EFFECT OF GAMMA RAY IRRADIATION ON ACTIVITY OF RANEY-NICKEL CATALYST

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The activity of Raney Nickel (T-4) Catalyst has been found to diminish for the deuteration of organic compounds when the catalyst was irradiated by gamma rays. Surface area measurements of the catalyst support this observation as the surface area of irradiated catalyst was found to be considerably less.

INTRODUCTION

Metals of the first transition series and many of their compounds make good catalysts for various reactions. Effects of environment and maintenance of exact conditions in a method of preparation play an important role. The activity of the catalyst varies with slight changes in the method of preparation followed. The activity of the catalyst changes if the structure is changed either by the adsorption of certain gases on the surface, annealing or by induced surface reconstruction by radiations. Gamma irradiated nickel oxide (cf. Tezuka & Techuchi 1969; and Yamashina & Nagamatsuya 1966, 1968) and other catalysts (Sano *et al.* 1969; and Garnett *et al.* 1967) have been found to yield altogether different activity for different processes. Radiation has increased the activity for some reactions and decreased for others. The activity depends upon the active centres on the surface of the catalysts. For deuteration reactions two types of active centres are considered.

Exchange of deuterium between benzene or biphenyl and heavy water has been chosen to test the activity of the catalyst. The process is relatively simple and the reproducibility of the results is very good (Bajpai & Paul 1967). This kind of study is also important for the mechanistic and theoretical studies of the radiation induced interactions on catalytic surfaces (Garnett *et al.* 1967).

EXPERIMENTAL

(*a*) *Materials used :* Benzene—analar, B. D. H.; Heavy water—isotopic purity >99.4 atom per cent, procured from the Heavy Water Division, BARC; Raney Nickel alloy—B. D. H.; Raney Nickel Catalyst—prepared by the method described by Nishimura (1959). The catalyst was kept under ethyl alcohol and the necessary amount withdrawn in nitrogen atmosphere.

(*b*) *Deuteration method :* 2 ml of benzene, 4 ml of D_2O (isotopic purity>99.4 atom per cent) and 0.05 gms of catalyst were taken in a thick-walled tubing of 6″ in length and 15 mm in diam. The contents were frozen in a liquid nitrogen bath. The tubings were evacuated and sealed. The capsules so prepared were stirred in an

TABLE I

Effect of amount of catalyst on deuteration

Sl. no.	Amount of catalyst in grams	% deuteration observed
1	0	0
2	0.05	58.32
3	0.07	67.75
4	0.08	67.75
5	0.1	73.13
6	0.3	76.83
7	0.5	75.00
8	0.7	75.00

TABLE II

Effect of gamma irradition on the activity of the catalyst for deutration and on its surface area

(Amount of the catalyst used is 0.05 gms. for Benzene and 2.5 gms for Biphenyl deuteration)

Sl. No.	Hours of gamma irradiation	% deuteration observed		Surface area m^2/gm	
		Catalyst Batch 1 (Benzene)	Catalyst Batch 2 (Benzene)	Catalyst Batch 1	Catalyst Batch 2
1	0	57.42	—	83.6	98.9
2	8	—	43.67	—	79.2
3	16	49.70	40.85	70.8	59.4
4	24	—	26.06	53.0	48.0
5	40	0	24.65	51.7	26.6
6	80	0 (Biphenyl)	— (Biphenyl)	10.2	—
7	0	34.70	—	83.6	—
8	16	21.30	—	70.8	—

oil-bath maintained at 150°C. After 48 hours the capsules were removed, the seals broken and the upper layers of benzene got analysed for the extent of deuteration on varian analytical NMR spectrometer A–60 A. Procedure with biphenyl was similar to above and described earlier (Bajpai & Paul 1967). The weight of the biphenyl taken was one gram.

(*c*) *Surface area measurements :* Surface area was measured after degassing the catalyst at 150°C, by a BET volumetric apparatus using nitrogen as adsorbate at liquid nitrogen temperature.

(*d*) *Gamma irradiation :* Catalyst wasi rradiated in nitrogen atmosphere using Cobalt–60 irradiator made by Isotope Division, BARC (AECL 200 type) with the

activity of 3000 curies. The dose rate of 2.5×10^5 rads/hour was kept constant while the time of irradiation was varied.

Results

To determine the suitable amount of catalyst, various amounts of the unirradiated catalysts were taken in different tubes. The results are summarised in Table I.

From Table I it will be seen that for the experimental conditions employed in the present case 0.1 gm of the catalyst is just about the optimum amount for effecting maximum deuteration in benzene. Half of this amount was taken for irradiation effect studies.

Table II shows as to how the deuteration in benzene goes on diminishing as the hours of gamma irradiation of the catalyst go on increasing.

Discussion

The results of the gamma irradiation effect on the catalytic activity for the deuteration of benzene and biphenyl clearly indicate that the activity of the catalyst is markedly decreased as the radiation dose is increased.

A catalytic reaction or an adsorption process depends on the overall action of a number of surface atoms. The most important consideration is the number of active sites in the process. These sites vary for different reactions.

Raney Nickel contains Ni-H sites which are considered for the deuteration process. Gamma irradiation may induce desorption of hydrogen resulting in loss of activity of the catalyst. Alternatively gamma irradiation may produce secondary photon or compton electrons which may produce lattice defects (Opolinska & Ciborowski 1962) that might completely alter the activity of the catalyst. In fact the radiation can induce complete reconstruction of the surface.

B 5 type of sites are usually found on steps of the catalyst surface. The reconstruction of the surface resulting in the reduction of the surface area as in the present case indicate smoothening of such steps resulting in loss of sites as well as surface area.

Further information to confirm the mechanism of the deuteration reactions is underway. Thermodynamic quantities like heats and entropies of adsorption as a function of surface coverage will determine the change of surface heterogeneity. The X-ray diffraction and electron microcopy of the catalyst may also be useful in understanding the phenomenon.

The effect and control of environment in deciding the catalyst specificity and activity for a particular process is an important consideration. Such studies may lead one to get an insight into the correlation between surface structure and the activity of the catalyst. The detailed knowledge of surface structure is useful in many processes such as catalysis and its related field adsorption, crystal growth, sintering, adhesion and mechanical strength.

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