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Reactivity of Spillover Hydrogen

Reactivity of Unsaturated Compounds

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Different unsaturated carboxylic acids (benzoic acid, cyclohexene carbonic acid, acetylene dicarbonic acid, maleic acid, and acrylic acid) were adsorbed on an oxide carrier (γ-Al_2O_3) in the presence of a Pt/Al_2O_3 catalyst. After an investigation of the thermal stability, spillover experiments were performed. Although under the given conditions HD exchange with the OH groups of the carrier took place, and tungsten bronze was formed under similar conditions, none of the acids were hydrogenated. This implies that the spiltover hydrogen leading to HD exchange is not able to hydrogenate unsaturated compounds to a detectable degree.

1. INTRODUCTION

Since the description of hydrogen spillover by Khoobiar (*1*) in 1964, many aspects of this effect have been investigated. Thus Levy and Boudard (*2*) observed the catalytic action of platinum during the reduction of WO_3, forming tungsten bronze. Teichner *et al.* (*3, 4*) report on the ability of a carrier (Al_2O_3, SiO_2) to hydrogenate ethene after a spillover experiment. Surface methoxy groups were observed to react with spillover hydrogen (*5*). On the other hand Antonucci *et al.* (*6*) claim to have found but little diffusion of active hydrogen to the oxide surface. In the system Pt/Al_2O_3, benzene will not react with the diffusing species but only with hydrogen atoms trapped on surface defects. The TPD experiment of Kramer and Andre (*7*) gave identical peaks for hydrogen desorption from spillover samples as from others obtained by an electric discharge in a hydrogen atmosphere. This is taken as evidence for some kind of atomic species spilled over.

In our investigations we attempted to test the nature of the species which are diffusing in a fast reaction across the layer of alumina in the Pt/Al_2O_3 system, in accordance with other investigations (*8–10*). Reducible carboxylic acids were adsorbed on the oxide component, and Fourier transform (FT)IR spectrometry should be able to detect whether or not they may react with spilledover hydrogen.

2. EXPERIMENTAL

Fourier transform–infrared spectroscopic measurements were made with a Bio-Rad spectrometer (FTS-15E) using a cell described earlier (*11*). Samples of γ-Al_2O_3 (Degussa type C) were impregnated with $H_2[PtCl_6]$ or $[Pt(NO_2)_2(NH_3)_2]$ and reduced, giving a Pt weight loading of 3%. A second sample was prepared from oxide partially covered with the carboxylic acid. Finally, a wafer was pressed from a mixture of both samples to avoid direct contact of metal and acid to ensure that reaction could only occur after surface diffusion of the hydrogen species across the oxide. Tungsten oxide was mechanically mixed with Pt/Al_2O_3 in a separate experiment. All samples were pretreated in helium at the reaction temperature before reaction with a hydrogen–helium stream (50 ml/min, 100 mm Hg H_2 partial pressure, 1 mm Hg = 133.32 Pa). During the reaction, spectra were taken every 5 min. All spectra were plotted in the form of absorbance with the spectrum of

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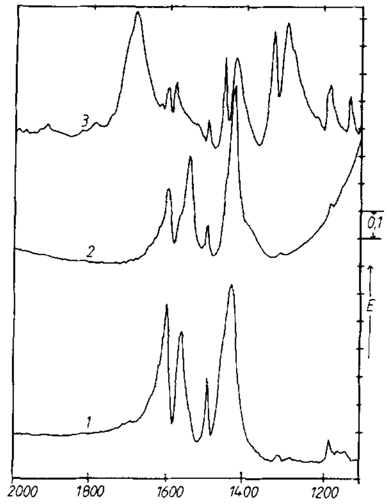

FIG. 1. State of benzoic acid adsorbed to γ-Al_2O_3: IR spectra (absorbance vs wavenumber). 1, benzoic acid adsorbed on γ-Al_2O_3 (type C); 2, aluminum benzoate in KBr; 3, benzoic acid in KBr.

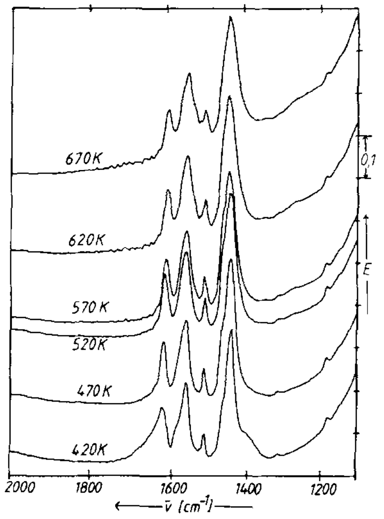

FIG. 2. Thermal stability of benzoic acid adsorbed on γ-Al_2O_3: IR spectra (absorbance vs wavenumber) taken after 30 min at temperature indicated.

the empty cell as background (resolution, 8 cm^{-1}).

3. RESULTS AND DISCUSSION

From investigations of Kummert and Stumm (*12*) it follows that alcohols, aldehydes, and carboxylic acids all form carboxylates on alumina; thus we chose the acids for adsorption. The adsorption of carboxylic acids has been also investigated by other authors (*13–16*). Figure 1 gives spectra of aluminum benzoate, adsorbed benzoic acid, and free benzoic acid.

In Fig. 2 spectra of adsorbed benzoic acid are shown. The samples were treated at different temperatures for about 30 min each in helium. Up to about 620 K no decomposition could be observed. Above this temperature the intensity of the bands slowly decreases without formation of new bands attributable to possible decomposition products.

The possible reaction of hydrogen with the adsorbate in the absence of platinum was tested by heating each sample for 120 min at 320, 470, and 570 K. As shown in Fig. 3, as an example at 470 K, no reduction takes place. This confirms that any reaction that takes place in the presence of platinum would be due to spilledover hydrogen. For comparison Fig. 4 shows the spectra of benzoic acid and its possible hydrogenation products cyclohexene- and cylcohexane carbonic acid, assuming that the carboxylic

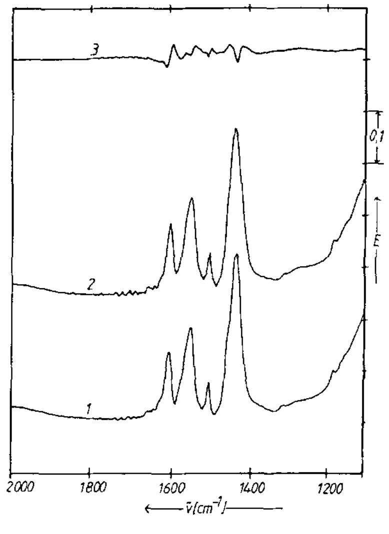

FIG. 3. Benzoic acid on γ-Al_2O_3 (T = 470 K): IR spectra (absorbance vs wavenumber). 1, Sample measured in He; 2, sample after 120 min in H_2/He; 3, difference spectrum.

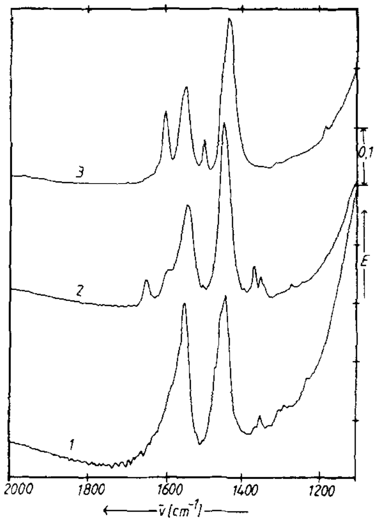

FIG. 4. Spectra of benzoic acid and its possible hydrogenation products (T = 470 K). 1, cyclohexane carbonic acid; 2, cyclohexene carbonic acid; 3, benzoic acid.

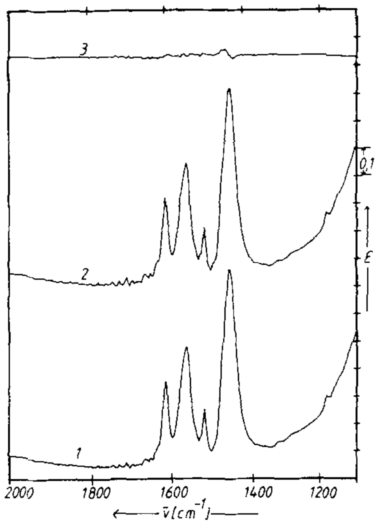

FIG. 5. Benzoic acid on Pt/γ-Al_2O_3 (T = 470 K): IR spectra (absorbance vs wavenumber). 1, sample measured in He; 2, sample after 120 min in H_2/He; 3, difference spectrum.

group does not react with spilledover hydrogen. Spillover experiments were performed at 320, 370, 420, 470, 520, 570, and 620 K, with reaction times of 120 min. Figure 5 is representative for all results: no reaction could be observed. The difference spectrum does not show any new bands, especially in the regions where the IR bands from cyclohexene- or cyclohexane carbonic acid adsorbates would be expected.

Two further measurements were performed to ensure that hydrogen spillover took place under the given conditions. First, after each spillover experiment, hydrogen was replaced by deuterium, to test the deuteration of surface hydroxyl groups. As to be seen from Fig. 6 the hydroxyl groups are extensively converted to deuteroxyl groups after 20 min at 470 K. This HD exchange was not caused by traces of water or oxygen, as was shown earlier (8–10) and it occurs without any change in the bands of the benzoate groups, even without deuteration of these groups. Second, experiments in the system WO_3–Pt/Al_2O_3 showed that formation of tungsten bronze took place at temperatures as low as 290 K within 5 min. Within this time the

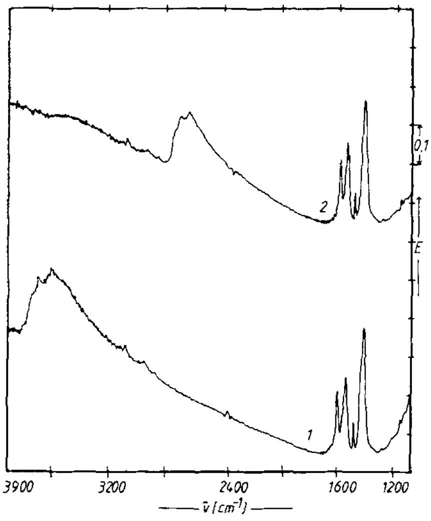

FIG. 6. Deuteration of surface hydroxyl groups of alumina on Pt/Al_2O_3 with adsorbed benzoic acid (T = 470 K); reaction time-20 min). 1, i.r. spectrum before reaction; 2, i.r. spectrum after reaction with D_2.

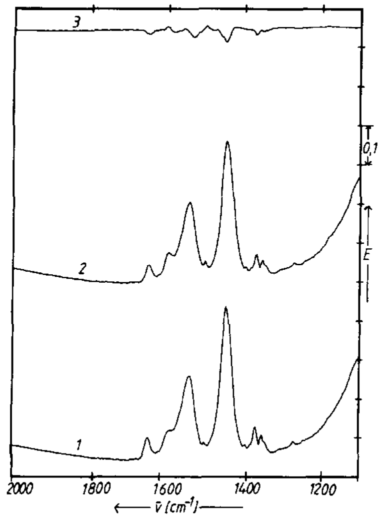

FIG. 7. Cyclohexene carbonic acid on Pt/Al_2O_3. 1, in helium; 2, after 120 min in H_2/He; 3, difference spectrum.

transmittance of the wafer dropped to about 1% of its original value—measured in helium. Visual inspection revealed that indeed the intensive blue bronze had formed.

The fact that benzoic acid did not react, though spillover took place, cannot be explained by thermodynamic limitations (*17*), since thermodynamic data favor the formation of cyclohexane from benzene below 560 K. The influence of the carboxyl group should be small in this respect. A variation of the reaction temperatures over a wide range should exclude that the reaction did not take place because of the stability of the benzoate. To exclude any remaining doubts, equivalent measurements were made with adsorbed cyclohexene carbonic acid, where the equilibrium is clearly on the side of the hydrogenation product. As Fig. 7 shows no reaction is observed in this case, except the desorption of the reactant, leading to a decrease in the cyclohexane carboxylate bands in the difference spectra.

Last, doubts about the reactivity might arise from steric problems, which might apply especially to the benzoate ion, as this ion is adsorbed with the benzene ring perpendicular to the oxide surface (*18*). Thus the interaction between the π-electron system and hydrogen, fixed to the surface, might be too small for a reaction. This problem should not arise with adsorbed maleic acid, but even in this system no reaction could be seen.

Finally experiments were carried out with acrylic- and acetylene carbonic acids. Even in these experiments there is no evidence of reaction.

As a consequence of these experiments we conclude that hydrogen spillover does not necessarily lead to the formation of active hydrogen species on the oxide surface, which are able to hydrogenate aromatic, olefinic, or acetylenic systems, yet the spilledover hydrogen is able to effect exchange of surface hydroxyls or formation of tungsten bronze. We therefore question the importance of spilledover hydrogen in direct reactions during catalytic conversion of hydrocarbons at least for alumina as a carrier.

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REFERENCES

1. Khoobiar, S., *J. Phys. Chem.* **68,** 411 (1964).
2. Levy, R. B., and Boudart, M., *J. Catal.* **32,** 304 (1974).
3. Teichner, S. J., *et al., J. Catal.* **38,** 135 (1975).
4. Teichner, S. J., et al., J. Catal. **59,** 467 (1979).
5. Teichner, S. J., *et al., J. Catal.* **68,** 411 (1981).
6. Antonucci, P., *et al., J. Catal.* **75,** 140 (1982).
7. Kramer, R., and André, M., *J. Catal.* **58,** 287 (1979).
8. Baumgarten, E., and Denecke, E., *J. Catal.* **95,** 286 (1985).
9. Baumgarten, E., and Denecke, E., *J. Catal.* **95,** 296 (1985).
10. Baumgarten, E., and Denecke, E., *J. Catal.* **100,** 377 (1986).
11. Baumgarten, E., and Weinstrauch, F., *Spectrochim. Acta A* **34A,** 1155 (1978).

12. Kummert, R., and Stumm, W., *J. Colloid Interface Sci.* **75,** 373 (1980).

13. Hall, T., and Hansma, P. K., *Surf. Sci.* **76,** 61 (1978).

14. Deflin, M., Eltantawy, I. M., and Baverez, M., *J. Catal.* **54,** 345 (1978).

15. Kuiper, A. E. T., *et al., J. Catal.* **29,** 40 (1973).

16. Cederberg, A. A., and Kirtley, J. R., *Solid State Commun.* **30,** 381 (1979).

17. D'Ans Lax: Taschenbuch für Chemiker and Physiker Band II'' (E. Lax, Ed.), Springer-Verlag, Berlin, 1964.

18. Groff, R. P., *J. Catal.* **79,** 259 (1982).