Selective Hydrogenation of Aromatic Compounds Containing Epoxy Group over Rh/Graphite

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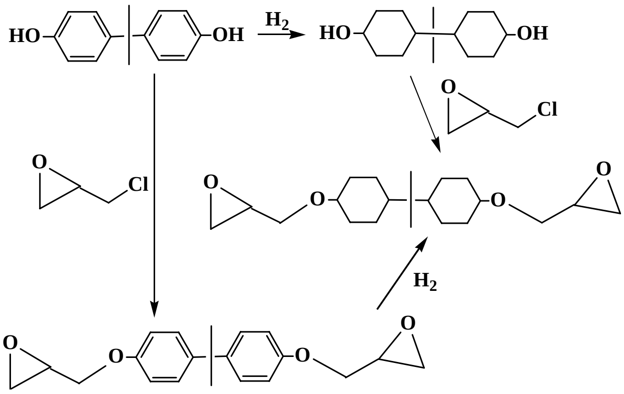
(Received August 22, 2002; CL-020712)

Catalytic hydrogenation of aromatic compounds containing epoxy group to alicylic compounds has been investigated. Rh supported on graphite with high surface area exhibited superior performance to other supported catalysts for the selective reduction of the aromatic group while retaining epoxy group.

Controlling selectivity in the reduction of the organic compounds which have both reduciable groups is one of the most important key technologies in academia as well as in industry. For instance, many efforts have been made for the hydrogenation of α,β-unsaturated aldehydes or ketones to give α,β-unsaturated alcohols.[1–3] We describe herein the effect of catalyst metal and supports on the catalytic property for the hydrogenation of a bisphenol A diglycidyl ether which has widely used for the epoxy cured resins. Catalytic hydrogenation of aromatic compounds to alicyclic ones is now easily accomplished over many platinum group catalysts under relatively mild condition.[4] However, highly selective catalytic hydrogenation of an aromatic ring in the vicinity of an epoxy group is a unique problem because the epoxy groups are vulnerable to acid and base and can easily undergo hydrogenolysis. It is of great importance to establish the technology for the transformation taking into account the industrial applications. Epoxy resins prepared from a diglycidyl ether of hydrogenated bisphenol A are characterized to be superior in weatherability and electric property to those from the aromatic counterparts. There have been known two ways to produce diglycidyl ether of hydrogenated bisphenol A as depicted in Scheme 1. The first is reacting epichlorohydrin with hydrogenated bisphenol A, whereas another is directly hydrogenating bisphenol A deglycidyl ethers.



Scheme 1.

The product obtained from the former process contains a large amount of chlorines and it is unsuitable for electric uses. On the other hand, the problems in the latter process to be solved are to find out the selective hydrogenation catalysts which can exclusively hydrogenate the aromatic ring while retaining epoxy group. There have been scare literatures referring to the reaction of kinds except a few patents disclosed in which RuO_2 and Rh/active carbon were employed as catalysts.[5–7] Table 1 shows the effect of various kinds of hydrogenation catalyst.

Table 1. Various catalysts for hydrogenation of bisphenol A diglycidyl ether

Catalyst	Conversion of aromatic group/%	Residual epoxy group /%
RuO_2	100	92
Ru/active carbon	30	99
Ru/SiO_2	0	99
Pd/active carbon	0	44
Rh/Al_2O_3	35	50
Rh/SiO_2	0	98
Rh/active carbon	100	77
Rh/graphite[a]	100	92
Rh/graphite[b]	70	93
Rh/graphite[c]	9	100

Reaction conditions: bisphenol A diglycidyl ether 5 g, THF 5 g, catalyst 0.25 g, H_2 15 MPa (at room temp.), 50 °C, 3 h. Metal loading of supported catalysts were 5 wt% and all the catalysts used except Rh/graphite were commercially available. Rh/graphite was prepared by wet impregnation of graphite with a aqueous solution of $RhCl_3$ followed by H_2 gas reduction at 300 °C for 2 h. [a]Lonza, HSAG100, surface area 130 m^2/g, [b]Lonza, HSAG300, surface area 280 m^2/g, [c]Kishida F08126D, surface area 3 m^2/g.

Catalytic property significantly changed by the catalyst metals as well as their supports. Ru and Rh have tendency to hydrogenate aromatic ring, whereas Pd predominantly attacks the epoxy group and Rh is much more active than Ru. Support also exerts an influence on the reaction feature. SiO_2 was quite inert in both Ru and Rh catalyst and Al_2O_3 is liable to decompose epoxy group possibly due to its acidic character. Active carbon support gave relatively high catalytic activity and selectivity, which is probably due to high surface area and relatively neutral property (acidity-basicity) on the surface. Therefore, we have focused on a series of carbonaceous supports as suitable for the reaction.

Graphite with a certain surface area (SA) of 100 m^2/g turned out to exhibit extraordinary catalytic behavior. No significant difference in Rh particle size (<50 Å) between HSAG100 and HSAG 300 was observed from XRD though Rh particle supported on graphite with SA of 3 m^2/g was surely large (~200 Å). In order to accurately compare the catalytic performance between Rh/active carbon and Rh/graphite, the hydrogenation were carried out monitoring H_2 uptake at the constant pressure as listed in

Table 2. Comparison between Rh/active carbon and Rh/graphite

Substrate	Catalyst	Conversion of aromatic group/%	Initial rate[a] /mol/g-cat.h	Residual Epoxy group/%
Phenyl glycidyl ether	5 wt%Rh/active carbon	100	0.75	64
Phenyl glycidyl ether	5 wt%Rh/graphite[b]	100	0.85	91
Bisphenol A diglycidyl ether	5 wt%Rh/active carbon	70	0.23	
Bisphenol A diglycidyl ether	5 wt%Rh/graphite[b]	100	0.32	97

Reaction conditions: substrate 50 g, THF 50 g, catalyst 0.5 g, H_2 7 MPa, 85 °C, 2.5 h.

[a]rate constant calculated by assuming zero order.

[b]Lonza, HSAG100.

Table 2. Catalysts are required to have activity enough to work under as low temperature as possible to suppress the undesired side reactions associated with the loss of epoxy group. Rh/graphite has outstanding characteristics in several respects. For instance, the hydrogenation of bisphenol A diglycidyl ether catalyzed by Rh/active carbon could not go into completion at the prescribed conditions, while by Rh/graphite the reaction can be achieved 100% conversion. Besides that, Rh/graphite is much less likely to decompose epoxy group. For the hydrogenation of phenyl glycidyl ether, 91% of epoxy group was retained during hydrogenation over the Rh/graphite.

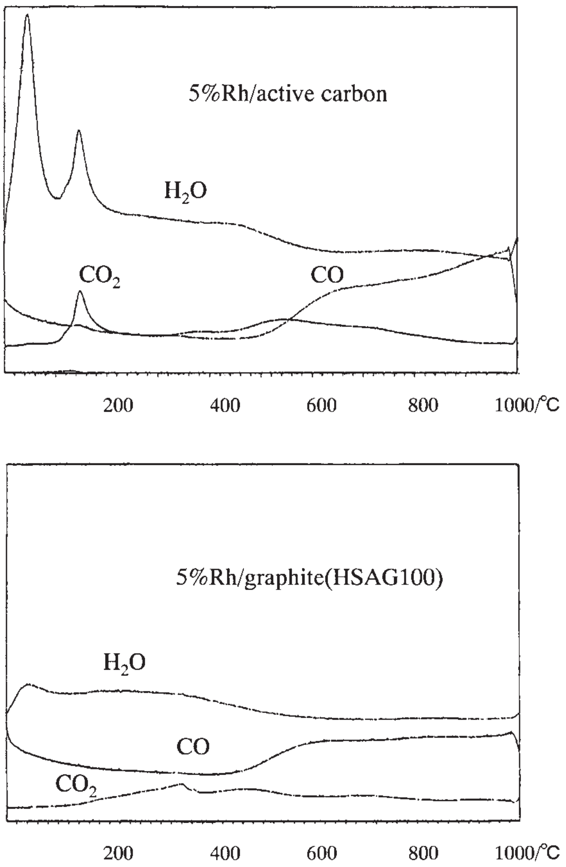


Figure 1. TG-MS spectra of Rh/active carbon and Rh/graphite. He 100 ml/min. 20 °C/min.

On the other hand, a considerable amount of decomposition of epoxy group took place for the reaction catalyzed by Rh/active carbon. Thus, Rh/graphite catalyst showed not only high catalytic activity for aromatic ring hydrogenation but a preference for the retention of epoxy group compared to the conventional Rh/active carbon which has been known to be the best candidate for the reaction so far. Fig. 1 illustrates TG-MS spectra of both catalysts. CO and CO_2 evolved are known to reflect the extent of functionalization, that is, concentration of the polar group like carboxyl, lactone and phenolic carbonyl group present on the support surface.[8–10] These polar sites are supposed to adsorb strongly H_2O which can cause hydrolysis of epoxy group and attack epoxy group as nucleophiles or electrophiles. As a result, surface properties of the catalyst are one of crucial factors in controlling the selectivity. Rh/graphite has overwhelmingly less functional group on the surface. That is partly why Rh/graphite exhibits high retention of epoxy group.

In conclusion, we have found a simple and convenient method for the alicylic compounds containing epoxy groups directly from the corresponding aromatic ones by using Rh/graphite. But why the phenomenon that catalyst activity greatly alters with its surface area having optimal value remains still obscure. We are now on the way for the characterization of Rh/graphite.

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