A Direct Correlation between Dispersion, Metal Area, and Vapour Phase Hydrogenation of Aniline; a First Report

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Aniline hydrogenation activity is correlated with dispersion, crystallite size, and metal area over Rh/Al_2O_3 catalyst.

Hydrogenation of aniline to cyclohexylamine is an important process because of the large amount of cyclohexylamine used as an intermediate for a variety of amine derivatives in numerous industries. Invariably dicyclohexylamine is formed as a by-product,[1—4] and is employed in the extraction of natural products as a chemical intermediate and in the medical field. The reaction is usually carried out in the liquid phase using supported ruthenium, rhodium, and nickel catalysts. Studies on the vapour phase hydrogenation of aniline are scarce and no correlation between the dispersion of a metal over the support, crystallite size and metal area, and the conversion and selectivity for this reaction has been reported so far. In this communication such a correlation is reported for the first time on rhodium supported on an alumina catalyst.

Supported Rh catalysts of different metal loadings in the region 0.5—7.0 wt% were prepared by impregnating aqueous solutions of $RhCl_3 \cdot 3H_2O$ of appropriate concentrations on alumina (Harshaw Al-11161E, surface area = 220 $m^2 g^{-1}$; particle size = 1400—1800 μm; pore volume = 0.65 $cm^3 g^{-1}$). Fresh catalysts were dried overnight at 423 K and then calcined in air at 623 K for 3 h. *Ca.* 0.3 g of the calcined catalyst was packed in between glass beads in a vertical glass reactor (OD = 1.5 cm). The catalyst is reduced in a hydrogen flow (0.265 mol h^{-1}). Aniline (GR) was fed from the top of the reactor at the required flow rate using a calibrated motorised syringe. Hydrogen was used as a reductant and as a carrier gas. The reaction temperature, 473 K, was chosen on the basis of preliminary experimental data. The liquid products were analysed by GC (column: 10% Carbowax 20 M on Chromosorb W). The major products were cyclohexylamine and dicyclohexylamine with minor constituents, cyclohexane and 4-phenylcyclohexylamine. Metal surface area, dispersion, and crystallite size were calculated from hydrogen adsorption isotherm data at room temperature using a conventional

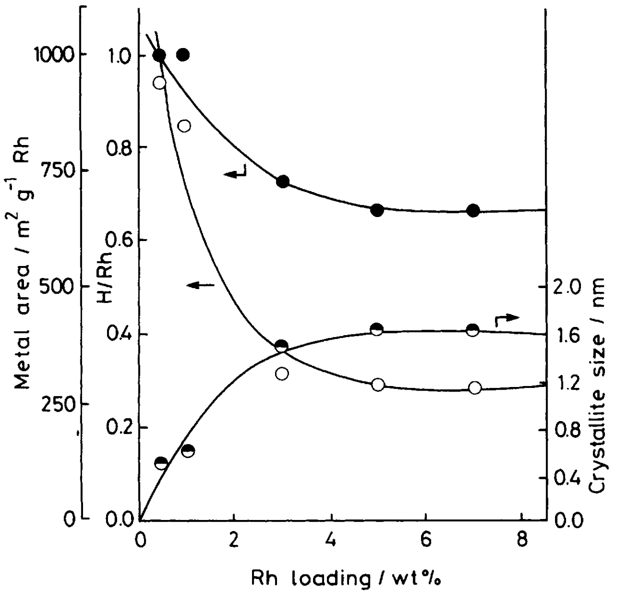

Figure 1. Effect of metal loading on dispersion (●), crystallite size (◓), and metal area (○).

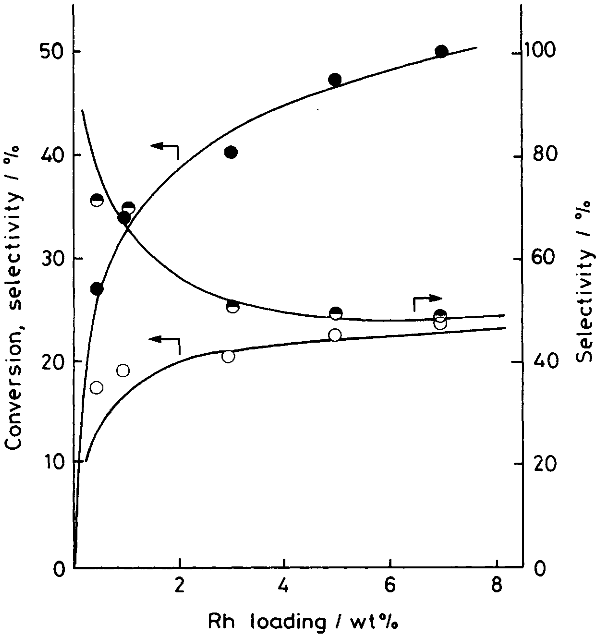

Figure 2. Effect of metal loading on aniline hydrogenation: conversion (●), selectivity for cyclohexylamine (○), and selectivity for dicyclohexylamine (◓).

volumetric system.[5,6] *X*-ray diffraction patterns of the catalysts were obtained using a Philips PW 1051 *X*-ray diffractometer. Activity is calculated in terms of turn-over frequency (TOF), defined as the number of molecules of aniline converted per atom of exposed rhodium per unit time.

Figure 1 depicts the variation of metal area, dispersion, and crystallite size with metal loading. Rh on Al_2O_3 samples with 0.5 and 1 wt% of the metal have nearly 100% dispersion and the crystallite size is of about 0.4 nm. At higher than 3 wt% of rhodium loading the dispersion decreased to about 70%. Crystallite size, however, showed an opposite trend, increasing with metal loading and remaining steady above 3 wt% of rhodium. On the other hand metal area shows a sharp decrease with metal loading up to 3 wt%, thereafter remaining nearly the same. A constant dispersion (70%) with relatively uniform crystallite size (1.6 nm) with increasing metal loading indicate the absence of any large agglomeration of metallic rhodium. *X*-ray diffraction patterns of the calcined and reduced samples of catalysts also support this observation as there is no evidence of large metal crystallites. However, the decrease in the metal surface area with increasing metal loading may be attributed to the nonavailability of a number of metal crystallites for hydrogen adsorption, which is a measure of metal area.

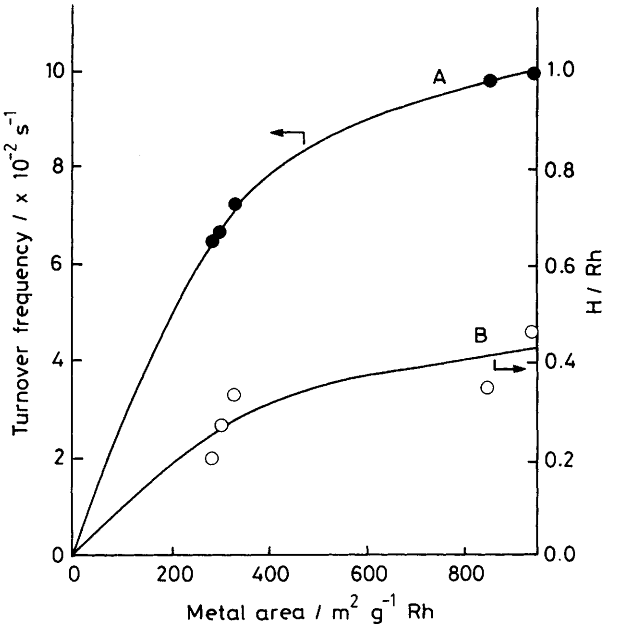

Figure 3. A correlation between metal area, dispersion (○), and TOF (●) for aniline hydrogenation.

The effect of metal loading on hydrogenation of aniline and selectivity for cyclohexylamine and dicyclohexylamine is shown in Figure 2. The total conversion of aniline increases with increasing metal loading. Selectivity for cyclohexylamine was rather steady around 20% throughout the metal loading. On the other hand, the selectivity for dicyclohexylamine decreases with increase in metal loading up to 3 wt%, thereafter remaining steady.

It is interesting to see the variation in aniline hydrogenation activity, as expressed by TOF, with metal area and dispersion (Figure 3). TOF increases with metal area irrespective of metal loading. It can also be seen clearly that the dispersion of metal also increases with metal area. Comparison of the two plots (Figure 3A and B) leads to a correlation of smooth variation of aniline hydrogenation activity and dispersion with metal area. From Figures 1 and 3, one could infer that an increase in rhodium loading, especially above 3 wt%, does not necessarily increase the metal area available for hydrogen adsorption or hydrogenation of aniline, even though dispersion and crystallite size do not vary much.

Thus vapour phase hydrogenation of aniline over Rh/Al_2O_3 catalyst together with hydrogen adsorption experiments reveal that the TOF for aniline conversion decreases with an increase in metal loading beyond 3 wt% and increases with metal surface area per gram of rhodium, indicating that all the possible metal atoms are not available for hydrogen adsorption and hydrogenation activity. Increase of rhodium loading beyond 3 wt% has no significant effect on the TOF of aniline hydrogenation. Selectivity for cyclohexylamine and dicyclohexylamine is constant for a given crystallite size and dispersion irrespective of metal area, especially beyond 3 wt% of rhodium loading. This may be compared with the benzene hydrogenation activity over Pt/SiO_2, which is constant for a range of platinum crystallite size distribution.[7]

Hydrogenation of aniline can result in the formation of cyclohexylamine, dicyclohexylamine, 4-phenylcyclohexylamine, cyclohexane, benzene, and ammonia depending on the mode of decomposition and coupling. The mechanism of formation of some of these compounds is explained by Greenfield.[4] Moss and Kemball[8] have reported unusual catalytic decomposition of cyclohexylamine at 407 K over evaporated platinum film. With the help of mass spectral analysis, it was observed that the decomposition of cyclohexylamine gave benzene rather than cyclohexane as a first step, even in presence of excess hydrogen. This was explained on the basis of a favourable thermodynamic equilibrium condition for benzene formation. However, in the present study, benzene was not identified in the product and no effort was made to detect ammonia, although other products were present. That benzene was not identified does not in any way preclude the possibility of formation of benzene *in situ* during the reaction. One possibility is that benzene would have been hydrogenated completely to cyclohexane which is still thermodynamically favourable under the reaction conditions (473 K and H/aniline, mole ratio = 4.0) studied. The presence of benzene in the product, as an intermediate, introduces competition in the hydrogenation of the main reactant, aniline. It is believed that hydrogenation of benzene is easier than hydrogenation of aniline. This is possibly one of the reasons why only cyclohexane was identified in the product and not benzene. Further studies on the influence of crystallite size on the mechanism of the formation of various products on several supported metal systems are under way.

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