

NOTE

On the Chemical Nature of Hydrogen Spillover

INTRODUCTION

A study by Benson, Kohn and Boudart (1) showed that hydrogen spillover plays an important role in the room temperature reduction of WO_3 but the chemical nature of this activated, diffusing hydrogen was not established. Observation of a reaction between adsorbed ion free radicals and spilled-over hydrogen could clarify the nature of this hydrogen species. The ion radicals provide a strong ESR signal on zeolites (2) and a reduction in signal intensity upon contact with spilled-over hydrogen would imply that hydrogen migrates as H^\cdot .

EXPERIMENTAL AND RESULTS

Four different samples were used: SK-200 (0.5% Pt/Ca-Y zeolite), 0.1% Pd supported on a Ce-exchanged Y zeolite, 4% Pt black/Ce-Y and 6% Pt black/Ce-Y. The Pd/Ce-Y sample was prepared in this laboratory and the two physical mixtures of Pt black/Ce-Y were prepared by grinding with a mortar and pestle. A sample of Ca-Y zeolite was used as a blank for comparison with the SK-200. Ce-Y zeolite was used as a blank for the other catalyst systems. All samples were activated under flowing air at temperatures between 400 and 600°C for 2-5 hr.

Anthracene or perylene (K&K Chemicals) was dissolved in CCl_4 , added to the catalyst in an ESR tube, and the CCl_4 was removed under vacuum. The ESR signal due to the positive ion radical of either anthracene or perylene was monitored with a Varian 4502-11 EPR spectrometer as a function of time at 22 or 57°C, first in

vacuum then under a hydrogen pressure of 300 Torr.

Anthracene, perylene, or hydrogen adsorbed on Pt black gave no ESR signal. In addition, the four catalysts did not give an ESR signal if they were exposed to hydrogen in the absence of anthracene or perylene.

All the catalysts exhibited similar behavior: The ESR signal height, which is proportional to the free radical concentration, was reduced more rapidly and more completely in the presence of Pt or Pd than in the blanks. Examples of this behavior are represented in Fig. 1-3 for anthracene and in Fig. 4 for perylene. Ordinate values were obtained by dividing the ESR peak height by the signal level. The absolute magnitude of the ordinate directly reflects the loss of unpaired spins and therefore the amount of diffused hydrogen. The change in standardized signal height shown in Fig. 3 corresponds to a spillover of approximately 20 $\mu\text{mole H}_2/\text{g}$ of sample. The number in parentheses next to each run represents the percent loss of the initial signal height.

After exposure to hydrogen, analyses of the catalysts by mass spectrometry gave a distribution of mass numbers from 178 up to and including 192 when anthracene was the adsorbate. The 192 peak, assumed to be perhydroanthracene, was found to be the most intense of the hydrogenated species. The amount of hydrogenation was substantially greater than that found to occur only on the Pt black.

To determine the amount of hydrogenation due to the Pt black alone, excess

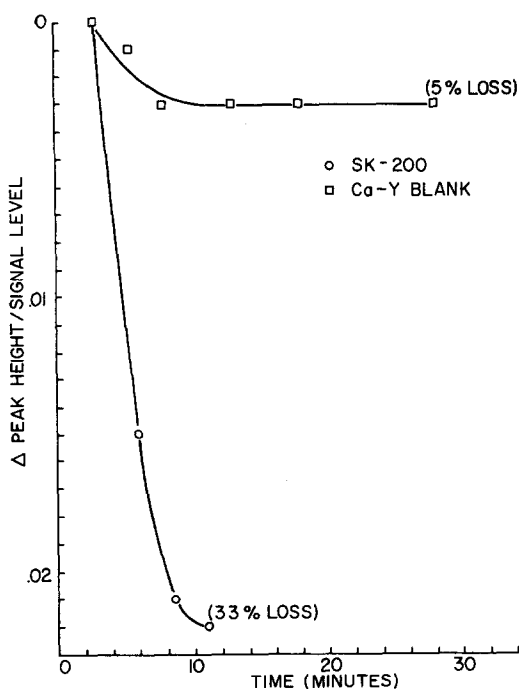


FIG. 1. Disappearance of anthracene ion radicals after H_2 exposure at $22^\circ C$.

anthracene was adsorbed on a pure Pt black sample whose weight was 10 times the weight of Pt black in the 6% Pt/Ce-Y sieve sample. The specific surface area of the Pt black in different samples was assumed equal. Upon exposure to hydrogen at $57^\circ C$, the anthracene was converted to

perhydroanthracene but the relative intensity of the mass spectrometer signal was only 1.5 times larger than the corresponding signal from the Pt black/Ce-Y sieve mixture. Since the Pt blank would be expected to give an intensity 10 times greater if hydrogenation were due to Pt alone, the synergistic effect of mixing Pt black and Ce-Y sieve upon hydrogenation is shown.

DISCUSSION

Hydrogen spillover (the diffusion of hydrogen from a surface capable of dissociating H_2 onto the surface of an adjoining solid) has been observed in a number of systems (3). The results presented here indicate that the migrating hydrogen possesses an electron capable of pairing with an unpaired free radical electron. Atomic diffusion is the simplest model to explain these data.

Diffusion of a proton onto and across the surface of the zeolite with simultaneous electron transfer through the zeolite to the adsorption site of the free radical does not appear reasonable since zeolite conductivity has been found experimentally to be due to cation migration. The fact that zeolites possess no measurable conductivity attributable to electrons (4, 5) is not surprising since Khoobiar *et al.* (6) found the band gap in $\eta-Al_2O_3$ to be 9.6eV; a band gap of similar magnitude is reasonable for

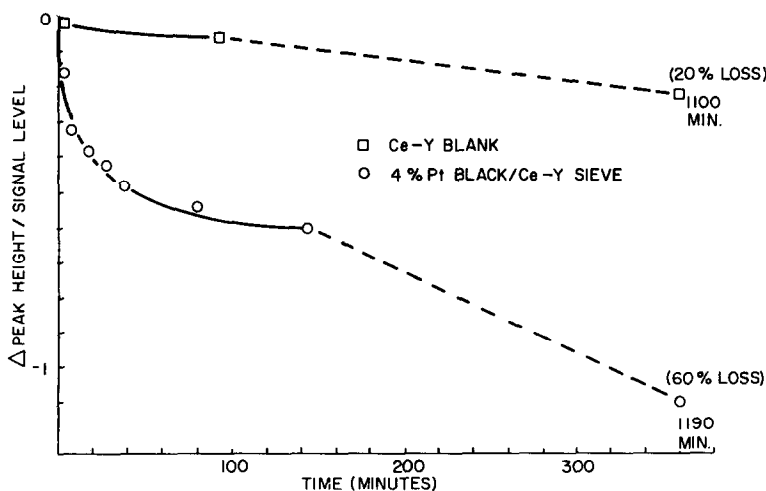


FIG. 2. Disappearance of anthracene ion radicals after H_2 exposure at $22^\circ C$.

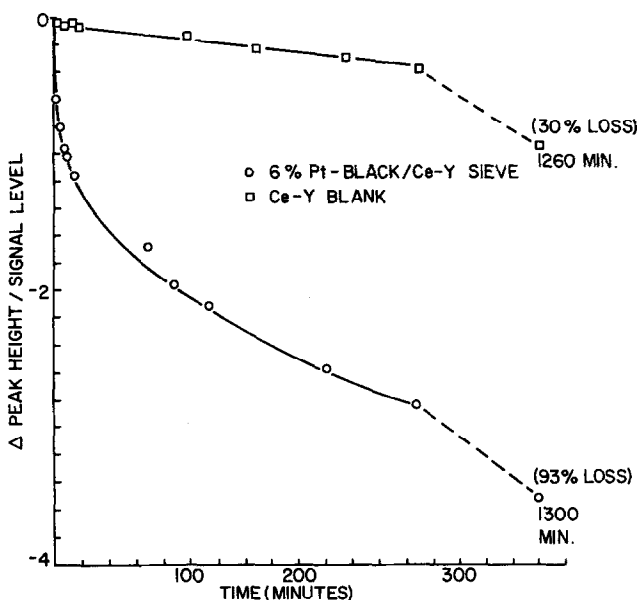


Fig. 3. Disappearance of anthracene ion radicals after H_2 exposure at $57^\circ C$.

a zeolite system. Extrapolation of data on $\eta-Al_2O_3$ (6) to $57^\circ C$ gives a conductivity value of $10^{-25} \text{ ohm}^{-1} \text{ cm}^{-1}$. Using this value to approximate the electronic conductivity in our zeolite system, we calculate the electron transport to be 10 orders of magnitude less than that observed, even if an electric field of 10^4 V cm^{-1} were applied across the sample.

The average distance between Ce ions ($\sim 10 \text{ \AA}$) is too great to allow electron transport by this mechanism. At this time though, we cannot preclude the possibility of electron transfer via electron exchange between ion free radicals and neutral molecules.

Incorporation of hydrogen as a hydride ion into the free radical would not of itself

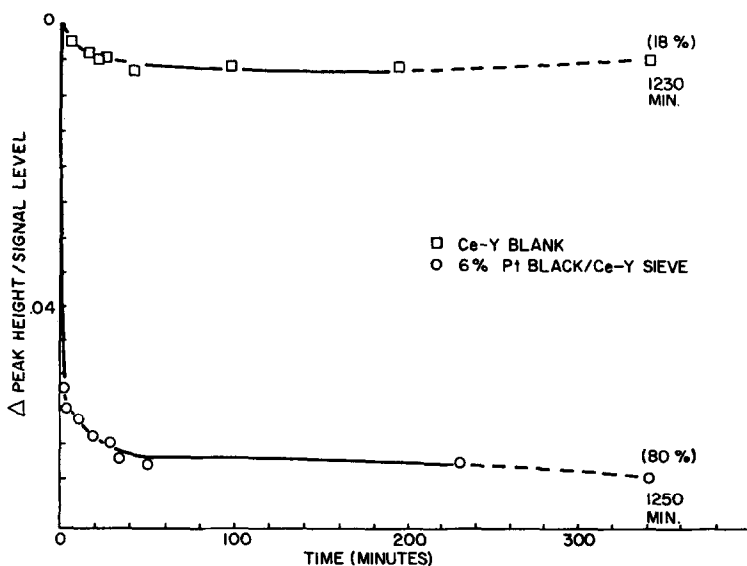


Fig. 4. Disappearance of perylene ion radicals after H_2 exposure at $57^\circ C$.

cause a decrease in the ESR signal intensity. However, the eventual coupling of partially hydrogenated free radicals produced by this mechanism cannot be discounted. Both this mechanism and the electron exchange process are complicated by the necessity for charge balance on the platinum. Experiments are in progress to evaluate the contribution of these pathways and others to the destruction of ion radicals in these systems.

Lewis (7) suggested that hydrogen spillover may occur in zeolite systems. This suggestion was later reinforced by Boudart (8). Our verification of this must make one aware of problems which may arise when selective chemisorption measurements are made on supported catalysts to calculate dispersion values. Conclusions, based on high hydrogen uptakes in zeolite systems, that metals are atomically dispersed may not be warranted.

REFERENCES

1. BENSON, J. E., KOHN, H. W., AND BOUDART, M., *J. Catal.* **5**, 307 (1966).
2. NEIKAM, W. C., *J. Catal.* in press. (1971).
3. BOUDART, M., VANNICE, M. A., AND BENSON, J. E., *Z. Phys. Chem. N.F.* **64**, 171 (1969).
4. FREEMAN, D. C., AND STAMIREN, D. N., *J. Chem. Phys.* **35**, 799 (1961).
5. BEATTIE, I. R., *Trans. Faraday Soc.* **50**, 581 (1954).
6. KHOBIAR, S., CARTER, J. L., AND LUCCHESI, P. J., *J. Phys. Chem.* **72**, 1682 (1968).
7. LEWIS, P. H., *J. Catal.* **11**, 162 (1968).
8. BOUDART, M., *Adv. Catal. Relat. Subj.* **20**, 157 (1969).

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