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A Contribution to the Investigation of Constitution and Operation of a Ni-on-SiO_2 Catalyst

In separating xylene isomers by selective chlorination (*1*), a mono-chlorinated xylene mixture is obtained which consists of 2-Cl-*m*-xylene, 4-Cl-*m*-xylene (together 90%) and 2-Cl-*p*-xylene (10%). The dechlorination of this residue for the purpose of regaining the xylenes can be effected by heterogeneous catalytic hydrogenolysis over Ni/SiO_2. In searching for the most effective catalyst it was found that the thermal treatment during catalyst preparation has a profound influence on the activity behavior.

The raw catalysts were produced by impregnation of silica gel (Fa. Schuchardt, screen fraction ASTM 10–20) with water-soluble Ni salts, conversion into $Ni(OH)_2$ with subsequent calcination, and reduction. The Ni content was 13–14%. Several water-sobule Ni salts were used to impregnate the silica gel, but their nature was of no influence on the efficiency of the catalyst. The preparative procedure was performed according to Refs. (*2,5*).

For evaluating the influence of the thermal treatment, samples of the raw catalyst were submitted to calcination in N_2 atmosphere at 400°C for various times (1 hr, catalyst I; 3 hr, catalyst III; 5 hr, catalyst V). The temperature of the subsequent reduction and hydrogenolysis was 300°C.

The catalytic efficiency was measured in a tube reactor using an apparatus similar to that described by Sabatier (*3,5*). The chloroxylene feed was first evaporated and thoroughly mixed with H_2 in an evaporator. This mixture was led to the active catalyst (volume, 80–100 ml) for reaction. The flow rate of H_2 was 20–25 liters/hr, and the chloroxylene addition rate was 20–25 ml/hr.

The feed for the reaction was a mixture according to (*1*) consisting of 10 mol% 2-Cl-*p*-xylene, 27 mol% 2-Cl-*m*-xylene and 63 mol% 4-Cl-*m*-xylene. The composition of the liquid reaction products was examined by gas chromatography using a Perkin-Elmer F 21 fractometer with columns of 4 m length (62 S 52.45: bentone 34 + di-*n*-decylphthalate); the carrier gas was N_2 at a flow rate of 60–80 ml/min, the temperature was programmed, and a flame ionization detector was used. The catalysts were examined by electron probe microanalysis (EPMA) using a JEOL JXA-3 microanalyzer to observe the distribution of the elements in the catalyst grains, which were embedded in polyester resin. Conductance of the specimen was obtained by vapor-deposited carbon.

The hydrogenolytic activity of catalysts calcined for different times was examined with 60 ml of the feed by analyzing the liquid reaction products after each 20 ml. After these analyses and an intermediate activation at 500°C in H_2 a further examination of the hydrogenolytic activity was performed. Because of the fact that the chosen catalysts selectively dechlorinate 2-Cl-*p*-xylene and 4-Cl-*m*-xylene and do not affect the 2-Cl-*m*-xylene (*4*), the amount of reacted *m*-xylene is a measure for the activity of the catalyst. Therefore a yield of 63 mol% *m*-xylene equals 100% catalytic activity.

The results of the activity investigations and the microanalyses are shown in Table

TABLE 1

Feed (ml)	m-Xylene (mol%) before and after intermediate activation in H_2 at 500°C					
	Catalyst I		Catalyst III		Catalyst V	
	Before	After	Before	After	Before	After
20	56	52	45	55	41	62
40	37.5	53.5	40	51	31	61
60	30	35	38	53	33	63

1 and in Figs. 1–3. In Table 1 the dependence of the catalytic activity on the amount of chloroxylene feed can be seen.

Figures 1–3 show the Ni distribution in the peripheral area of a catalyst grain, by means of the characteristic X-ray micrograph. The right lower corner of the picture represents the internal part of the catalyst grain. As far as catalyst I is concerned it appears that the catalytic activity of the original catalyst and the catalyst after intermediate activation at 500°C is almost the same and decreases with increasing feed addition. In Fig. 1 it is clearly shown that the main part of the nickel is on the surface of the grain, with only a little inside the grain.

The activity behavior and the Ni distribution of catalyst III, the catalyst which was calcined for 3 hr, was different. From the X-ray micrograph (Fig. 2) it appears that the major part of the nickel is inside the grain, with only a small fraction in the form of a thin skin remaining on the surface. The activity behavior shows that the initial activity at 300°C has decreased in comparison with catalyst I, whereas the activity after intermediate activation has increased. The activity diminution during feed addition is still present in the unac-

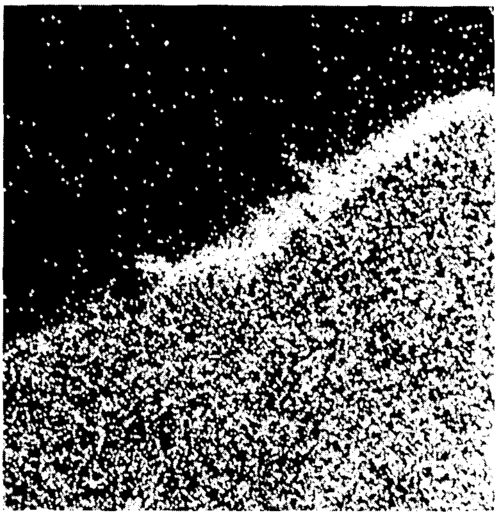
FIG. 2. Nickel distribution in cat. III; area 170 × 170 μm.

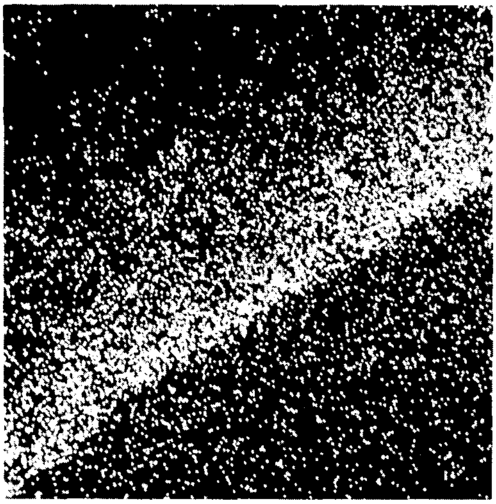
FIG. 1. Nickel distribution in cat. I; area 170 × 170 μm.

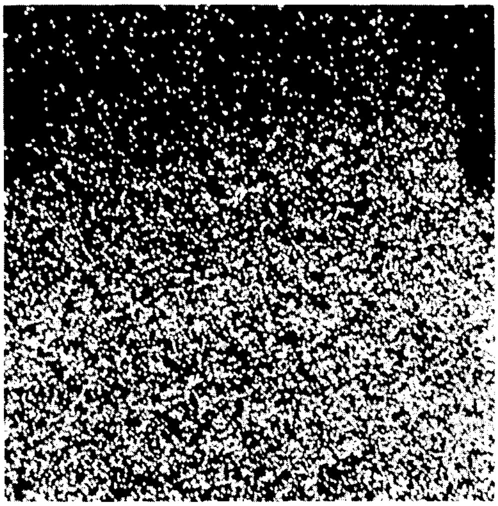
FIG. 3. Nickel distribution in cat. V; area 170 × 170 μm.

tivated catalyst, but not in the activated catalyst.

The same changes, only quantitatively reinforced, are observed with catalyst V. The Ni distribution (Fig. 3) clearly shows that the metal has completely migrated into the silica gel grain. The initial activity has further decreased, the catalytic activity after intermediate activation has further increased and reached a 100% activity for selective dechlorination of 2-Cl-*p*-xylene and 4-Cl-*m*-xylene. This means that 2-Cl-*m*-xylene remains completely unreacted.

The comparison of the element-specific pictures demonstrates an increase of Ni content inside the SiO_2 grain with increasing calcination times. The concentration increases from about 6% in catalyst I to about 13% in catalyst V; the latter is composed of completely homogeneous grains without any enrichment of Ni on the surface. Therefore the term "impregnation catalyst" is wrong for these very efficient catalysts.

It is evident that the Ni content inside the grains must be caused by the diffusion of NiO into the structureless gel of the carrier during the calcination, because *reduced* Ni is not able to diffuse into the gel, as is shown in the pictures of catalysts I and III (Figs. 1 and 2). The H_2 treatment at 300°C of the catalysts calcined for a long time is therefore not able to reduce the whole NiO amount. This is shown in the initial activity of the catalysts, which decreases with increasing calcination times, because NiO is inactive in this respect. The only active substance is metallic Ni with a well-ordered lattice, as was proved by X-ray analysis (*5*).

The intermediate activation at 500°C in H_2 caused complete reduction of the NiO and the catalytic activities of the catalyst calcined for a long time could be increased considerably after this further H_2 treatment. The reason why the initial catalytic activity of catalyst I is higher than the activity after intermediate activation is that most of the NiO is on the surface and can therefore easily be reduced even at 300°C.

For the catalysts calcined for a short time, the strong decrease of the catalytic activity which results from feed addition may be caused by the fact that the metallic Ni, which exists as a relatively thick skin on the surface, is more deactivated by the HCl produced by the hydrogenolysis than the Ni of the catalysts calcined for a long time, which is in the form of atom aggregates (*6*) embedded and protected in the SiO_2-gel matrix.

The increase of the catalytic activity after intermediate activation is caused by the fact that, owing to the extremely large specific surface of the silica gel, the embedded Ni has a larger surface area than the Ni which forms a compact sintered skin in the surface of the grain.

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