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Study of the Interaction of Aliphatic Alcohols on TiO_2

In Reply to S. Siddhan

Siddhan has made an interesting comment to one of our recent papers on alcohol decomposition in this Journal (*1*) clearly stating the relations existing between the 1-olefin/2-olefin ratio in 2-butanol decomposition and the basicity of the catalysts (i.e., the higher the basicity the higher this ratio) and between the *cis*-2-olefin/*trans*-2-olefin ratio and *syn* and *anti* modes of elimination (i.e., the higher this ratio the more the *anti* mode of elimination). On the basis of these statements he suggests that our results on TiO_2 (1-olefin/2-olefin = 0.5 and *cis*-2/*trans*-2 = 2) are in accordance with the *anti* mode of elimination in the decomposition of 2-butanol.

First of all, we would like to make the point that we have not tried to make any generalization in the sense that 1-olefin and *syn* mode of elimination are complementing though, in fact, an error exists on p. 196 in our paper (*1*) where it says ". . . the reaction giving the *Hoffman olefin* on ThO_2 via *cis*-E_2. . . ." Actually, it should have said *Saytzeff olefin,* which probably has introduced some confusion.

In our opinion it is not clear, looking into the literature, that Siddhan's statements had been applied to our case in a correct form. So, Table 1 includes data taken from Noller *et al.* (*2*) (Ref. (*22*) in our paper) for 2-butanol decomposition on several orthophosphates. It seems that $CaHPO_4$ and $Ba_3(PO_4)_2$ catalysts, having ratios 1-olefin/2-olefin and *cis*-2/*trans*-2 rather similar to those found by us on TiO_2, would show an *anti* mode of elimination using Siddhan's arguments. However, 70% *syn* mode has been calculated for these catalysts using deuterated 2-butanols (incidentally, this is an example in which Saytzeff preference and *syn* mode of elimination simultaneously occur). The same holds for $Ca_3(PO_4)_2$ (85% *syn* mode), whilst $AlPO_4$ produces 2-olefins by a 55% *anti* mode in spite of its low *cis*-2/*trans*-2 ratio. Hydroxyapatite, studied by Hall *et al.* (*3*), gives another example of *syn* mode of elimination with ratios 1-olefin/2-olefin = 0.46, *cis*-2/*trans*-2 = 1.81, close to our values for TiO_2.

Our work was designed, in principle, to examine the behavior of the adsorbed phase present on a TiO_2 surface, which is now well known to us (*4–7*), to see whether information could be obtained on the nature of the sites involved in water elimination from alcohols on this oxide. In fact, our studies by TPD show the evolution of the adsorbed phase, giving a picture of the dynamic nature of the surface species when going from a fully covered surface to its almost free state, at increasing temperatures. So, Fig. 1a (reproducing Fig. 3 in our paper (*1*)) indicates for instance, that the small amount of alcohol molecules existing on the surface at 275°C mainly give *cis*-2-butene by decomposition. This means either that alcohol molecules leading to 1-butene have been exhausted

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TABLE 1

Decomposition of 2-Butanol on Alkaline-Earth Orthophosphates[a]

Catalyst	$Ca_3(PO_4)_2$	$CaHPO_4$	$Ba_3(PO_4)_2$	$AlPO_4$
1-olefin/2-olefin	0.39	0.47	0.33	0.30
cis-2/*trans*-2	1.06	1.61	2.26	0.97
syn/*anti*	85/15	70/30	70/30	45/55

[a] From Ref. (*2*).

at lower temperatures or, as we said in the paper, that 2-butanol molecules in sites originally giving the 1-olefin rearrange on these sites and lead now to the *cis*-2-olefin. In favor of the latter assumption we must remark that the sharp change in olefin composition just starts at the onset of the desorption of the water formed during the alcohol decomposition (see Fig. 5 in our previous paper (*8*)) which will facilitate the rearrangements of the alcohol molecules remaining at the surface, as described in our paper. It is difficult to admit that under our TPD conditions at $t > 225°C$ rehydroxylation would occur at the TiO_2 surface (*5–7*), as suggested by Siddhan to explain the increase in 2-olefins.

On the other hand, we must point out that although kinetic parameters calculated from TPD peaks agree with those obtained in a catalytic reactor, when measured under appropriate conditions (*8*), saturation coverages existing under catalytic pseudozero-order conditions are, in principle, quite different from those occurring during TPD scanning which may affect the olefins distribution if steric effects are important. (That is, now the surface would remain always saturated by the alcohol in equilibrium with the gas phase which immediately replaces the water produced during decomposition restoring the complete alcohol monolayer at each temperature.) This is shown by our results in Fig. 1b, corresponding to the olefin evolution during catalytic decomposition (*9*) of 2-butanol on the same TiO_2 sample used in our work. Though kinetic parameters also coincide in this case with those found by TPD analysis, olefin distribution was different and remained unchanged for all contact times used. It is noteworthy in this figure that the olefin distribution at the lower temperatures agrees with that found at the early stages during TPD scanning (i.e., when the surface remains saturated by alcohol and water molecules at $t < 225°C$). In our opinion, this actually indicates that as long as the TiO_2 surface remains saturated by alcohol molecules the rearrangement of the adsorbed molecules,

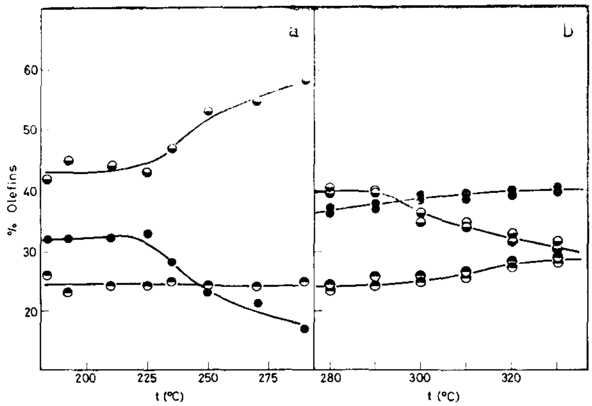

FIG. 1. Olefin evolution in the decomposition of 2-butanol on TiO_2 (anatase), (a) during TPD-scanning of the alcohol adsorbed on the surface (taken from Ref. (*1*, Fig. 3)); (b) during catalytic decomposition under pseudozero-order conditions. Contact times: 0.01–1 s; ●, 1-butene; ⊖, *cis*-2-butene; ◓, *trans*-2-butene.

leading to changes from 1-olefin toward *cis*-2-olefin evolution observed in TPD does not occur, so 1-butene evolution remains almost constant (ca. 38% compared with 32% in TPD).

In addition, Fig. 1b shows that under catalytic conditions the *cis*-2/*trans*-2 ratio changes from ca. 2 to 1 with increasing temperatures. In principle, one is led to ascribe this to an increasing E_1-mechanism. However, we must rule out an important contribution of this mechanism, since olefin distribution remains the same for a wide range of contact times and far removed from the thermodynamic equilibrium. Several alternative explanations can be given. One is to assume that reversible reduction and dehydroxylation of the TiO_2 surface in the alcohol atmosphere produce both sites with a lower steric hindrance (i.e., by removal of O^{2-}) acting in the *trans*-2-olefin formation by a *syn* mode of elimination and new strongly basic O^{2-} ions (i.e., by removal of basic OH groups at 3730 cm^{-1}) involved in the 1-olefin formation. Both reduction and dehydroxylation of TiO_2 are now documented in the literature under rather similar conditions.

Individual activation energies calculated for the three olefins during the catalytic process indicate that the *trans*-2-butene requires ca. 4 kcal mol^{-1} more than the *cis*-2-butene on our nonporous (*10*) TiO_2 surface, suggesting that the reaction leading to that olefin has to take place necessarily by the *syn* mode from the strained symperiplanar or synclinal conformation. In this sense, we think that both *anti* and *syn* modes are competitives on our TiO_2 surface though, of course, a study using deuterated 2-butanols would definitely settle this point.

In fact, an exact knowledge of the actual state of the surfaces during catalysis seems of paramount importance in the assessment of the role of sites stereochemistry in these reactions. In our opinion, it may be risky to afirm, viz., "sodium modifies Al_2O_3 basicity resulting in increased 1-olefin evolution while the mode of elimination just remains *anti* . . .," unless the formation of a new phase (i.e., aluminate) under catalytic conditions had been ruled out.

In spite of the dynamic character of the catalytic surface our results on TiO_2 seems to support Noller's statement (*2*), viz., "we would suppose that the selection between *cis* and *trans*(*syn* and *anti*) is mainly due to steric effects."

REFERENCES

1. Carrizosa, I. and Munuera, G., *J. Catal.* **49**, 189 (1977).
2. Thomke, K., and Noller, H., *in* "Proceedings, 5th Intern. Congress on Catalysis" (J. Hightower, Ed.), Vol. 2, p. 1183. North-Holland, Amsterdam, 1973.
3. Kibby, C. L., Lande, L. L., and Hall, W. K., *J. Amer. Chem. Soc.* **94**, 214 (1972).
4. Munuera, G., Moreno, F., and Gonzalez, F., *in* "Proceedings, 7th Intern. Symposium on Reactivity of Solids," p. 681. Chapmann & Hall, London, 1973.
5. Munuera, G., Gonzalez, F., Moreno, F., and Prieto, J. A., *in* "Proceedings, 5th Intern. Congress on Catalysis" (J. Hightower, Ed.), Vol. 2, p. 1159. North-Holland, Amsterdam, 1973.
6. Parfitt, G. D., *in* "Progr. Surfaces Membrane Sci.," Vol. 11, p. 181. Academic Press, New York, 1976, and references therein.
7. Gonzalez, F., Munuera, G., and Prieto, J. A., *J. Chem. Soc. Faraday Trans.* 1, **74**, 1517 (1978).
8. Carrizosa, I., and Munuera, G., *J. Catal.* **49**, 174 (1977).
9. Carrizosa, I., Cano, R., to be published.
10. Carrasco, J., Gonzalez, F., and Munuera, G., *Anal. Quim.* **67**, 561 (1971).

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