

## ISOPROPYLBENZENE DECOMPOSITION AND HIGH TEMPERATURE ADSORPTION OF PYRIDINE ON HYDROREFINING CATALYSTS

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Received November 15th, 1982

The acidic properties of various oxidic and sulphided hydrorefining catalysts have been studied by means of isopropylbenzene decomposition at 400°C in a pulse reactor, and of the adsorption of pyridine at 300°C. Isopropylbenzene reacted in two parallel reactions, forming benzene and propene by cracking, and  $\alpha$ -methylstyrene by dehydrogenation. Sulphidation influences more the strength than the concentration of acidic sites. A correlation between the rate constants for the cracking of isopropylbenzene and the  $b$  constants of Langmuir isotherm for pyridine adsorption is presented.

Of the various properties of hydrorefining catalysts, also their acidity has got attention recently. Most work has been dealing with the IR spectra of adsorbed basic molecules<sup>1-3</sup>; also the extent of the adsorption or acid catalyzed model reactions have been studied.

In the present communication, we describe the results of the study of isopropylbenzene decomposition and of the high temperature adsorption of pyridine in a series of hydrorefining catalysts of different origin in oxidic and sulphided forms.

### EXPERIMENTAL

*Catalysts.* Samples 2 to 5 reported in the preceding paper<sup>4</sup> were utilized in this work. A commercial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (HO 417 Houdry Hüls) which was used as a carrier for the preparation of samples 2 and 3 was also included into the measurements.

*Isopropylbenzene decomposition.* Helium (BOC) used as carrier gas was dried over molecular sieve 13X, and isopropylbenzene (chromatographic standard Merck) was used directly. The experiments were carried out in a pulse reactor which consisted of a stainless steel tube 4.8 mm i.d., connected to a chromatographic column with the following characteristics: Stainless steel, length 2 m, 4 mm i.d., packed with 10 wt.% polyethyleneglycol on Celite 0.125–0.177 mm. The temperature of the column was 120°C and of the flame ionization detector 200°C. The catalyst sample (0.08–0.16 mm) was mixed with an inert and placed in the central zone of the reactor between glass wool plugs. The reactor was then attached to the column and heated in He from room temperature to 400  $\pm$  3°C in 2 h. Fifteen 0.4  $\mu$ l pulses of isopropylbenzene were injected into the reactor. Conversions were calculated for each pulse from the areas of the corresponding peaks and those obtained daily by injection of isopropylbenzene and benzene standards through the reactor filled with an inert. Exploratory experiments were made and it was

decided that with the size of particles used and with He flows from 40 to 60  $\text{cm}^3 \text{min}^{-1}$  no mass transfer limitations or chromatographic effects were present in the reactor. Isopropylbenzene was simultaneously dealkylated to benzene and propene and dehydrogenated to  $\alpha$ -methylstyrene. Strong deactivation was observed during the fifteen pulses injected. An example of products composition is shown in Fig. 1.

The identification of  $\alpha$ -methylstyrene was carried out by means of the following procedure: Catalyst 4 was charged in a glass flow reactor and reduced with  $\text{H}_2$  at 400°C during 4 h, operating at 450°C and 0.99  $\text{h}^{-1}$ , 15 wt.% of  $\alpha$ -methylstyrene was present in the reaction product. It was separated in a preparative gas chromatograph and identified by NMR using a Hitachi H 6013 spectrometer.

**Pyridine adsorption.** Pyridine (BDH) was purified by bulb to bulb distillation in the same high vacuum adsorption apparatus. A McBain balance was used for the measurements of the adsorption at  $300 \pm 3^\circ\text{C}$ , oxidic or sulphided samples (0.016–0.25 mm) were activated under high vacuum (better than  $1.3 \cdot 10^{-3} \text{ Pa}$ ) at 400°C during 4 h.

## RESULTS AND DISCUSSION

**Isopropylbenzene decomposition.** Both the overall conversion of isopropylbenzene  $X_i$  and the conversion to cracked products  $X_c$  were extrapolated to the fresh

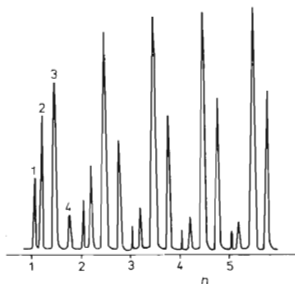


FIG. 1

Typical chromatogram of the products of the decomposition of isopropylbenzene in pulse reactor. 1 Propene, 2 benzene, 3 isopropylbenzene, 4  $\alpha$ -methylstyrene

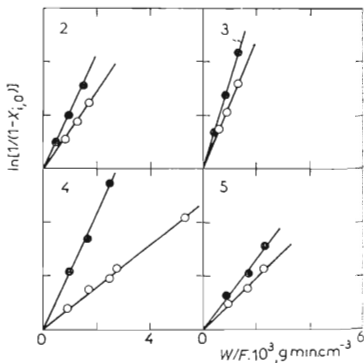


FIG. 2

First order plots of the overall conversion of isopropylbenzene. The numbering of the graphs corresponds to the numbering of the catalysts. O Oxide form, ● sulphided form

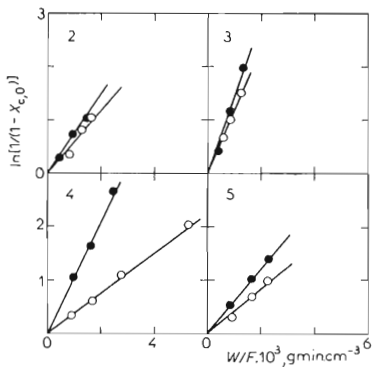


FIG. 3

First order plots of the conversion to cracked products. For explanation see Fig. 2

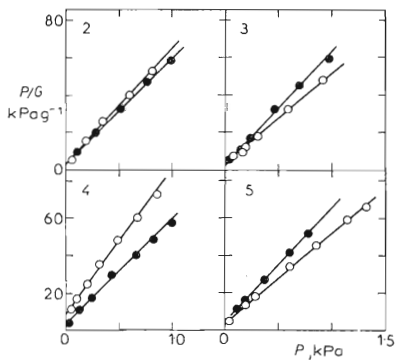


FIG. 4

Fit of the data on pyridine adsorption to the linear form of Langmuir isotherm. For explanation see Fig. 2

surface, *i.e.* to the zeroth pulse using the minimum squares procedure for the relations  $\ln X_{i,n}$  and  $\ln X_{c,n}$  vs pulse number  $n$ ; the data from the first three to five pulses agreed reasonably with this assumption. In Figs 2 and 3 are shown the first order plots of the overall conversion of isopropylbenzene  $X_{i,0}$ , and of the conversion to cracked products  $X_{c,0}$ . The rate constants for cracking  $k_c$  and dehydrogenation  $k_d$  were evaluated from the slopes of these plots using the relations

$$\ln 1/(1 - X_{i,0}) = (k_c + k_d) W/F \quad (1)$$

$$\ln 1/(1 - X_{c,0}) = k_d W/F \quad (2)$$

The corresponding values are listed in Table I.

*Pyridine adsorption.* The data on pyridine adsorption are shown in Fig. 4 in the form of the linear plots of Langmuir isotherm:

$$P/G = 1/bG_{\max} + P/H_{\max} \quad (3)$$

$P$  denotes pressure (kPa),  $G$  adsorbed pyridine (mmol),  $b$  and  $G_{\max}$  are constants. The fit to this isotherm is as good as to justify the use of the  $b$  constant as a measure of the relative strength of adsorption sites and of the maximum weight adsorbed  $G_{\max}$  as a measure of the relative concentration of these sites. The results of the calculation of these parameters are shown in Table II. Irreversible adsorption varied from 25 to 50 percent of the maximum weight adsorbed and in no respect to catalyst activity or acid strength.

TABLE I

First order rate constants ( $\text{cm}^3 \text{g}^{-1} \text{min}^{-1}$ ) for cracking and dehydrogenation of isopropylbenzene

Sample	Oxidic		Sulphided	
	$k_c$	$k_d$	$k_c$	$k_d$
2 (Mo-Al <sub>2</sub> O <sub>3</sub> )	685	41	725	308
3 (Ni-Mo-Al <sub>2</sub> O <sub>3</sub> )	1 180	80	1 537	74
4 (Ni-Mo-Al <sub>2</sub> O <sub>3</sub> )	326	62	1 055	21
5 (Ni-Mo-Al <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub> )	440	55	613	35

The values of  $b$  show that the nature of acidic sites is rather different on  $\text{Al}_2\text{O}_3$  and on the other samples, whilst  $G_{\text{max}}$  are comparable for  $\text{Al}_2\text{O}_3$  and for supported samples.  $\text{Al}_2\text{O}_3$  exhibits the highest  $b$  values; this contrasts with its negligible activity in isopropylbenzene cracking at conditions in which the rest of the samples were very active.

TABLE II  
Constants of Langmuir isotherm for pyridine adsorption

Sample	Oxidic		Sulphided	
	$b$ $\text{kPa}^{-1}$	$G_{\text{max}}$ $\text{mmol g}^{-1}$	$b$ $\text{kPa}^{-1}$	$G_{\text{max}}$ $\text{mmol g}^{-1}$
$\text{Al}_2\text{O}_3$	29.55	0.260	30.75	0.210
2	21.23	0.201	0.201	0.218
3	21.83	29.78	29.78	0.205
4	8.40	0.164	17.85	0.225
5	9.75	0.269	14.40	0.206

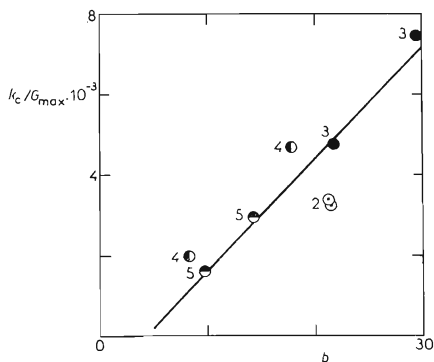


FIG. 5

Correlation of the ratios  $k_c/G_{\text{max}}$  with the  $b$  constants for pyridine adsorption on oxidic and sulphided forms of the catalysts. The numbering of the points corresponds to catalyst numbering

A similar behaviour was reported by Vyskočil and Zdražil<sup>5</sup> for cyclohexene isomerization. Studying the adsorption of pyridine by IR spectroscopy, Kiviat and Petrakis<sup>1</sup>, Fransen and coworkers<sup>2</sup>, and Mone<sup>3</sup> have shown that very low if any Bronsted type surface acidity can be found in  $\text{Al}_2\text{O}_3$  which exhibits a high Lewis acidity. The impregnation with Mo resulted in a development of Bronsted acidity and a reduction of the relative amount of Lewis sites. This could explain the differences in activities observed for  $\text{Al}_2\text{O}_3$  and  $\text{Mo-Al}_2\text{O}_3$  for cracking and isomerization reactions.

In our case, the addition of Ni to  $\text{Mo-Al}_2\text{O}_3$  (comparing oxidic samples) causes an increase in the number of sites accompanied by a small change in their strength. Sulphidation of the catalysts increases more the strength than changes the concentration of sites. In the case of  $\text{Al}_2\text{O}_3$ , a decrease in  $G_{\text{max}}$  was observed with a slight increase in  $b$ ; this was reported also by Ratnasamy and coworkers<sup>7</sup> who studied the adsorption of ammonia on  $\text{Al}_2\text{O}_3$  in oxidic and sulphided forms. With  $\text{Mo-Al}_2\text{O}_3$  a small influence of sulphidation was observed.

The correlation of the constants for the cracking of isopropylbenzene normalized to the concentration of acidic sites with the  $b$  constants for pyridine adsorption, both for oxidic and sulphided samples is shown in Fig. 5 and it appears that this type of correlation is valid for hydrorefining catalysts ( $R = 0.89$ ).

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