April, 1990] © *1989 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn., 63, 1275—1277 (1990)* 1275

Hydrogenation of Monoalkylbenzenes over Supported Pt Catalysts. Influence of Different Variables on the Catalytic Activity

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(Received June 15, 1989)

Synopsis. The catalytic activity of various supported Pt systems used in the hydrogenation of monoalkylaromatic hydrocarbons is markedly influenced by different variables involved in the catalyst synthesis (support, solvent, metal salt, and reduction temperature of the precursor). By analyzing the influence of the substrate structure, we found the following reactivity order: *t*-butylbenzene>isopropylbenzene>ethylbenzene>toluene>benzene. The results obtained conform to the Hammet equation.

The gas-phase hydrogenation of benzene has been used as a reference for a series of studies of catalytic activity[1–3] and to analyze the possible adsorbed states of benzene and other arenes on active sites.[4,5]

In our investigations, hydrogenation reactions were carried out in vapor phase by using a pulse reactor. The results found show the influence of the impregnating salt and the solvent used in the preparation of the metal precursor, the precursor reduction temperature, and the nature of the support on the activity of the resultant catalyst. We also analyzed the structure-reactivity relationship for alkylbenzenes investigated. The experiments were carried out in a pulse reactor fitted to a gas chromatograph. This technique, used by some authors for the determination of kinetic data[3,6,7] offers major advantages in catalysis.

Experimental

Supports. The catalysts were prepared by using six different supports named F, F72, P2, PM2, S, and PS. The first four consisted of SiO_2-$AlPO_4$ (80:20 w/w) gelled in different media. The so-called support S was commercial silica (Merck ref. 7734), while support PS was a natural Spanish sepiolite. The synthesis, texture properties and acidity of these supports were described in detail elsewhere.[8]

Table 1. Metal Surface Area and Dispersion of the Pt Systems as Calculated by Hydrogen Chemisorption

Catalyst	Reduction T/°C	Area (m^2/gPt)	Dispersion[a)]
$Pt_{0.5}$F72	600	207	0.55
$Pt_{0.5}$F72	500	212	0.57
$Pt_{0.5}$F72	400	238	0.63
$Pt_{0.5}$F72	300	322	0.86
$Pt_{0.5}$F72	200	346	0.92
$Pt_{0.5}$F	400	222	0.59
$Pt_{0.5}$S	200	128	0.34
$Pt_{0.5}$PM2	200	148	0.39
$Pt_{0.5}$P2	200	134	0.36
$Pt_{0.5}$PS	200	350	0.93

a) The dispersion was calculated from the metal surface area by assuming a fully disperse catalyst to be made up of spherical Pt atoms half-inlaid in the support.

Catalysts. The catalysts contained 0.5% of platinum by weight and were prepared by impregnation from aqueous, methanol, and acetone solutions of 3.8×10^{-3} M (1 M=1 mol dm^{-3}) $H_2PtCl_6\cdot6H_2O$ or K_2PtCl_6. Both precursors were reduced in situ in the pulse reactor by passing a hydrogen (99.995%) stream at a flow rate of 50 mL min^{-1}. In every case, the metal loading, measured by atomic absorption, was 0.5% by weight. The catalysts were fully isolated from external contaminants by flowing a hydrogen stream (25 mL min^{-1}) through the catalytic bed.

The metal surface of the Pt systems thus obtained was determined by a volumetric procedure based on hydrogen chemisorption and on the assumption of an H:Pt stoichiometry of 1:1[9] and spherical particles. In Table 1 are listed the surface area and dispersion values obtained for the different catalysts reduced at their temperature of greatest activity and at various other temperatures in the case of catalyst F72. These catalysts were prepared from an aqueous solution of $H_2PtCl_6\cdot6H_2O$.

Experimental Setup. The different metal precursors were reduced and arenes hydrogenated in a pulse reactor fitted to a gas chromatograph.[10] The experiments were carried out by using 0.05 g of the catalyst (7.5×10^{-4} g of Pt), a hydrogen stream of 50 mL min^{-1} and a reaction temperature of 120 °C. The precursors were reduced for 1 h and no variation in the resultant activity was found in catalysts reduced for up to 8 h. No diffusion phenomena were observed under the reaction conditions used. In addition, none of the different elements of the systems used was found to be involved in the catalytic process.

Results and Discussion

Table 2 which shows the activity values found at a constant conversion (i.e. in the zone where the conversion obtained is independent of the amount injected) for catalyst $Pt_{0.5}$F72 reduced at different temperatures and synthesized from an aqueous solution of K_2PtCl_6 (column a) and from solutions of H_2PtCl_6 in water (b), methanol (c), and acetone (d). Al can be seen, the optimum reduction temperature varies with the solvent used and, as a rule, the catalysts obtained by aqueous impregnation are more active than those obtained in methanol or acetone. The most active catalyst was that synthesized from an aqueous solution of hexachloroplatinic acid and reduced at 500 °C.

For catalyst $Pt_{0.5}$F72, the optimum reduction temperature was between 500 and 400 °C, the most active systems being those obtained from an aqueous solution of H_2PtCl_6 which was also used subsequently to synthesize the catalysts studied.

We also analyzed the influence of the support used in the preparation of the metal catalyst. As shown in Table 2 for catalyst $Pt_{0.5}$F72, the activity of the catalysts varied with the reduction temperature. In Table 3 are given the activities of the catalysts corresponding

Table 2. Activity (%) at a Constant Conversion (8.5×10^{-5} mol reactant) of $Pt_{0.5}F72$ Systems Obtained by Using K_2PtCl_6 in H_2O (a), and H_2PtCl_6 in H_2O (b), CH_3OH (c), and $(CH_3)_2CO$ (d), and Reduced at Different Temperatures

Reactant	Reduction temperature/°C																		
	200				300				400				500				600		
	a	b	c	d	a	b	c	d	a	b	c	d	a	b	c	d	a	b	c
Benzene	24	29	6	21	26	31	30	27	31	41	57	33	29	64	55	24	11	17	30
Toluene	36	30	10	31	37	35	35	37	39	44	73	40	34	69	64	29	15	19	32
Ethylbenzene	42	54	19	55	50	55	51	54	53	65	86	57	49	80	82	47	21	32	46
Isopropylbenzene	47	65	22	66	60	67	57	64	68	77	91	68	62	89	89	59	30	35	56
t-Butylbenzene	54	80	42	86	80	85	73	74	82	87	96	88	71	98	94	80	39	41	72

Table 3. Influence of the Support on the Catalytic Activity in the Hydrogenation of Alkylbenzenes

Catalyst	Reduction temperature/°C[a]	Constant-conversion activity				
		Reactant				
		a	b	c	d	e
$Pt_{0.5}F72$	500	64	69	80	89	98
$Pt_{0.5}F$	400	40	47	57	72	83
$Pt_{0.5}S$	200	48	53	77	96	100
$Pt_{0.5}PM2$	200	30	49	63	75	92
$Pt_{0.5}P2$	200	21	32	45	61	85
$Pt_{0.5}PS$	200	29	36	53	74	90

a) The reduction temperatures given are those resulting in the optimum activity for each support. a=benzene, b=toluene, c=ethylbenzene, d=isopropylbenzene, and e=*t*-butylbenzene. Amount of reactant: 8.5×10^{-5} mol.

to the reduction temperature at which they showed their greatest activity in the hydrogenation of arenes.

The order of activity found for the catalysts reduced at their optimum temperature was

$$Pt_{0.5}F72 > Pt_{0.5}S > Pt_{0.5}F > Pt_{0.5}PM2 > Pt_{0.5}PS > Pt_{0.5}P2.$$

In general, catalysts F72 (SiO_2-$AlPO_4$ gelled in ammonia) and F ($AlPO_4$ gelled in ammonia) have higher optimum reduction temperatures (500 and 400 °C, respectively), while the catalysts consisting of SiO_2-$AlPO_4$ gelled in propylene oxide (P2 and PM2), that of pure silica (S) and the natural sepiolite (PS) reach their optimum activity upon reduction at 200 °C, above which it starts to decrease.

A comparison of the catalytic activity with the metal surface areas of the catalysts (Table 1) reveals the absence of a direct relationship between the activity and the average metal particle size. In addition, sintering was observed as a result of increasing the precursor reduction temperature.

As regards the influence of the reactant structure on the activity and as can be seen from the results given in Tables 2 and 4, *t*-butylbenzene is hydrogenated more readily than the other alkylbenzenes with all the catalysts studied. The order of activity found was

t-butylbenzene > isopropylbenzene >
ethylbenzene > toluene > benzene.

Our results are consistent with those previously reported by other authors for the hydrogenation of the same arenes on Ni/Al_2O_3[11] or Pt catalysts not sensitive to sulfur poisoning.[12] However, some authors have observed the opposite reactivity trend when using Rh catalysts at 100 atm in methanol solutions, probably due to steric effect.[13]

Under the present experimental conditions, the hydrogenation rate increased as the length of the alkyl branch of the arene did, thus suggesting an electronic effect of the substituent rather than a steric effect. In order to assess this electronic effect, our results were fitted to Hammett's equation,[14] taking toluene as reference,

$$\ln x/x_o = \sigma\rho$$

where x and x_o denote the conversion obtained in the hydrogenation of the arene and toluene, respectively; σ is the electron-releasing strength of the substituent ($\sigma_{tol}=-0.046$, $\sigma_{eb}=-0.057$, $\sigma_{ib}=-0.065$, and $\sigma_{tb}=-0.074$) and ρ stands for the specific reaction rate constant. Following Best's criteria,[15] toluene was chosen as a reference instead of benzene as, according to this author, the latter is adsorbed in a nearly planar conformation on the catalyst surface, standing aside from Hammett's plot. A good correlation coefficient ($r>0.99$) was obtained in all cases.

The results found suggest that it is the inductive effects (+I) from the alkyl groups which play the prevailing role in the reactivity shown by the different arenes. Accordingly, the hydrocarbons should be preferentially adsorbed on electron-deficient metal atoms, although the adsorption of the reactants on the support cannot be ruled out. These reactants might undergo a spillover process from the support to the metal, thereby favoring the subsequent hydrogenation stage.

This work was supported by a grant from the Dirección General de Investigación Cientifica y Tecnica (Project PA-86-0065).

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