whether the metal was in an oxidized or reduced form (*6*). However, in our case, both B- and C-type samples undergo a reducing treatment: From the point of view of the preparation method, indeed, only type A catalysts are peculiar. This is confirmed by reflectance spectroscopy in the visible region: While B and C samples give flat spectra (their colors varying between dark brown and black), A samples give stronger absorptions in the range of 350–500 nm, probably due to the presence, on the surface of the catalysts, of compounds like $[PdCl_4]^{2-}$ (480 nm), $[Pd(H_2O)_4]^{2+}$ (370 nm), and similar oxo and chloro compounds (*7–9*). Some preliminary ESCA measurements (*10*) have further confirmed that palladium is present in different oxidation states in fresh A and C catalysts, which nevertheless exhibit similar behavior in our reaction.

Furthermore, we could not find, by transmission electron microscopy on extractive replicas, any significant difference in palladium particle size distribution of samples reduced with hydrogen and, respectively, with hydrazine. Therefore, it seems likely that both the metal oxidation state and its dispersion, in the fresh catalysts, have to be excluded as a cause of the dual-state behavior of our catalysts.

All this suggests that the different behavior observed between palladium-on-alumina catalysts calcined in air or reduced with hydrazine, on one hand, and those reduced with hydrogen, on the other, is probably due to more subtle phenomena involving the surface of the catalyst. This is in agreement with the explanations suggested by Taylor *et al.* (*11*) for a similar dual-state behavior of ruthenium and other noble-metal catalysts in reactions such as NO reduction, water–gas shift reaction, NH_3 decomposition and hydrocarbon synthesis ($CO + H_2$). In particular it was suggested (*11*) that the final treatment of the catalyst could be the cause of a surface reconstruction or could exert an influence on the metal–support interaction. Even if no choice can be made between these two factors in explaining the dual-state behavior of our catalysts, we wish to point out that the support plays a relevant role in this reaction: In fact, when palladium is supported on silica or on $CaCO_3$, good selectivities to styrene can be achieved only at conversion values much lower than those ($>90\%$) we used in the Pd/Al_2O_3 tests: Thus, conversion of VCE: Pd/SiO_2, 22.0%; $Pd/CaCO_3$: 55.0%; Selectivity to STY: Pd/SiO_2: 61.7%; $Pd/CaCO_3$: 43.7%; (after 1.75 hr, at 157°C). When temperature and, therefore, VCE conversion are increased, the main product is CO_2.

ACKNOWLEDGMENT

We are grateful to Dr. R. Covini and Dr. P. Cavalieri D'Oro for helpful discussions, and to Mr. W. Grazioli and Mr. G. Sgrinzato for experimental work.

REFERENCES

1. U. S. Patent 3,502,736, Maruzen Oil Co. (1970).
2. German Patent Appl. 2,612,082, Montedison, (1976).
3. Italian Pat. Appl. 23747-A/76, Montedison, (1976).
4. Rylander, P. N., "Organic Synthesis with Noble Metals Catalysts," Academic Press, New York, 1973.
5. See, for example: Herington, E. F. G., and Rideal, E. K., *Proc. Roy. Soc. A*, **190**, 289 (1947).
6. Cullis, C. F., Keene, D. E., and Trimm, D. L., *Proc. Roy. Soc. A*, **325**, 121 (1971).
7. Bozon-Verduraz, F., Omar, A., Escard, J., and Pontvianne, B., "II Seminaire Soviétique-Français sur la Catalyse, Kiev," 1974.
8. Bozon-Verduraz, F., Tardy, M., Bugli, G., Pannetier, G., and Leclère, C., *in* "Preparation of Catalysts,"—Proceedings, International Symposium Brussels, 1975 (Delmon, B., Jacobs, P. A., and Poncelet, G., Eds.), p. 265. Elsevier, Amsterdam 1976.
9. Tauszik, G. R., Marzi, A., and Covini, R., *React. Kinet. Catal. Lett.*, in press.
10. Mattogno, G., personal communication.
11. Taylor, K. C., Sinkevitch, R. M., and Klimisch, R. L., *J. Catal.* **35**, 34 (1974).

A. Castellan
G. R. Tauszik

Montedison S. p. A.
Research Center of Bollate
Via San Pietro 50,
20021 Bollate (Milan), Italy

Received June 28, 1976; revised April 25, 1977